

Estimation of the Heat Capacities of Organic Liquids as a Function of Temperature Using Group Additivity.

I. Hydrocarbon Compounds

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A second-order group additivity method has been developed for the estimation of the heat capacity of liquid hydrocarbons as a function of temperature in the range from the melting temperature to the normal boiling temperature. The temperature dependence of group contributions and structural corrections has been represented by a polynomial expression. The adjustable parameters in the polynomials have been calculated using a weighted least squares minimization procedure. Recommended heat capacities from a large compilation of critically evaluated data that contains over 1300 organic liquids served as a database both for the development and testing of the method.

Key words: estimation; group contribution approach; heat capacity of liquids; hydrocarbons; temperature dependence.

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1. Introduction

Heat capacity is a basic thermodynamic property. It is used in chemical engineering calculations to obtain the differences in thermodynamic functions between two different temperatures. Experimental liquid heat capacity data are available for only a fraction of the total number of compounds encountered in industrial processes. In addition, for only a small number of compounds does the extant data cover the temperature interval that is often required in applications, i.e. from the melting temperature up to the normal boiling temperature. Estimation methods are an obvious choice to provide heat capacities for compounds for which there is a complete lack of data or for which data are available only over a limited temperature interval.

Additivity schemes that correlate thermophysical and thermodynamic properties with molecular structure have become widely used for data estimation. Because a molecular property is calculated by summing up atomic, bond, or group contributions, the additivity methods are purely empirical. The additivity approach applied to the estimation of thermophysical properties was systematically developed by S.W. Benson and coworkers (58BEN/BUS, 69BEN/CRU, 70BEN/ONE, 73EIG/GOL, 77LUR/BEN, 77SHA/GOL, 77STE/GOL, 91BEN/GAR). From the beginning, attention has been focused primarily towards the estimation of thermodynamic properties for the gas phase.

Several additivity methods have been proposed for the estimation of liquid heat capacities (55JOH/HUA, 65MIS, 69SHA, 73CHU/SWA1, 73CHU/SWA2, 77LUR/BEN, 81OGI/ARA, 82CHU/NGU, 88DOM/HEA). Some methods utilize a second order additivity routine that takes into account the nearest-neighbor interactions in the definition of structural units into which molecules are divided. Guthrie and Taylor (84GUT/TAY) developed an additivity method for the estimation of the heat capacity of vaporization that is defined as the difference between the gas and the liquid heat capacities.

All additivity methods developed for the estimation of the liquid heat capacity so far, with the exception of 77LUR/BEN, provide contributions either at a single temperature, typically near 25 °C, or at a few discrete temperatures (65MIS). Luria and Benson (77LUR/BEN) developed group contributions that permit the estimation of the liquid heat capacity in an analytical form that represents the dependence of the heat capacity of a hydrocarbon on temperature. In chemical engineering calculations, an analytical equation for the heat capacity as a function of temperature is preferred to discrete values of heat capacities given at a few temperatures.

The current project has been concerned with the revision of the existing group contributions and structural corrections developed by Luria and Benson (77LUR/BEN) and the extension of the method to cover a broad range of organic liquids containing the elements: carbon, hydrogen, oxygen, nitrogen, sulfur, and halogens. The second-order additivity method provides for the estima-

tion of the heat capacity of organic liquids and yields the heat capacity as a function of temperature in an analytical form. Thus, the method can be implemented readily in chemical engineering calculations to establish energy balances or to evaluate the effect of temperature on phase and reaction equilibria.

The development of the method has been made possible as a large compilation of experimental calorimetrically measured heat capacities has become available (88ZAB/RUZ, 93ZAB/RUZ). The compilation contains critically evaluated data for over 1300 organic compounds. The evaluated heat capacities served as the input data in the development of the present estimation method. This paper presents group and structural correction parameters for hydrocarbons. A total of 29 groups and 24 structural corrections are given which include those for families such as alkanes, alkenes, alkynes, aromatic hydrocarbons, and saturated and unsaturated cyclic hydrocarbons.

2. Development of the Method

2.1. Additivity Scheme

We have used the following expression to estimate the heat capacity of organic liquids, C , as a function of temperature:

$$\frac{C}{R} = \sum_{i=1}^k n_i \Delta c_i \quad (1)$$

where R is the gas constant ($R = 8.31451 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$, 88COH/TAY), n_i is the number of additivity units of type i , Δc_i is the dimensionless value of the additivity unit of type i , and k is the total number of additivity units in a molecule. The additivity units include groups and structural corrections.

Several functional forms for the dependence of Δc_i on temperature have been considered and examined (92RUZ/DOM). Finally, a simple expression has been chosen:

$$\Delta c_i = a_i + b_i \frac{T}{100} + d_i \left(\frac{T}{100} \right)^2 \quad (2)$$

where T is temperature in K and a_i , b_i , d_i are adjustable parameters. Other, more complex expressions were rejected as adjustable parameters are highly correlated. Insufficient accuracy of the heat capacity data, a narrow interval of available data for some compounds, poor choice of structural units into which molecules are broken, and inadequacy of the model are possible explanations for the parameter correlation. We believe that the first two items are the most probable causes that prevent the use of a more extensive functional form for the dependence of Δc_i with temperature.

2.2. Temperature Range

The present estimation method is applicable from the melting temperature to the normal boiling temperature which is the range for the liquid phase most often re-

quired in chemical engineering calculations. At present, it is not possible to develop an empirical method to estimate heat capacities of organic liquids over a wider temperature range as experimental data above the normal boiling temperature are scarce. The method can be extrapolated to temperatures above the normal boiling point; however, the predictive accuracy deteriorates as the extent of the temperature extrapolation increases. Near the critical point deviations between observed and estimated heat capacities become large as the liquid heat capacity becomes infinite at the critical point.

When comparing recommended heat capacities and those estimated using additive contributions reported here we have encountered only few instances where it was necessary to use temperature outside the range of one or more groups present in the compound. We found that the temperature extrapolation up to 80 K outside the range of a group has no considerable effect upon the error of prediction. It was shown by 93RUZ/DOM that extrapolated group values calculated outside the temperature limits are reasonable when using the eqn. (2) for the dependence of contributions Δc_i with temperature.

Due to the limited temperature range to which the method applies, no distinction was made between the isobaric heat capacity, C_p , and the saturation heat capacity, C_{sat} . At low saturation pressures below 0.1 MPa, C_p and

C_{sat} are nearly equal in magnitude. The difference between C_p and C_{sat} at the normal boiling temperature lies typically below 0.2 % and only becomes significant far above the normal boiling temperature. Even when the method is applied above the normal boiling temperature the deviations between observed and estimated heat capacities exceed the differences between C_p and C_{sat} .

2.3. Group Notation

We have followed the group notation developed by Benson and coworkers (58BEN/BUS, 69BEN/CRU). The group is defined as a central atom together with its nearest-neighbor atoms and ligands. We have adopted the short form of the notation for multiple bonded atoms C_d , C_t , C_B , and C_a that omits the atom at the other end of the multiple bond. C_d is a double bonded carbon atom attached to a second double bonded carbon atom and to two other monovalent ligands, C_t is a triple bonded carbon atom attached to a second triple bonded carbon atom and to another monovalent ligand, C_B is a carbon atom in a benzene ring attached to two other benzene ring carbon atoms and to another monovalent ligand, C_a is the double bonded carbon atom located in the middle of the allenic group $>C=C=C<$. Table 1 lists all groups that we have used together with a sample group assignment for some typical molecules.

TABLE 1. List of groups

Group	Number of Atoms		Sample group assignment
	C	H	
$C-(H)_3(C)$	1	3	propane: 2 $C-(H)_3(C)$, 1 $C-(H)_2(C)_2$
$C-(H)_2(C)_2$	1	2	<i>n</i> -hexane: 2 $C-(H)_3(C)$, 4 $C-(H)_2(C)_2$
$C-(H)(C)_3$	1	1	2-methylpentane: 3 $C-(H)_3(C)$, 2 $C-(H)_2(C)_2$, 1 $C-(H)(C)_3$
$C-(C)_4$	1	0	2,2-dimethylbutane: 4 $C-(H)_3(C)$, 1 $C-(H)_2(C)_2$, 1 $C-(C)_4$
$C_d-(H)_2$	1	2	ethene: 2 $C_d-(H)_2$
$C_d-(H)(C)$	1	1	1-propene: 1 $C-(H)_3(C)$, 1 $C_d-(H)_2$, 1 $C_d-(H)(C)$
$C_d-(C)_2$	1	0	2-methyl-1-propene: 2 $C-(H)_3(C)$, 1 $C_d-(H)_2$, 1 $C_d-(C)_2$
$C_d-(H)(C_d)$	1	1	1,3-butadiene: 2 $C_d-(H)_2$, 2 $C_d-(H)(C_d)$
$C_d-(C)(C_d)$	1	0	2-methyl-1,3-butadiene: 1 $C-(H)_3(C)$, 2 $C_d-(H)_2$, 1 $C_d-(H)(C_d)$, 1 $C_d-(C)(C_d)$
$C-(H)_2(C)(C_d)$	1	2	1-butene: 1 $C-(H)_3(C)$, 1 $C_d-(H)_2$, 1 $C_d-(H)(C)$, 1 $C-(H)_2(C)(C_d)$
$C-(H)(C)_2(C_d)$	1	1	3-methyl-1-butene: 2 $C-(H)_3(C)$, 1 $C_d-(H)_2$, 1 $C_d-(H)(C)$, 1 $C-(H)(C)_2(C_d)$
$C-(C)_3(C_d)$	1	0	3,3-dimethyl-1-butene: 3 $C-(H)_3(C)$, 1 $C_d-(H)_2$, 1 $C_d-(H)(C)$, 1 $C-(C)_3(C_d)$
$C-(H)_2(C_d)_2$	1	2	1,4-pentadiene: 2 $C_d-(H)_2$, 2 $C_d-(H)(C)$, 1 $C-(H)_2(C_d)_2$
$C_t-(H)$	1	1	1-butyne*: 1 $C-(H)_3(C)$, 1 $C-(H)_2(C)(C_d)$, 1 $C_t-(H)$, 1 $C_t-(C)$
$C_t-(C)$	1	0	2-butyne: 2 $C-(H)_3(C)$, 2 $C_t-(C)$
$C_t-(C_B)$	1	0	ethynylbenzene ^b : 5 $C_B-(H)$, 1 $C_t-(C_B)$, 1 $C_B-(C_d)$, 1 $C_t-(H)$
C_a	1	0	1,2-butadiene: 1 $C-(H)_3(C)$, 1 $C_d-(H)_2$, 1 $C_d-(H)(C)$, 1 C_a
$C_B-(H)$	1	1	benzene: 6 $C_B-(H)$
$C_B-(C)$	1	0	toluene: 5 $C_B-(H)$, 1 $C_B-(C)$, 1 $C-(H)_3(C)$
$C_B-(C_d)$	1	0	ethenylbenzene: 5 $C_B-(H)$, 1 $C_B-(C_d)$, 1 $C_d-(H)_2$, 1 $C_d-(H)(C_d)$
$C_B-(C_B)$	1	0	1,1'-biphenyl: 10 $C_B-(H)$, 2 $C_B-(C_B)$
$C-(H)_2(C)(C_B)$	1	2	ethylbenzene: 5 $C_B-(H)$, 1 $C_B-(C)$, 1 $C-(H)_2(C)(C_B)$, 1 $C-(H)_3(C)$
$C-(H)(C)_2(C_B)$	1	1	1-methylethylbenzene: 5 $C_B-(H)$, 1 $C_B-(C)$, 1 $C-(H)(C)_2(C_B)$, 2 $C-(H)_3(C)$ ^a
$C-(C)_3(C_B)$	1	0	(1,1-dimethylethyl)benzene: 5 $C_B-(H)$, 1 $C_B-(C)$, 1 $C-(C)_3(C_B)$, 3 $C-(H)_3(C)$
$C-(H)_2(C_B)_2$	1	2	1,1'-methylenebisbenzene: 10 $C_B-(H)$, 2 $C_B-(C)$, 1 $C-(H)_2(C_B)_2$
$C-(H)(C_B)_3$	1	1	1,1',1''-methylidenetrisbenzene: 15 $C_B-(H)$, 3 $C_B-(C)$, 1 $C-(H)(C_B)_3$
$C_{BF}-(C_{BF})(C_B)_2$	1	0	naphthalene: 8 $C_B-(H)$, 2 $C_{BF}-(C_{BF})(C_B)_2$
$C_{BF}-(C_{BF})_2(C_B)$	1	0	phenanthrene: 10 $C_B-(H)$, 2 $C_{BF}-(C_{BF})(C_B)_2$, 2 $C_{BF}-(C_{BF})_2(C_B)$
$C_{BF}-(C_{BF})_3$	1	0	fluoranthene: 10 $C_B-(H)$, 1 $C_{BF}-(C_{BF})(C_B)_2$, 4 $C_{BF}-(C_{BF})_2(C_B)$, 1 $C_{BF}-(C_{BF})_3$

^aThe approximation $C-(H)_2(C)(C_t) \equiv C-(H)_2(C)(C_d)$ was used.

^bThe approximation $C_B-(C_t) \equiv C_B-(C_d)$ was used.

Benson *et al.* (69BEN/CRU) and many other authors who have developed a second-order additivity method for the estimation of thermophysical properties arbitrarily assigned values to some groups either when groups exist in conjugate pairs or when data for the calculation of a group are unavailable. We have utilized some of the assignments mainly as it reduced the colinearity of adjustable parameters (93RUZ/DOM). The list of equivalent groups is given in Table 2.

TABLE 2. List of equivalent groups

$C-(H)_3(C) \equiv C-(H)_3(C_d) \equiv C-(H)_3(C_i) \equiv C-(H)_3(C_B)$
$C-(H)_2(C)(C_i) \equiv C-(H)_2(C)(C_d)$
$C_B-(C_i) \equiv C_B-(C_d)$
$C_d-(H)(C_B) \equiv C_d-(H)(C_d)$
$C_d-(C)(C_B) \equiv C_d-(C)(C_d)$
$C_B-(C)(C_B)(C_{BF}) \equiv C_B-(C)$
$C_B-(C_i)(C_B)_2 \equiv C_B-(C_d)(C_B)_2$

We have adopted the approach proposed by Benson and coworkers (69BEN/CRU, 76BEN) to estimate the heat capacity of saturated and unsaturated cyclic hydrocarbons. The heat capacity of a cyclic hydrocarbon is estimated by summing up group contributions developed for acyclic compounds and then adding a structural correction that is specific for the particular cyclic compound. As the corrections reflect the internal ring strain imposed on a molecule, they are denoted as ring strain corrections, or rsc. Table 3 lists all structural corrections that we have used together with typical sample group assignments.

2.4. Next-to-Nearest Neighbor Interactions

The second-order additivity method makes no allowance for next-to-nearest neighbor interactions. Some authors have found that such interactions have considerable influence on molecular properties and therefore included corrections to account for next-to-nearest neighbor interactions. The *gauche*, *cis*, and *ortho* corrections developed by Benson *et al.* (69BEN/CRU) or the methyl repulsion correction suggested by Domalski and Hearing (88DOM/HEA) are some examples of the approach.

It is worthwhile to include a correction for a next-to-nearest neighbor interaction if it accounts for a difference between observed and estimated molecular property that is almost equal in magnitude or larger than the uncertainty in the estimated values. When examining the recommended heat capacities taken from the compilation 93ZAB/RUZ, we have found that the largest differences in heat capacities of *cis* and *trans* isomers of alkenes and of saturated cyclic hydrocarbons and of *ortho*, *meta*, and *para* isomers of substituted benzene are approximately as large as the uncertainty of the present estimation method. For some compounds the differences in heat capacities of two isomers change in magnitude or even change from a positive to a negative value in the temperature interval where the data for both isomers are available. This is most probably due to an experimental error of the original data. Thus, we have not developed corrections for next-to-nearest neighbor interactions due to the lack of sufficiently accurate data.

TABLE 3. List of structural corrections

Structural correction	Sample group assignment
cyclopropane rsc	cyclopropane: 3 C-(H) ₂ (C) ₂ , 1 cyclopropane rsc
cyclobutane rsc	cyclobutane: 4 C-(H) ₂ (C) ₂ , 1 cyclobutane rsc
cyclopentane (unsub) rsc	cyclopentane: 5 C-(H) ₂ (C) ₂ , 1 cyclopentane (unsub) rsc
cyclopentane (sub) rsc	methylcyclopentane: 1 C-(H) ₃ (C), 4 C-(H) ₂ (C) ₂ , 1 C-(H)(C) ₃ , 1 cyclopentane (sub) rsc
cyclohexane rsc	cyclohexane: 6 C-(H) ₂ (C) ₂ , 1 cyclohexane rsc
cycloheptane rsc	cycloheptane: 7 C-(H) ₂ (C) ₂ , 1 cycloheptane rsc
cyclooctane rsc	cyclooctane: 8 C-(H) ₂ (C) ₂ , 1 cyclooctane rsc
spiropentane rsc	spiropentane: 4 C-(H) ₂ (C) ₂ , 1 C-(C) ₄ , 1 spiropentane rsc
cyclopentene rsc	cyclopentene: 1 C-(H) ₂ (C) ₂ , 2 C _d -(H)(C), 2 C-(H) ₂ (C)(C _d), 1 cyclopentene rsc
cyclohexene rsc	cyclohexene: 2 C-(H) ₂ (C) ₂ , 2 C _d -(H)(C), 2 C-(H) ₂ (C)(C _d), 1 cyclohexene rsc
cycloheptene rsc	cycloheptene: 3 C-(H) ₂ (C) ₂ , 2 C _d -(H)(C), 2 C-(H) ₂ (C)(C _d), 1 cycloheptene rsc
cyclooctene rsc	cyclooctene: 4 C-(H) ₂ (C) ₂ , 2 C _d -(H)(C), 2 C-(H) ₂ (C)(C _d), 1 cyclooctene rsc
cyclohexadiene rsc	1,3-cyclohexadiene: 2 C _d -(H)(C), 2 C _d -(H)(C _d), 2 C-(H) ₂ (C)(C _d), 1 cyclohexadiene rsc
cyclooctadiene rsc	1,5-cyclooctadiene: 4 C _d -(H)(C), 4 C-(H) ₂ (C)(C _d), 1 cyclooctadiene rsc
cycloheptatriene rsc	1,3,5-cycloheptatriene: 2 C _d -(H)(C), 4 C _d -(H)(C _d), 1 C-(H) ₂ (C) ₂ , 1 cycloheptatriene rsc
cyclooctatetraene rsc	1,3,5,7-cyclooctatetraene: 8 C _d -(H)(C _d), 1 cyclooctatetraene rsc
indan rsc	indan: 1 C-(H) ₂ (C) ₂ , 4 C _B -(H), 2 C _B -(C), 2 C-(H) ₂ (C)(C _B), 1 indan rsc
1H-indene rsc	1H-indene: 1 C _d -(H)(C), 1 C _d -(H)(C _d), 1 C-(H) ₂ (C) ₂ , 4 C _B -(H), 1 C _B -(C), 1 C _B -(C _d), 1 1H-indene rsc
tetrahydronaphthalene rsc	1,2,3,4-tetrahydronaphthalene: 2 C-(H) ₂ (C) ₂ , 4 C _B -(H), 2 C _B -(C), 2 C-(H) ₂ (C)(C _B), 1 tetrahydronaphthalene rsc
decahydronaphthalene rsc	decahydronaphthalene: 8 C-(H) ₂ (C) ₂ , 2 C-(H)(C) ₃ , 1 decahydronaphthalene rsc
hexahydroindan rsc	hexahydroindan: 7 C-(H) ₂ (C) ₂ , 2 C-(H)(C) ₃ , 1 hexahydroindan rsc
dodecahydrofluorene rsc	dodecahydro-9-methylfluorene: 1 C-(H) ₃ (C), 8 C-(H) ₂ (C) ₂ , 5 C-(H)(C) ₃ , 1 dodecahydrofluorene rsc
tetradecahydrophenanthrene rsc	tetradecahydrophenanthrene: 10 C-(H) ₂ (C) ₂ , 4 C-(H)(C) ₃ , 1 tetradecahydrophenanthrene rsc
hexadecahydropyrene rsc	3-ethylhexadecahydropyrene: 1 C-(H) ₃ (C), 10 C-(H) ₂ (C) ₂ , 7 C-(H)(C) ₃ , 1 hexadecahydropyrene rsc

3. Determination of Additivity Unit Values

A multiple linear least squares method has been used for the calculation of adjustable parameters in Eq. (2). The minimized objective function has the following form:

$$S = \sum_{j=1}^m w_j (C_j^{\text{rec}} - C_j^{\text{std}})^2 \quad (3)$$

where the subscript j denotes j -th data point, C_j^{rec} is the recommended liquid heat capacity, C_j^{std} is the estimated heat capacity. The weight, w_j , is equal to the reciprocal of the variance of the j -th data point $\sigma^2(C_j)$. It is estimated for each j -th value on the basis of the assumed accuracy of the recommended heat capacities. The input information is the percentage error of the recommended data, σ, C . Thus, the weight of the j -th data point is expressed as:

$$w_j = 1 / \left(\frac{C_j \cdot \sigma, C}{100} \right)^2 \quad (4)$$

The adjustable parameters were calculated by simultaneous minimization of the recommended heat capacities for families of structurally similar compounds in a series of five successive steps. In the first step, 16 group parameters were determined using selected data on 39 alkanes, alkenes including dienes, and alkynes. In all consecutive steps of the parameterization scheme, adjustable parameters were calculated for additivity units that occur in another family of compounds while the previously determined parameters were fixed. In the second step, 13 group parameters were calculated using selected data on 36 aromatic hydrocarbons including multi-ring hydrocarbons and biphenyls. In the third step, 8 structural corrections were determined using selected data on 24 mono-cycloalkanes. In the fourth step, 11 structural cor-

rections were calculated using selected data on 18 unsaturated cyclic hydrocarbons. In the last step, 5 structural corrections were determined using selected data on 16 perhydroindans, perhydronaphthalenes, perhydrofluorenes, perhydrophenanthrenes, and perhydropyrenes. The list of selected compounds is given in Table 4 together with the temperature ranges for the recommended data and literature references to sources of original data that served for the generation of recommended heat capacities. The adjustable parameters for the calculation of group contributions and structural corrections are given in Tables 5 and 6. The appendix gives a sample calculation for *n*-heptane at 300 K.

3.1. Database of Liquid Heat Capacities

The recommended heat capacities were obtained from an extensive compilation that contains all currently available calorimetrically measured heat capacities for over 1300 liquid organic compounds (88ZAB/RUZ, 93ZAB/RUZ). The compilation includes parameters of a smoothing equation obtained from a critical assessment of experimental data. Parameters are accompanied by a rating that represents the expected overall accuracy of the data. The rating was expressed as a percentage error and served as the input information for the calculation of weights in the least squares parameterization (see Eq. (4)).

A PC-version of the database that provides parameters of a smoothing equation, tables of heat capacities over a specified temperature interval, and enthalpy and entropy difference between two specified temperatures, will be available from the Standard Reference Data Program of the National Institute of Standards and Technology, Gaithersburg, Maryland.

TABLE 4. List of selected compounds used for the calculation of adjustable parameters

Compound	Temperature range/K	References
1st step of the parameterization scheme		
propane	81–230	38KEM/EGA, 65CUT/MOR, 78GOO
pentane	149–310	67MES/GUT, 75GRI/RAS, 88MEL/VER
hexane	180–400	31HUF/PAR, 46DOU/HUF2, 51CON/SAG, 69WIL/ROT, 75GRI/RAS, 76KAR/GRO, 80KAL/JED, 81GRO/ING, 82WIL/ING, 84BEN/DAR, 84BRA/PIN, 86BEN/DAR, 88MEL/VER, 88SAI/TAN
heptane	210–420	47OSB/GIN, 54DOU/FUR, 61HUF/GRO, 66KLE, 79SCH/OFF, 80KAL/JED, 87WIL/ING
octane	223–440	47OSB/GIN, 54FIN/GRO, 75GRI/RAS, 81GRO/ING, 84ROU/GRO, 85LAI/GRO, 86BEN/DAR
decane	247–462	54FIN/GRO, 75GRI/RAS, 84GRO/ING, 84ROU/GRO, 86GAT/WOO, 88KUZ/KHA
octadecane	300–379	49PAR/MOO, 67MES/GUT
2,2-dimethylbutane	177–366	46DOU/HUF2, 46KIL/PIT, 50AUE/SAG, 83BEN/DAR, 84BEN/DAR, 86BEN/DAR, 89OHN/FUJ
2-methylpentane	117–303	46DOU/HUF2, 83BEN/DAR, 84BEN/DAR, 86BEN/DAR
2,3-dimethylpentane	85–385	76FIN/MES
2,4-dimethylpentane	161–307	61HUF/GRO
3,3-dimethylpentane	147–351	76FIN/MES
3-ethylpentane	161–299	61HUF/GRO
2,2,3-trimethylbutane	253–313	61HUF/GRO
3,3-diethylpentane	243–365	76FIN/MES, 79FUC/PEA
2,2,3,3-tetramethylpentane	269–393	76FIN/MES

TABLE 4. List of selected compounds used for the calculation of adjustable parameters — Continued

Compound	Temperature range/K	References
2,2,4,4-tetramethylpentane	213–380	76FIN/MES
1-propene	93–250	31HUF/PAR, 39POW/GIA, 50AUE/SAG
1,2-butadiene	140–290	47AST/SZA
1,3-butadiene	165–300	45SCO/MEY
1-butyne	150–275	50AST/MAS
2-butyne	249–284	41YOS/OSB
1-butene	90–270	36TOD/PAR, 46AST/FIN, 49SCH/SAG
2-methyl-1-propene	139–253	36TOD/PAR
2-methyl-1,3-butadiene	130–304	37BEK/WOO, 70MES/TOD
3-methyl-1,2-butadiene	162–315	70MES/TOD
1,2-pentadiene	142–308	70MES/TOD
1,4-pentadiene	128–310	70MES/TOD
2,3-pentadiene	151–315	70MES/TOD
2-methyl-1-butene	140–293	47TOD/OLI
2-methyl-2-butene	141–301	30PAR/HUF, 47TOD/OLI
3-methyl-1-butene	111–298	47TOD/OLI
1-pentene	126–320	47TOD/OLI, 49SCH/SAG
3,3-dimethyl-1-butene	166–296	38KEN/SHO
1-hexene	136–308	57MCC/FIN1, 85KAL/WOY
1-heptene	157–300	57MCC/FIN1
1-octene	175–309	57MCC/FIN1
1-decene	211–356	57MCC/FIN1
2nd step of the parameterization scheme		
benzene	287–493	48OLI/EAT, 56DUF/EVE, 65FIN/GRU, 71KHA/SUB, 75RAS/GRI, 75SAN, 76FOR BEN2, 77WIL/GRO, 78GRO/WIL, 82GRO/ING, 82TAN, 82WIL/FAR, 85OGA/MUR, 85TAN, 87TAN, 89LAI/ROD
methylbenzene	162–503	62SCO/GUT, 66HWA/ZIE, 73AKH/EKS, 75HOL/ZIE, 75RAS/GRI, 76FOR/BEN1, 76SAN/MEL, 77WIL/GRO, 79AND/GRI, 82GRO/ING, 82WIL/FAR, 86ROU/GRO
ethynylbenzene	228–330	31SMI/AND, 82LEB/BYK
ethenylbenzene	247–353	46PIT/GUT, 50KUR
1,2-dimethylbenzene	252–463	43PIT/SCO, 75RAS/GRI, 79FOR/BEN
1,3-dimethylbenzene	231–540	43PIT/SCO, 75RAS/GRI, 75SAN
1,4-dimethylbenzene	288–573	47COR/GIN, 75RAS/GRI, 79FOR/BEN, 79OTT/GOA, 88MES/FIN
ethylbenzene	178–393	44GUT/SPI, 45SCO/BRI, 76FOR/BEN2, 79AND/GRI, 79FOR/BEN, 83GRO/FAR1
1-methylethylbenzene	180–413	52SCH/SAG, 73KIS/SUG, 79AND/GRI
propylbenzene	181–371	48TSC, 65MES/TOD2, 83GRO/FAR2
1,2,3-trimethylbenzene	250–301	55TAY/JOH
1,2,4-trimethylbenzene	230–430	57PUT/KIL, 79AND/GRI
1,3,5-trimethylbenzene	230–424	55TAY/KIL, 77FOR/BEN, 79AND/GRI, 79WIL/FAR
butylbenzene	194–370	65MES/TOD2, 83GRO/FAR3
(1,1-dimethylethyl)benzene	220–294	30HUF/PAR
1-methyl-4-(1-methylethyl)benzene	211–356	31HUF/PAR, 47KUR
(1-methylpropyl)benzene	294–430	79AND/GRI
1,1'-methylenebisbenzene	302–353	30HUF/PAR, 31SMI/AND, 56DUF/EVE
1,1'-(1,2-ethyenediyl)bisbenzene	365–553	50KUR
(E)-1,1'-(1,2-ethenediyl)bisbenzene	403–553	33FER/THO, 50KUR
1,1'-(1,2-ethanediy)bisbenzene	324–472	33FER/THO, 41SCH, 50KUR, 88MES/FIN
1,1',1''-methylidenetrisbenzene	373–596	32SPA/THO, 50KUR
naphthalene	353–473	41SCH, 57MCC/FIN2
1-methylnaphthalene	248–352	57MCC/FIN2
2-methylnaphthalene	310–367	31HUF/PAR, 57MCC/FIN2
1,1'-biphenyl	350–589	32SPA/THO, 56MCE, 58WAL/BRO, 83ORO/MRA
1,8-dimethylnaphthalene	350–432	77FIN/MES
2,3-dimethylnaphthalene	385–415	88MES/FIN
2,6-dimethylnaphthalene	390–438	77FIN/MES
2,7-dimethylnaphthalene	373–391	77FIN/MES
phenanthrene	371–471	41SCH, 77FIN/MES
(1-methylethyl)-1,1'-biphenyl	293–671	56MCE, 63VAR/KOP, 64VUK/RAS
fluoranthene	386–452	71WON/WES
pyrene	431–479	71WON/WES
triphenylene	481–510	71WON/WES
1-(2-naphthalenylmethyl)naphthalene	343–423	77FIN/MES

TABLE 4. List of selected compounds used for the calculation of adjustable parameters – Continued

Compound	Temperature range/K	References
3rd step of the parameterization scheme		
cyclopropane	154–243	46RUE/POW
cyclobutane	185–285	53RAT/GWI
methylenecyclobutane	140–301	78LEB/TSV, 81FIN/MES
cyclopentane	180–300	46DOU/HUF1, 47SZA/MOR, 79FOR/DAR, 85TAN
methylcyclopentane	136–366	46DOU/HUF1, 51CON/SAG
1,1-dimethylcyclopentane	206–300	53GRO/OLI
<i>cis</i> -1,2-dimethylcyclopentane	223–303	53GRO/OLI
<i>trans</i> -1,3-dimethylcyclopentane	144–304	53GRO/OLI
ethylcyclopentane	140–302	53GRO/OLI
propylcyclopentane	162–365	65MES/TOD1
butylcyclopentane	168–368	65MES/TOD1
cyclohexane	282–380	43RUE/HUF, 50AUE/SAG, 64MOE/THO, 66KLE, 74WIL/ZET, 75JOL/BOI, 75SAN, 78GRO/WIL, 78SAF, 79FOR/DAR, 79WIL/GRO, 82GRO/ING, 82TAN, 85NKI/CHA, 85TAN/NAK
methylcyclohexane	144–309	46DOU/HUF1, 66HWA/ZIE, 75HOL/ZIE, 79WIL/GRO, 82GRO/ING, 85TAN
1,1-dimethylcyclohexane	243–304	49HUF/TOD
<i>cis</i> -1,3-dimethylcyclohexane	204–299	49HUF/TOD
<i>trans</i> -1,3-dimethylcyclohexane	188–299	49HUF/TOD
propylcyclohexane	186–373	65FIN/MES
butylcyclohexane	208–365	65FIN/MES
(1,1-dimethylethyl)cyclohexane	313–423	63GUD/CAM
1,2-dicyclohexylethane	313–483	63GUD/CAM
1,2-dicyclohexylpropane	313–483	62GOL/BEL, 63GUD/CAM
cycloheptane	269–300	56FIN/SCO, 75JOL/BOI, 79FOR/DAR
cyclooctane	294–322	56FIN/SCO, 79FOR/DAR, 85TAN
spiropentane	176–312	50SCO/FIN
4th step of the parameterization scheme		
cyclopentene	141–301	48HUF/EAT
1,3-cyclohexadiene	170–300	76GIE/WOL
1,4-cyclohexadiene	230–300	76GIE/WOL
cyclohexene	171–301	48HUF/EAT, 77HAI/SUG
1,3,5-cycloheptatriene	202–312	56FIN/SCO
(<i>Z</i>)-cycloheptene	219–303	89LEB/SMI
4-methylcyclohexene	161–321	88LEB/KUL
1,3,5,7-cyclooctatetraene	273–328	49SCO/GRO
1,5-cyclooctadiene	207–320	75LEB/TSV
cyclooctene	262–328	78LEB/LEB
1H-indene	280–375	61STU/SIN, 65ZIE
2,3-dihydroindene	240–320	61STU/SIN
1,2,3,4-tetrahydronaphthalene	248–319	57MCC/FIN2
1,1-dimethylindan	236–389	81LEE/FIN
4,6-dimethylindan	262–370	81LEE/FIN
4,7-dimethylindan	286–394	81LEE/FIN
1,1,4,6-tetramethylindan	286–378	81LEE/FIN
1,1,4,7-tetramethylindan	170–376	81LEE/FIN
5th step of the parameterization scheme		
<i>cis</i> -octahydro-1H-indene	239–367	72FIN/MCC
<i>trans</i> -octahydro-1H-indene	212–391	72FIN/MCC
ethyloctahydro-1H-indene	311–423	62GOL/BEL, 63GUD/CAM
octahydro(1-methylethyl)-1H-indene	311–423	62GOL/BEL, 63GUD/CAM
<i>cis</i> -decahydronaphthalene	234–423	57MCC/FIN2, 63GUD/CAM, 88SHI/OGA, 89OHN/FUJ
<i>trans</i> -decahydronaphthalene	249–413	53SEFY, 57MCC/FIN2, 88SHI/OGA, 89OHN/FUJ
decahydrodimethylnaphthalene	313–483	63GUD/CAM
ethyldecahydronaphthalene	313–483	63GUD/CAM
decahydro-1-(1-methylethyl)naphthalene	311–483	62GOL/BEL, 63GUD/CAM
decahydro-1-propylnaphthalene	311–483	62GOL/BEL, 63GUD/CAM
dodecahydro-9-methyl-1H-fluorene	313–483	63GUD/CAM
9-(2-ethylhexyl)dodecahydrofluorene	313–483	63GUD/CAM
tetradecahydrophenanthrene	313–483	63GUD/CAM
2-ethyltetradecahydrophenanthrene	313–483	63GUD/CAM
3-ethylhexahydropyrene	311–422	62GOL/BEL
diethylhexadecahydropyrene	313–483	63GUD/CAM

TABLE 5. Parameters for the dependence of group contribution Δc_i on temperature, $\Delta c_i = a_i + b_i(T/100) + d_i(T/100)^2$, T/K

Group	Adjustable parameters			Temperature range, K
	a_i	b_i, K^{-1}	d_i, K^{-2}	
C-(H) ₃ (C)	3.8452	-3.3997E-1 ^a	1.9489E-1	80-490
C-(H) ₂ (C) ₂	2.7972	-5.4967E-2	1.0679E-1	80-490
C-(H)(C) ₃	-4.2867E-1	9.3805E-1	2.9498E-3	85-385
C-(C) ₄	-2.9353	1.4255	-8.5271E-2	145-395
C _d -(H) ₂	4.1763	-4.7392E-1	9.9928E-2	90-355
C _d -(H)(C)	4.0749	-1.0735	2.1413E-1	90-355
C _d -(C) ₂	1.9570	-3.1938E-1	1.1911E-1	140-315
C _d -(H)(C _d)	3.6968	-1.6037	5.5022E-1	130-305
C _d -(C)(C _d) ^b	1.0679	-5.0952E-1	3.3607E-1	130-305
C-(H) ₂ (C)(C _d)	2.0268	2.0137E-1	1.1624E-1	90-355
C-(H)(C) ₂ (C _d) ^b	-8.7558E-1	8.2109E-1	1.8415E-1	110-300
C-(C) ₃ (C _d) ^b	-4.8006	2.6004	-4.0688E-2	165-295
C-(H) ₂ (C _d) ₂ ^b	1.4973	-4.6017E-1	5.2861E-1	130-300
C _r -(H) ^b	9.1633	-4.6695	1.1400	150-275
C _r -(C)	1.4822	1.0770	-1.9489E-1	150-285
C _a	3.0880	-6.2917E-1	2.5779E-1	140-315
C _r -(C _B)	1.2377E+1	-7.5742	1.3760	230-550
C _B -(H)	2.2609	-2.5000E-1	1.2592E-1	180-670
C _B -(C)	1.5070	-1.3366E-1	1.1799E-2	180-670
C _B -(C _d)	-5.7020	5.8271	-1.2013	230-550
C _B -(C _B)	5.8685	-8.6054E-1	-6.3611E-2	295-670
C-(H) ₂ (C)(C _B)	1.4142	5.6919E-1	5.3465E-3	180-470
C-(H)(C) ₂ (C _B)	-1.0495E-1	1.0141	-7.1918E-2	180-670
C-(C) ₃ (C _B) ^b	1.2367	-1.3997	4.1385E-1	220-295
C-(H) ₂ (C _B) ₂	-1.8583E+1	1.1344E+1	-1.4108	300-420
C-(H)(C _B) ₃ ^b	-4.6611E+1	2.4987E+1	-3.0249	375-595
C _{BF} -(C _{BF})(C _B) ₂	-3.5572	2.8308	-3.9125E-1	250-510
C _{BF} -(C _{BF}) ₂ (C _B)	-1.1635E+1	6.4068	-7.8182E-1	370-510
C _{BF} -(C _{BF}) ₃	2.6164E+1	-1.1353E+1	1.2756	385-480

^aParameter values given in the E notation. The first part of the number denotes the fractional part which is followed by the exponent to the base 10 (e.g. -3.3997E-1 means $-3.3997 \cdot 10^{-1}$).

^bAdjustable parameters were calculated from heat capacity data on a single compound only.

4. Results and Discussion

An extensive evaluation of the present method was made by comparing recommended heat capacities and those estimated using additive contributions reported here. The recommended heat capacities were taken from the compilation 93ZAB/RUZ. A total of 265 hydrocarbons and almost 4000 data points were included in these comparisons. Deviations between recommended and estimated values were calculated for the temperature range from the lower limit of the recommended data up to the normal boiling temperature or up to the upper limit of the recommended data if it lies below the normal boiling temperature. If the recommended data extend above the normal boiling temperature, a second set of deviations was determined using data for the entire temperature range. The standard deviation and average absolute percent deviation are given for each compound in Tables 7 to 13 where compounds were divided according to their molecular structures into the following families: *n*-alkanes, branched alkanes, alkenes, dienes, cycloalkanes, unsaturated cyclic hydrocarbons, and aromatic hydrocarbons.

We have also made comparisons using group contribution parameters developed by Luria and Benson

(77LUR/BEN). The comparisons involved a smaller set of compounds than that mentioned previously as we determined 11 more group contributions and 10 more structural corrections than reported by 77LUR/BEN. In addition, we found that there is apparently an error in parameter values for the C-(H)₂(C)(C_d) group given by 77LUR/BEN as deviations between recommended and estimated heat capacities are extremely high for hydrocarbons containing the C-(H)₂(C)(C_d) group in their molecular structure. Another indication of an erroneous value of parameters for the C-(H)₂(C)(C_d) group is that group values are large and negative in the entire temperature range. By contrast none of the group contribution values that we determined is negative, and the same is true for the group contribution values for the liquid heat capacity at 25 °C reported by 88DOM/HEA. The summary deviations between the recommended and estimated values using the parameters by 77LUR/BEN given separately for almost all families of hydrocarbons are given in Table 14. In this table, the summary deviations calculated using group values developed in this work are also presented for identical sets of compounds. As we determined parameters for more additivity units than presented by 77LUR/BEN, Table 14 also includes summary deviations for the entire families of hydrocarbons.

TABLE 6. Parameters for the dependence of structural correction Δc_i on temperature, $\Delta c_i = a_i + b_i(T/100) + d_i(T/100)^2$, T/K

Structural correction	Adjustable parameters			Temperature range, K
	a_i	b_i, K^{-1}	d_i, K^{-2}	
cyclopropane rsc ^b	4.4297	-4.3392	1.0222	155-240
cyclobutane rsc	1.2313	-2.8988	7.5099E-1 ^a	140-300
cyclopentane (unsub) rsc ^b	-3.3642E-1	-2.8663	7.0123E-1	180-300
cyclopentane (sub) rsc	2.1983E-1	-1.5118	2.3172E-1	135-365
cyclohexane rsc	-2.0097	-7.2656E-1	1.4758E-1	145-485
cycloheptane rsc ^b	-1.1460E+1	4.9507	-7.4754E-1	270-300
cyclooctane rsc ^b	-4.1696	5.2991E-1	-1.8423E-2	295-320
spiropentane rsc ^b	5.9700	-3.7965	7.4612E-1	175-310
cyclopentene rsc ^b	2.1433E-1	-2.5214	6.3136E-1	140-300
cyclohexene rsc	-1.2086	-1.5041	4.2863E-1	160-320
cycloheptene rsc ^b	-5.6817	1.5073	-1.9810E-1	220-300
cyclooctene rsc ^b	-1.4885E+1	7.4878	-1.10879	260-330
cyclohexadiene rsc	-8.9683	6.4959	-1.5272	170-300
cyclooctadiene rsc ^b	-7.2890	3.1119	-4.3040E-1	205-320
cycloheptatriene rsc ^b	-8.7885	8.2530	-2.4573	200-310
cyclooctatetraene rsc ^b	-1.2914E+1	1.3583E+1	-4.0230	275-330
indan rsc	-6.1414	3.5709	-4.8620E-1	170-395
1H-indene rsc ^b	-3.6501	2.4707	-6.0531E-1	280-375
tetrahydronaphthalene rsc ^b	-6.3861	2.6257	-1.9578E-1	250-320
decahydronaphthalene rsc	-6.8984	6.6846E-1	-7.0012E-2	235-485
hexahydroindan rsc	-3.9271	-2.9239E-1	4.8561E-2	210-425
dodecahydrofluorene rsc	-1.9687E+1	8.8265	-1.4031	315-485
tetradecahydrophenanthrene rsc	-6.7632E-1	-1.4753	-1.3087E-1	315-485
hexadecahydropyrene rsc	6.1213E+1	-3.0927E+1	3.2269	310-485

^aParameter values given in the E notation. The first part of the number denotes the fractional part which is followed by the exponent to the base 10 (e.g. -3.3997E-1 means $-3.3997 \cdot 10^{-1}$).

^bAdjustable parameters were calculated from heat capacity data on a single compound only.

An additional comparison of the present method with the method developed by Lee and Kesler (75LEE/KES) has been made. The Lee-Kesler method is a generalized corresponding states method that requires data for the critical temperature, critical pressure, acentric factor, and the heat capacity of the ideal gas for the estimation of the heat capacity of vapor and liquid phase as a function of temperature. We have included several representative compounds from each family in the comparison. The input data required for the application of the Lee-Kesler method were taken from the following sources. Critical properties and acentric factors were obtained from the database of physico-chemical properties of pure compounds CDATA (92RUZ/LAB) that contains recommended values based on the critical evaluation of a wide range of literature sources and includes also some estimated values. The heat capacity of the ideal gas was taken from the compilation by Bureš *et al.* (87BUR/HOL) that presents the heat capacity as a function of temperature in an analytical form. Several reliable data compilations were used to develop the parameters of correlating equations given in 87BUR/HOL. Deviations between the recommended and the estimated heat capacities for individual compounds are given in Tables 7 to 13. Table 15 presents a comparison of the summary deviations calculated for the present group contribution method and the generalized Lee-Kesler method. Deviations are compared for identical sets of compounds belonging to different families. A slightly smaller number of

data points that were included in the evaluation of the Lee-Kesler method is due to convergence problems in the calculation of density in the proximity of the critical point. Generally, in contrast to the present group contribution method, deviations for the Lee-Kesler method are significantly larger in the range from the low temperature limit to the normal boiling temperature than in the entire temperature range of data. An example of the agreement between the recommended and the estimated liquid heat capacity is demonstrated in Fig. 1 for 1-pentene.

4.1. *n*-Alkanes

The heat capacity data on *n*-alkanes are the most abundant with regard to the number of members within a family, the temperature range that these data cover, and measurements by different authors. The *n*-alkanes exhibit the most typical dependence of the heat capacity with temperature. For the majority of *n*-alkanes, the first derivative of the heat capacity with respect to temperature is positive over the entire liquid region. For some members of this homologous series, in particular C₁ to C₃, C₅ to C₇, and C₉, a shallow minimum located a few degrees above the melting temperature is observed in very precise measurements. The present method does not account for the initial almost flat part of the curve and predicts a monotonically increasing heat capacity with temperature.

The heat capacity of methane cannot be predicted using the proposed method whereas the prediction for

TABLE 7. Deviations between recommended and estimated heat capacities of *n*-alkanes. Numbers of data points and values of standard and average deviations in parentheses apply to data up to the normal boiling temperature only. Temperature and heat capacity ranges correspond to the entire range of available data. Recommended data are from Záborský *et al.* (93ZAB/RUZ)

Compound	No. data points	Std.dev. ^a J·K ⁻¹ mol ⁻¹	Avg. dev. ^b %	Temp. range, K	Heat capacity range, J·K ⁻¹ mol ⁻¹	Avg. dev. ^c (Lee-Kesler) %
ethane	22 (10)	35.9 (7.4)	19.3 (10.6)	91–298	68–211	5.3 (8.0)
propane	22 (16)	4.5 (1.7)	2.8 (1.4)	81–289	84–115	10.6 (14.7)
butane	26 (15)	9.1 (2.5)	4.3 (2.0)	140–365	113–179	3.2 (4.6)
<i>n</i> -pentane	28 (18)	4.0 (2.4)	1.8 (1.3)	149–380	142–200	3.1 (4.1)
<i>n</i> -hexane	31 (18)	3.9 (1.7)	1.3 (0.7)	180–463	171–273	1.8 (2.3)
<i>n</i> -heptane	36 (20)	12.0 (3.7)	1.5 (1.0)	183–520	203–408	2.0 (2.9)
<i>n</i> -octane	27 (19)	2.8 (1.8)	0.7 (0.5)	223–462	233–342	1.2 (1.3)
<i>n</i> -nonane	12 (12)	4.2	1.0	225–314	265–292	2.3
<i>n</i> -decane	25 (22)	6.3 (5.1)	1.4 (1.2)	247–462	297–416	1.2 (1.2)
<i>n</i> -undecane ^d	21 (21)	8.2	1.6	252–433	330–424	1.5
<i>n</i> -dodecane	8 (8)	4.6	1.0	267–317	364–386	2.7
<i>n</i> -tridecane	5 (5)	6.3	1.4	272–306	397–411	3.7
<i>n</i> -tetradecane	18 (18)	14.4	2.3	283–433	432–527	1.8
<i>n</i> -pentadecane	6 (6)	7.5	1.5	285–313	465–478	4.1
<i>n</i> -hexadecane	14 (14)	15.1	2.0	298–413	502–574	2.2
<i>n</i> -heptadecane	10 (10)	7.4	1.1	302–384	535–597	2.2
<i>n</i> -octadecane	9 (9)	7.5	1.1	300–379	567–626	2.6
<i>n</i> -nonadecane	17 (17)	22.5	2.4	305–453	595–729	1.6
<i>n</i> -eicosane	9 (9)	13.9	2.0	325–400	653–748	4.8
<i>n</i> -heneicosane	14 (14)	25.0	2.7	316–433	666–776	1.3
<i>n</i> -docosane	16 (16)	23.9	2.2	318–453	702–845	2.0
<i>n</i> -tricosane	14 (14)	20.7	1.9	321–445	735–877	
<i>n</i> -tetracosane	15 (15)	29.0	2.5	324–453	771–915	
<i>n</i> -pentacosane	6 (6)	4.9	0.5	333–373	816–865	
<i>n</i> -hexacosane	15 (15)	25.2	2.2	329–454	847–1005	
<i>n</i> -octacosane	14 (14)	29.8	2.2	334–453	912–1072	
<i>n</i> -triacontane	1 (1)	33.7	3.3	339–339	1008–1008	5.0
<i>n</i> -dotriacontane ^e	14 (14)	155.0	13.9	350–475	994–1131	
<i>n</i> -tritriacontane	5 (5)	9.1	0.7	353–383	1113–1152	
<i>n</i> -tetratriacontane	13 (13)	26.6	1.7	346–452	1138–1313	
<i>n</i> -hexatriacontane	17 (17)	83.7	4.8	349–500	1201–1417	
<i>n</i> -tetracontane	2 (2)	72.1	5.1	355–363	1414–1414	
<i>n</i> -dotetracontane	12 (12)	21.4	1.3	357–454	1433–1654	
<i>n</i> -octatetracontane	11 (11)	56.4	2.6	363–452	1618–1818	

^aStandard deviation is calculated as

$$SD = \sqrt{\frac{1}{n_p} \sum (C^{rec} - C^{estd})^2}$$

where n_p is the number of data points (usually 10 K apart).

^bAverage absolute percent deviation is calculated as

$$APD = 100 \cdot \frac{1}{n_p} \sum \left| \frac{C^{rec} - C^{estd}}{C^{rec}} \right|$$

^cAverage absolute percent deviation calculated by the above equation between the recommended heat capacities and those estimated by the Lee-Kesler method (75LEE/KES).

^dFor all *n*-alkanes higher than *n*-decane no experimental data above the normal boiling temperature are available.

^eData are uncertain, possibly subject to a systematic error.

ethane is poor with an average percent deviation of 11% in the range from the melting temperature to the normal boiling temperature. Past experience shows that first members of homologous series often do not conform easily to a group additivity in comparison to other members. We have thus not included data on ethane in the basic data set used to calculate parameters despite the fact that there are extensive accurate measurements of the heat capacity of this compound over almost the entire vapor-liquid saturation region.

Deviations between observed and estimated heat capacities for all *n*-alkanes are given in Table 7. Deviations slightly higher than the average, reaching a maximum value of about 6 %, have been found for almost all *n*-alkanes starting with undecane at temperatures above 400 K. The deviations are almost constant for all higher *n*-alkanes thus indicating that the dependence of a group contribution on the length of the carbon chain would not result in an improved estimation of the heat capacity. The use of 4 adjustable parameters in Eq. (2) to describe the

TABLE 8. Deviations between recommended and estimated heat capacities of branched alkanes. Numbers of data points and values of standard and average deviations in parentheses apply to data up to the normal boiling temperature only. Temperature and heat capacity ranges correspond to the entire range of available data. Recommended data are from Zábanský *et al.* (93ZAB/RUZ)

Compound	No. data points	Std. dev. ^a J·K ⁻¹ mol ⁻¹	Avg. dev. ^a %	Temp. range, K	Heat capacity range, J·K ⁻¹ mol ⁻¹	Avg. dev. ^b (Lee-Kesler) %
2-methylpropane	29 (16)	12.8 (3.8)	6.0 (3.1)	115–378	100–195	3.8 (5.6)
2,2-dimethylpropane	4 (4)	10.4	6.6	258–279	152–162	1.1
2-methylbutane	21 (21)	1.8	1.2	114–298	123–165	6.5
2,2-dimethylbutane	22 (17)	2.7 (2.9)	1.6 (1.7)	177–367	150–219	1.3 (1.7)
2,3-dimethylbutane	18 (18)	2.5	1.4	147–307	145–192	8.7
2-methylpentane	21 (21)	0.3	0.2	117–303	147–196	6.2
3-methylpentane	24 (24)	2.0	1.0	119–327	146–202	6.3
2,2-dimethylpentane	17 (17)	3.2	1.3	155–298	165–221	1.9
2,3-dimethylpentane	33 (30)	4.4 (3.5)	1.7(1.5)	85–385	156–259	5.9 (6.7)
2,4-dimethylpentane	16 (16)	2.2	1.0	161–307	170–229	8.4
3,3-dimethylpentane	24 (24)	1.1	0.5	147–351	166–240	3.6
3-ethylpentane	16 (16)	3.5	1.8	161–299	174–220	3.1
2-methylhexane	16 (16)	0.9	0.4	160–301	181–224	3.0
3-methylhexane	21 (21)	2.6	1.3	91–289	166–216	6.8
2,2,3-trimethylbutane	9 (9)	1.0	0.4	253–313	194–220	1.5
3,3-dimethylhexane	2 (2)	3.7	1.2	291–306	247–255	1.5
2,5-dimethylhexane	6 (6)	2.1	0.8	286–313	242–257	0.4
2-methylheptane	22 (22)	2.4	0.8	178–370	213–288	10.4
3-methylheptane	25 (25)	3.1	1.0	157–376	204–289	10.7
4-methylheptane	6 (6)	2.0	0.7	287–313	244–259	0.8
2,2,3,3-tetramethylbutane	2 (2)	5.3	1.9	375–378	280–282	
2,2,4-trimethylpentane	22 (22)	5.9	2.2	171–366	186–274	2.8
2,3,3-trimethylpentane	2 (2)	3.8	1.3	291–306	246–253	1.0
2,3,4-trimethylpentane	18 (18)	4.6	1.6	173–324	190–276	
3,3-diethylpentane	15 (15)	3.2	1.0	243–365	246–320	
2,2,3,3-tetramethylpentane	16 (16)	4.0	1.3	269–393	255–327	
2,2,4,4-tetramethylpentane	19 (19)	2.7	0.6	213–380	221–315	
2,7-dimethyloctane	8 (8)	3.5	0.9	223–295	269–299	
2-methylnonane	10 (10)	5.6	1.4	200–298	279–309	
3-methylnonane	11 (11)	2.5	0.8	190–298	263–305	1.4
4-methylnonane	12 (12)	2.7	0.9	180–298	264–315	2.2
5-methylnonane	11 (11)	1.0	0.3	190–298	265–311	1.8
2-methyldecane	18 (18)	4.2	1.0	235–385	313–396	
11-decyloheicosane	2 (2)	13.3	1.4	282–298	927–938	

^a Standard deviation and average absolute percent deviation defined in Table 7.

^b See footnote c at the bottom of Table 7.

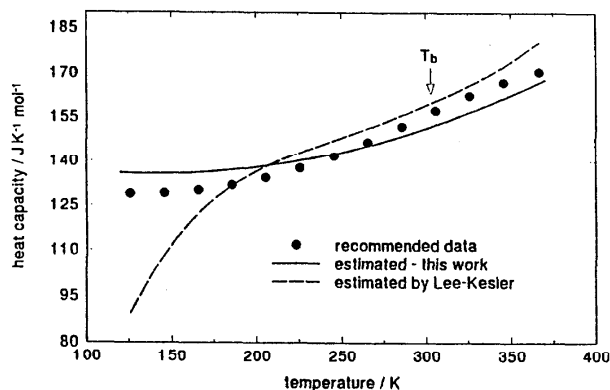


Fig. 1. The agreement between the recommended and the estimated liquid heat capacities of 1-pentene. The recommended data are from Zábanský *et al.* (93ZAB/RUZ).

dependence of Δc_p on temperature does not lead to substantially better predictions at higher temperatures as well. The most plausible explanation lies in the selection of compounds used for the calculation of adjustable parameters. The set of selected compounds (see Table 4) contains predominantly short-chain hydrocarbons simply because there are no data available for long-chain hydrocarbons other than *n*-alkanes.

4.2. Branched Alkanes

Deviations in the family of branched alkanes are in general low (Table 8). There are no data for branched alkanes higher than C₁₀ except for 2-methyldecane and 11-decyloheicosane. Somewhat larger deviations for two compounds, 2-methylpropane and 2,2-dimethylpropane, can be possibly explained by a methyl repulsion for a ternary and quaternary carbon atoms. The methyl repulsion correction was proposed and applied to the estimation of enthalpies of formation of substituted alkanes by

TABLE 9. Deviations between recommended and estimated heat capacities of alkenes. Numbers of data points and values of standard and average deviations in parentheses apply to data up to the normal boiling temperature only. Temperature and heat capacity ranges correspond to the entire range of available data. Recommended data are from Záborský *et al.* (93ZAB/RUZ)

Compound	No. data points	Std. dev. ^a J·K ⁻¹ mol ⁻¹	Avg. dev. ^a %	Temp. range, K	Heat Capacity range, J·K ⁻¹ mol ⁻¹	Avg. dev. ^c (Lee-Kesler) %
ethene	8 (8)	6.0	8.9	107-169	69-67	2.9
1-propene	28 (14)	15.3 (2.2)	7.8 (1.9)	93-344	92-152	10.1 (12.1)
1-butene	31 (19)	9.1 (1.9)	4.2 (1.5)	90-366	109-163	9.1 (14.4)
(E)-2-butene	12 (12)	2.7	1.9	171-271	111-122	4.7
(Z)-2-butene	26 (15)	8.8 (0.9)	3.6 (0.6)	134-366	114-163	5.6 (6.6)
2-methyl-1-propene	14 (14)	2.7	1.8	139-253	107-121	4.7
2-methyl-1-butene	16 (16)	2.6	1.8	140-293	133-155	
2-methyl-2-butene	18 (18)	1.6	1.1	141-301	133-154	
3-methyl-1-butene ^b	21 (19)	0.1 (0.1)	0.1 (0.1)	111-298	121-156	
1-pentene	27 (20)	2.9 (2.8)	1.9 (1.8)	126-366	129-170	5.7 (6.6)
(E)-2-pentene	19 (19)	3.3	2.0	135-302	128-158	
(Z)-2-pentene	18 (18)	2.4	1.6	129-295	133-150	
2,3-dimethyl-2-butene	14 (14)	10.2	6.1	204-318	154-181	1.3
3,3-dimethyl-1-butene ^b	14 (14)	0.3	0.2	166-296	144-186	
1-hexene	20 (20)	2.4	1.4	136-308	154-187	14.1
1-heptene	17 (17)	2.0	0.9	157-300	181-212	4.1
1-octene	16 (16)	1.4	0.5	175-309	213-245	3.4
2,4,4-trimethyl-1-pentene	13 (13)	0.6	0.2	178-296	190-232	
2,4,4-trimethyl-2-pentene	15 (15)	7.3	2.8	170-299	192-236	
1-decene	17 (17)	2.2	0.4	211-356	276-329	2.3
1-undecene	12 (12)	3.4	0.6	227-311	308-337	
1-dodecene	8 (8)	4.2	0.8	240-306	342-364	3.2
1-hexadecene	5 (5)	8.5	1.7	279-304	477-488	

^a Standard deviation and average absolute percent deviation defined in Table 7.

^b The heat capacity values for the compound were used as a single source of data to determine the adjustable parameters.

^c See footnote c at the bottom of Table 7.

TABLE 10. Deviations between recommended and estimated heat capacities of dienes. Numbers of data points and values of standard and average deviations in parentheses apply to data up to the normal boiling temperature only. Temperature and heat capacity ranges correspond to the entire range of available data. Recommended data are from Záborský *et al.* (93ZAB/RUZ)

Compound	No. data points	Std. dev. ^a J·K ⁻¹ mol ⁻¹	Avg. dev. ^b %	Temp. range, K	Heat capacity range, J·K ⁻¹ mol ⁻¹	Avg. dev. ^c (Lee-Kesler) %
1,2-butadiene	16 (15)	1.7 (1.5)	1.2 (1.0)	140-290	110-123	
1,3-butadiene	16 (11)	0.0 (0.0)	0.0 (0.0)	165-300	103-125	2.1 (2.7)
2-methyl-1,3-butadiene ^b	19 (19)	0.3	0.2	130-304	123-153	7.7 (7.7)
3-methyl-1,2-butadiene	18 (17)	0.3 (0.3)	0.2 (0.2)	162-315	131-157	
1,2-pentadiene	18 (18)	0.2	0.1	142-308	131-153	
(E)-1,3-pentadiene	16 (15)	3.7 (3.4)	2.0 (1.8)	189-316	130-155	
(Z)-1,3-pentadiene	21 (21)	5.1	2.8	138-316	130-152	
1,4-pentadiene ^b	20 (19)	0.2 (0.2)	0.1 (0.1)	128-301	128-148	
2,3-pentadiene	19 (19)	1.7	1.1	151-315	136-156	
1,5-hexadiene	3 (3)	8.4	4.7	297-310	175-180	

^a Standard deviation and average absolute percent deviation defined in Table 7.

^b The heat capacity values for the compound were used as a single source of data to determine the adjustable parameters.

^c See footnote c at the bottom of Table 7.

Domalski and Hearing (88DOM/HEA). However, we do not observe a similar behavior in other branched hydrocarbons that is exemplified by unusual deviations between the recommended and estimated heat capacities of 2-methylpropane and 2,2-dimethylpropane as well as for other branched alkanes. We reject the possibility of explaining the large deviations by the poor quality of the data as the data for both compounds come from reliable sources (2-methylpropane: 37PAR/SHO, 38SAG/LAC, 40AST/KEN; 2,2-dimethylpropane: 36AST/MES, 69ENO/SHI).

4.3. Alkenes and Dienes

Testing of the present method in the family of alkenes and dienes (Tables 9 and 10) shows that the estimated heat capacities agree well with the recommended data with a few exceptions. Large deviations for ethene, 1-propene, and 1-butene can be explained by an unusual dependence of the heat capacity with temperature that exhibits a rather deep minimum which is shifted more than 50 K above the melting temperature (92ZAB/BUR).

4.4. Alkynes

The heat capacities of liquid alkynes as a function of temperature are available for two compounds only, 1-butyne and 2-butyne. The compounds have been used for the determination of group contributions; therefore, they are not reported in tables of deviations between the recommended and estimated heat capacities.

4.5. Saturated Cyclic Hydrocarbons

The heat capacity data in the family of saturated cyclic hydrocarbons are quite abundant. The family includes data for a large number of compounds that contain up to 27 carbon atoms in the molecule. To account for the difference in the ring strain correction for the unsubstituted and substituted cyclopentane, we followed the approach by 88DOM/HEA and developed two sets of parameters. Somewhat larger deviations for some high molecular weight cycloalkanes may be attributed either to poor quality of the data as recommended data for many of these compounds are rated as medium quality in the compilation 93ZAB/RUZ, or to a model deficiency.

4.6. Unsaturated Cyclic Hydrocarbons

The deviations for unsaturated cyclic hydrocarbons reported in Table 12 are very low because, due to the limited amount of available data, many compounds have been used as a single source of data to determine the structural corrections.

4.7. Aromatic Hydrocarbons

Aromatic hydrocarbons including multi-ring hydrocarbons conform to the additivity rules well as is demon-

strated by the small deviations given in Table 13. Slightly larger deviations for 1,2,3,4-tetramethylbenzene might be attributed to a lower quality of data in particular at temperatures above 300 K, where data from only a single source (47KUR) are available. The heat capacity of 5'-phenyl-1,1':3',1''-terphenyl was measured in a single laboratory only, 82LEB/BYK. As heat capacities of other terphenyls are predicted well, we suspect that these data may have a higher uncertainty than originally expected and found for 5'-phenyl-1,1':3',1''-terphenyl in Table 13.

5. Conclusion

Parameters for a group contribution method that permits estimation of heat capacities of liquid hydrocarbons have been determined. Summation of group contributions and structural corrections represented by a second order polynomial enables one to obtain an analytical expression for the heat capacity as a function of temperature. The method is applicable for the estimation of heat capacities of liquid alkanes, alkenes, alkynes, saturated and unsaturated cyclic hydrocarbons, and aromatic hydrocarbons.

A total of almost 4000 comparisons for 265 C_2 to C_{48} hydrocarbons have been made between a recommended value and one calculated using the additive group contributions reported here. It has been demonstrated that the method can be used in the range from the melting temperature to the normal boiling temperature where it gives an average deviation of 1.9 %. It has been shown that the estimated heat capacities are also correct above the normal boiling temperature. The proposed method fails in the vicinity of the critical point where the heat capacity rises quickly and becomes unbounded at the critical point.

The present estimation method compares favorably with a similar additivity method developed by Luria and Benson (77LUR/BEN) despite a smaller number of parameters used in this work for the description of the temperature dependence of contributions Δc_i . A small number of adjustable parameters for each additivity unit is essential to allow a realistic extrapolation outside the temperature limits to which the parameters relate (93RUZ/DOM). A small number of parameters also reduces the colinearity of parameters, in particular for families of compounds other than hydrocarbons. The application of a more complex expression for the dependence of Δc_i with temperature is limited by unavailability of accurate heat capacity data.

A comparison of the group contribution method developed here with the generalized three-parameter corresponding states method of Lee-Kesler (75LEE/KES) shows that the present estimation method is superior, in particular, in the region up to the normal boiling temperature.

To improve and further develop the estimation scheme, more data are required in a broad temperature interval covering the range from the melting temperature

to the normal boiling temperature. There is a lack of data for higher molecular weight hydrocarbons, in particular branched alkanes and alkenes. The heat capacity data for liquid alkynes are restricted to two compounds only.

The second paper of the series will present adjustable parameters for the estimation of heat capacities as a function of temperature for organic compounds containing the elements C,H,O,N,S, and halogens.

TABLE 11. Deviations between recommended and estimated heat capacities of saturated cyclic hydrocarbons. Numbers of data points and values of standard and average deviations in parentheses apply to data up to the normal boiling temperature only. Temperature and heat capacity ranges correspond to the entire range of available data. Recommended data are from Záborský *et al.* (93ZAB/RUZ)

Compound	No. data points	Std. dev. ^a J·K ⁻¹ mol ⁻¹	Avg. dev. ^a %	Temp. range, K	Heat capacity range, J·K ⁻¹ mol ⁻¹	Avg. dev. ^d (Lee-Kesler) %
cyclopropane ^b	11 (10)	0.0 (0.0)	0.0 (0.0)	154–243	75–81	4.2 (4.2)
cyclobutane	12 (12)	1.4	1.1	185–285	90–106	5.0
methylenecyclobutane	19 (19)	0.4	0.3	140–301	107–132	
spiropentane ^b	17 (17)	0.1	0.1	176–312	109–139	
cyclopentane ^b	14 (14)	0.1	0.1	180–300	100–127	3.0
cyclohexane	27 (9)	20.9 (2.8)	5.5 (1.4)	282–523	150–319	2.5 (2.0)
methylcyclopentane	26 (23)	1.4 (1.3)	0.8 (0.8)	136–366	125–187	7.1 (8.3)
cycloheptane ^b	6 (6)	0.0	0.0	269–300	170–182	
1,1-dimethylcyclopentane	12 (12)	4.2	2.3	206–300	153–187	2.5
cis-1,2-dimethylcyclopentane	10 (10)	3.0	1.7	223–303	162–191	1.9
trans-1,2-dimethylcyclopentane	14 (14)	5.7	3.4	162–294	150–185	7.8
trans-1,3-dimethylcyclopentane	18 (18)	3.5	2.1	144–304	145–191	7.9
ethylcyclopentane	18 (18)	3.5	2.1	140–302	147–188	2.5
methylcyclohexane	19 (19)	1.2	0.7	144–309	139–190	9.9
cyclooctane ^b	5 (5)	0.1	0.0	295–322	214–226	7.7
1,1-dimethylcyclohexane	8 (8)	3.1	1.5	243–304	184–212	3.9
cis-1,2-dimethylcyclohexane	10 (10)	1.2	0.5	228–299	182–211	2.0
trans-1,2-dimethylcyclohexane	14 (14)	1.2	0.6	184–301	166–211	4.3
cis-1,3-dimethylcyclohexane	12 (12)	1.1	0.5	204–299	172–210	2.5
trans-1,3-dimethylcyclohexane	14 (14)	4.1	2.0	188–299	172–213	4.4
cis-1,4-dimethylcyclohexane	14 (14)	4.7	2.2	189–303	174–215	4.7
trans-1,4-dimethylcyclohexane	8 (8)	1.0	0.4	242–299	187–211	1.4
ethylcyclohexane	16 (16)	3.1	1.6	167–299	164–212	8.2
propylcyclopentane	23 (23)	2.8	1.3	162–365	174–248	12.6
cis-octahydro-1H-indene	15 (15)	2.8	1.1	239–367	186–254	
trans-octahydro-1H-indene	21 (21)	1.9	0.8	212–391	175–262	
butylcyclopentane	23 (23)	2.8	1.1	168–368	202–282	
propylcyclohexane	22 (22)	2.0	0.7	186–373	195–283	
1,1'-bicyclopentyl	13 (13)	32.0	12.3	311–423	229–289	
cis-decahydronaphthalene	22 (22)	0.5	0.2	234–423	202–314	5.5
trans-decahydronaphthalene	20 (20)	3.1	1.2	249–413	202–309	3.5
butylcyclohexane	19 (19)	2.3	0.8	208–365	228–311	
1,4-diethylcyclohexane	13 (13)	36.8	12.2	313–423	265–313	
(1,1-dimethylethyl)cyclohexane	13 (13)	4.6	1.4	313–423	264–353	
decahydro-1-methylnaphthalene	13 (13)	4.9	1.2	311–423	268–346	
decahydro-2-methylnaphthalene	13 (13)	14.3	4.8	311–423	254–339	
ethylcyclohexane	13 (13)	5.1	1.3	311–423	282–353	
1,1'-bicyclohexyl	22 (22)	11.6	2.9	277–470	269–414	
decahydrodimethylnaphthalene	19 (19)	17.9	3.9	313–483	303–464	
ethyldecahydronaphthalene	19 (19)	9.6	2.0	313–483	298–463	
1-ethyldecahydronaphthalene	13 (13)	7.1	1.6	311–423	303–378	
2-ethyldecahydronaphthalene	13 (13)	14.6	4.1	311–423	290–371	
octahydro (1-methylethyl)-1H-indene	13 (13)	16.8	4.2	311–423	330–377	
decahydro (1-methylethyl)naphthalene	13 (4)	25.3 (19.1)	5.9 (4.8)	373–483	373–482	
decahydro-1-(1-methylethyl)naphthalene	19 (19)	23.7	5.4	311–483	317–460	
decahydro-1-propylnaphthalene	19 (19)	7.4	1.6	311–483	336–481	
2-methyl-1,1'-bicyclohexyl	19 (19)	3.7	0.8	313–483	328–497	
1,1'-methylenebicyclohexane	19 (19)	12.4	2.5	311–483	356–436	
heptylcyclohexane	8 (8)	1.2	0.3	240–300	326–365	
dodecahydro-9-methyl-1H-fluorene	19 (19)	9.8	2.3	313–483	326–482	
tetradecahydrophenanthrene	19 (19)	2.9	0.7	313–483	331–467	
1-butyldecahydronaphthalene	19 (19)	19.7	3.7	311–483	355–498	
1-(cyclohexylmethyl)-2-methylcyclohexane	19 (19)	28.8	6.2	313–483	363–517	

TABLE 11. Deviations between recommended and estimated heat capacities of saturated cyclic hydrocarbons. Numbers of data points and values of standard and average deviations in parentheses apply to data up to the normal boiling temperature only. Temperature and heat capacity ranges correspond to the entire range of available data. Recommended data are from Záborský *et al.* (93ZAB/RUZ) – Continued

Compound	No. data points	Std. dev. ^a J·K ⁻¹ mol ⁻¹	Avg. dev. ^a %	Temp. range, K	Heat capacity range, J·K ⁻¹ mol ⁻¹	Avg. dev. ^d (Lee-Kesler) %
decahydro-1-(1-methylpropyl)naphthalene	19 (19)	22.7	4.9	311–483	351–511	
decahydro-1-(2-methylpropyl)naphthalene	19 (19)	31.1	6.7	313–483	360–507	
1,2-dicyclohexylethane	19 (19)	13.1	2.2	313–483	368–508	
(1,1-dimethylethyl)decahydronaphthalene	13 (13)	12.9	2.6	313–423	353–443	
2-ethyl-1,1'-bicyclohexyl	19 (19)	7.4	1.4	313–483	369–531	
1,1'-ethylidenebicyclohexane	19 (19)	13.6	2.6	313–483	352–518	
1,1':3',1"-tercyclopentane	19 (19)	26.9	4.3	313–483	365–503	
cyclohexyl(ethylcyclohexyl)methane (unsp.i.) ^f	19 (19)	16.8	2.8	313–483	403–554	
1-(cyclohexylmethyl)-2-ethylcyclohexane	19 (19)	13.3	2.5	311–483	412–568	
1,2-dicyclohexylpropane	19 (19)	14.0	2.1	313–483	397–555	
(1-methylethyl)-1,1'-bicyclohexyl	19 (19)	28.2	4.8	311–483	418–538	
decylcyclopentane	10 (10)	3.7	0.6	258–321	407–443	
1-cyclohexyloctahydro-3-methyl-1H-indene	19 (19)	46.2	8.9	313–483	404–559	
2-ethyltetradecahydrophenanthrene	19 (19)	4.1	0.8	313–483	401–556	
1,1'-(1-methyl-1,3-propanediyl)bicyclohexane	19 (19)	34.1	6.4	313–483	401–572	
cyclohexyl[(1-methylethyl)cyclohexyl]methane	19 (19)	23.9	3.3	313–483	429–585	
decylcyclohexyl	5 (5)	2.2	0.5	274–300	435–454	
cyclopentylbicyclohexyl (unsp.i.)	19 (19)	17.2	2.8	311–483	432–600	
bis(ethylcyclohexyl)methane (unsp.i.)	19 (19)	31.3	4.3	313–483	467–613	
1-cyclohexyl-1-(1-methylethyl)cyclohexylethane	19 (19)	21.1	3.0	313–483	467–640	
3-ethylhexahydro-pyrene	13 (13)	6.1	1.2	311–422	460–534	
1-cyclohexyloctahydro-1,3,3-trimethyl-1H-indene	19 (19)	22.2	3.7	311–483	458–668	
1,1':2',1"-tercyclohexane	19 (19)	23.8	4.0	311–483	423–630	
1,1':3',1"-tercyclohexane	19 (19)	22.6	3.7	311–483	460–644	
1,1-bis(ethylcyclohexyl)ethane (unsp.i.)	19 (19)	33.7	4.2	313–483	481–660	
dodecylcyclohexane	3 (3)	11.9	2.3	290–300	516–524	
hexaethylcyclohexane (unsp.i.)	19 (19)	42.5	4.7	313–483	431–685	
bis(2,4,6-trimethylcyclohexyl)methane	13 (13)	61.2	8.2	373–483	591–694	
4-heptyl-1,1'-bicyclohexyl	19 (19)	52.4	8.2	313–483	486–668	
1,1'-heptylidenebicyclohexane	19 (19)	20.9	2.8	311–483	532–711	
diethylhexadecahydro-pyrene	19 (19)	6.2	1.0	313–483	515–704	
1,1',1"-(1-propanyl-2-ylidene)tricyclohexane	13 (13)	19.6		2.5	373–483	638–765
4-nonyl-1,1'-bicyclohexyl	19 (19)	56.7	7.1	313–483	572–741	
4'-heptyl-1,1':3',1"-tercyclohexane	19 (19)	40.0	3.7	311–483	670–890	
4'-nonyl-1,1':3',1"-tercyclohexane	13 (13)	50.9	4.6	373–483	820–972	
(1-decylundecyl)cyclohexane	5 (5)	10.4	1.3	270–300	746–789	

^aStandard deviation and average absolute percent deviation defined in Table 7.

^bThe heat capacity values for the compound were used as a single source of data to determine the adjustable parameters.

^cUnspecified isomer.

^dSee footnote c at the bottom of Table 7.

TABLE 12. Deviations between recommended and estimated heat capacities of unsaturated cyclic hydrocarbons. Recommended data are from Záborský *et al.* (93ZAB/RUZ)

Compound	No. data points	Std. dev. ^a J·K ⁻¹ mol ⁻¹	Avg. dev. ^a %	Temp. range, K	Heat capacity range, J·K ⁻¹ mol ⁻¹	Avg. dev. ^d (Lee-Kesler) %
cyclopentene ^b	18	0.3	0.2	141–301	99–123	8.7
1,3-cyclohexadiene	15	1.6	1.1	170–300	117–145	
1,4-cyclohexadiene	9	2.6	1.3	230–300	133–146	
cyclohexene	15	3.6	2.6	171–301	116–149	6.7
1,3,5-cycloheptatriene ^b	14	0.0	0.0	202–312	141–167	
(Z)-cycloheptene ^b	11	0.0	0.0	219–303	149–174	
4-methylcyclohexene	19	4.5	2.6	161–321	143–190	
1,3,5,7-cyclooctatetraene ^b	8	0.0	0.0	273–328	179–193	
1,5-cyclooctadiene (unsp.s.i.) ^{b,c}	14	0.1	0.1	207–320	168–208	
cyclooctene (unsp.s.i.) ^b	9	0.0	0.0	262–328	191–221	

^aStandard deviation and average absolute percent deviation defined in Table 7.^bThe heat capacity values for the compound were used as a single source of data to determine the adjustable parameters.^cUnspecified stereoisomer.^dSee footnote c at the bottom of Table 7.TABLE 13. Deviations between recommended and estimated heat capacities of aromatic hydrocarbons. Numbers of data points and values of standard and average deviations in parentheses apply to data up to the normal boiling temperature only. Temperature and heat capacity ranges correspond to the entire range of available data. Recommended data are from Záborský *et al.* (93ZAB/RUZ)

Compound	No. data points	Std. dev. ^a J·K ⁻¹ mol ⁻¹	Avg. dev. ^a %	Temp. range, K	Heat capacity range, J·K ⁻¹ mol ⁻¹	Avg. dev. ^c (Lee-Kesler) %
benzene	24 (9)	3.1 (4.0)	1.8 (2.9)	287–493	134–207	2.5 (3.9)
methylbenzene	37 (24)	2.1 (0.8)	0.8 (0.5)	178–503	135–247	6.3 (8.6)
ethynylbenzene	13 (13)	1.0	0.5	228–330	163–189	
ethenylbenzene	14 (14)	1.6	0.8	247–353	169–194	
1,2-dimethylbenzene	24 (18)	3.0 (3.5)	1.4 (1.7)	252–463	174–251	1.7 (2.0)
1,3-dimethylbenzene	34 (20)	3.7 (1.5)	1.1 (0.7)	231–540	165–292	1.8 (2.3)
1,4-dimethylbenzene	32 (15)	6.0 (1.3)	1.8 (0.5)	288–573	179–318	1.8 (2.4)
ethylbenzene	25 (25)	1.6	0.8	178–393	157–219	6.8
1H-indene ^b	12 (12)	0.1	0.1	280–375	181–213	48.6
2,3-dihydroindene (indan)	10 (10)	1.5	0.8	240–320	170–200	
1-methylethenylbenzene	7 (7)	7.1	3.7	251–300	185–201	1.6
1-methylethylbenzene	27 (27)	2.6	0.6	180–413	180–262	5.4
propylbenzene	22 (22)	0.8	0.3	181–371	183–244	5.4
1,2,3-trimethylbenzene	8 (8)	5.1	2.4	250–301	200–217	1.9
1,2,4-trimethylbenzene	22 (22)	3.1	1.3	230–430	194–266	3.5
1,3,5-trimethylbenzene	22 (22)	2.6	1.0	230–424	185–261	3.6
naphthalene	14 (14)	7.4	3.0	353–473	217–268	0.6
1,2,3,4-tetrahydronaphthalene ^b	10 (10)	0.0	0.0	248–319	195–227	
butylbenzene	20 (20)	1.1	0.4	194–370	208–276	
(1,1-dimethylethyl)benzene ^b	8 (8)	0.0	0.0	220–294	209–236	
1-methyl-4-(1-methylethyl)benzene	17 (17)	4.1	1.6	211–359	206–275	
(1-methylpropyl)benzene	15 (15)	7.0	2.1	294–430	243–304	
1,2,3,4-tetramethylbenzene	14 (14)	14.2	4.6	277–380	231–291	
1,2,3,5-tetramethylbenzene	5 (5)	3.2	1.3	255–297	225–238	
1,2,4,5-tetramethylbenzene	14 (13)	9.8 (8.8)	2.8 (2.6)	352–472	267–303	
1-methylnaphthalene	14 (14)	0.7	0.3	248–352	204–248	
2-methylnaphthalene	7 (7)	2.8	1.1	310–367	229–252	
1,1-dimethylindan	18 (18)	2.6	0.9	236–389	221–298	
4,6-dimethylindan	14 (14)	2.9	1.1	262–370	225–278	
4,7-dimethylindan	14 (14)	2.4	0.8	286–394	235–289	
pentamethylbenzene	16 (16)	14.5	3.8	328–468	284–320	
1,1'-biphenyl	25 (18)	8.9 (5.2)	2.2 (1.6)	350–589	272–386	2.4 (1.8)
1,8-dimethylnaphthalene	10 (10)	3.7	1.2	350–432	279–321	
2,3-dimethylnaphthalene	5 (5)	3.6	1.2	385–415	298–311	
2,6-dimethylnaphthalene	6 (6)	2.7	0.9	390–438	294–318	
2,7-dimethylnaphthalene	4 (4)	0.7	0.2	373–391	286–295	

TABLE 13. Deviations between recommended and estimated heat capacities of aromatic hydrocarbons. Numbers of data points and values of standard and average deviations in parentheses apply to data up to the normal boiling temperature only. Temperature and heat capacity ranges correspond to the entire range of available data. Recommended data are from Zábanský *et al.* (93ZAB/RUZ) — Continued

Compound	No. data points	Std. dev. ^a J·K ⁻¹ mol ⁻¹	Avg. dev. ^a %	Temp. range, K	Heat capacity range, J·K ⁻¹ mol ⁻¹	Avg. dev. ^c (Lee-Kesler) %
cyclohexylbenzene	20 (20)	4.1	0.9	290–470	258–370	
hexamethylbenzene	5 (5)	12.4	3.2	443–473	377–398	
1,1'-methylenebisbenzene	7 (7)	6.5	1.9	302–353	266–287	
1,1,4,6-tetramethylindan	12 (12)	0.9	0.2	286–378	292–349	
1,1,4,7-tetramethylindan	23 (23)	1.8	0.5	170–376	240–350	
anthracene	7 (7)	6.8	1.3	497–541	371–379	
1,1'-(1,2-ethynediyl)bisbenzene	21 (21)	13.1	3.4	365–553	311–419	
phenanthrene	12 (12)	9.6	2.8	371–471	299–349	
(E)-1,1'-(1,2-ethenediyl)bisbenzene	17 (15)	3.5 (3.3)	0.8 (0.8)	403–553	351–422	
1,1'-(1,2-ethanediyl)bisbenzene	17 (17)	13.0	2.7	324–472	313–382	
1,1'-ethylidenebisbenzene	7 (7)	8.8	3.1	260–299	273–295	
4-methylphenanthrene	13 (13)	3.5	0.9	332–445	304–374	
(1-methylethyl)-1,1'-biphenyl	40 (32)	11.4 (11.9)	2.2 (2.3)	293–671	345–638	
fluoranthene	9 (9)	1.3	0.3	386–452	336–373	
pyrene	6 (6)	0.6	0.1	431–479	353–380	
triphenylene	4 (4)	2.9	0.6	481–510	446–462	
1,1':2',1"-terphenyl	4 (4)	10.0	2.4	330–356	390–407	
1,1':3',1"-terphenyl	12 (12)	8.9	1.8	432–534	453–512	
1,1':4',1"-terphenyl	11 (11)	14.5	2.8	487–580	486–560	
1-methyl-7-(1-methylethyl)phenanthrene	13 (13)	14.0	2.8	369–473	420–487	
ar,ar'-bis(1-methylethyl)-1,1'-biphenyl	18 (18)	11.0	1.6	422–589	521–657	
1,1',1"-methylidenetrisbenzene ^b	24 (24)	0.0	0.0	373–596	541–640	
1-(2-naphthalenylmethyl)naphthalene	10 (10)	0.9	0.1	343–423	440–503	
5'-phenyl-1,1':3',1"-terphenyl	5 (5)	39.0	6.1	446–480	616–654	
1,1':3',1":3",1"-quaterphenyl	12 (12)	23.7	3.7	431–534	597–670	
1,1-diphenyldodecane	4 (4)	3.3	0.3	283–298	586–595	
(1-cyclohexyldodecyl)benzene	2 (2)	2.9	0.4	282–297	603–606	
1,1',1"-(1,3,5-benzenetriyl) trisinaphthalene	10 (10)	42.3	4.4	472–560	870–967	

^aStandard deviation and average absolute percent deviation defined in Table 7.

^bThe heat capacity values for the compound were used as a single source of data to determine the adjustable parameters.

^cSee footnote c at the bottom of Table 7.

TABLE 14. Summary deviations between observed and estimated heat capacities. Values in parentheses apply to data up to the normal boiling temperature only

Family	No. cmpds.	No. data points	Std. dev. ^a J·K ⁻¹ mol ⁻¹	Avg. dev. ^b %	Temp. range, K	Heat capacity range, J K ⁻¹ mol ⁻¹
<i>n</i> -alkanes C ₂ to C ₄₈	34	485 (405)	20.8 (18.8)	2.8 (1.9)	81–520	68–1818
Luria-Benson	34	485 (405)	19.7 (17.1)	2.6 (1.4)		
branched alkanes						
C ₄ to C ₃₁	34	518 (497)	4.5 (3.3)	1.4 (1.2)	85–393	100–938
Luria-Benson	34	518 (497)	5.1 (3.8)	1.6 (1.3)		
alkenes C ₂ to C ₁₆	23	389 (343)	6.3 (3.6)	2.4 (1.6)	90–366	67–488
alkenes C ₂ to C ₆	8	141 (114)	8.6 (4.3)	3.8 (2.3)	93–366	67–181
Luria-Benson	8	141 (114)	6.7 (3.3)	3.2 (2.4)		
dienes C ₄ to C ₆	10	166 (157)	2.5 (2.5)	0.9 (0.9)	128–316	103–180
dienes C ₄ to C ₅	7	126 (117)	2.6 (2.6)	1.1 (1.1)	128–316	103–157
Luria-Benson	7	126 (117)	4.2 (4.2)	2.8 (2.8)		

saturated cyclic hydrocarbons

TABLE 14. Summary deviations between observed and estimated heat capacities. Values in parentheses apply to data up to the normal boiling temperature only — Continued

Family	No. cmpds.	No. data points	Std. dev. ^a J·K ⁻¹ mol ⁻¹	Avg. dev. ^b %	Temp. range, K	Heat capacity range, J K ⁻¹ mol ⁻¹
saturated cyclic hydrocarbons C ₃ to C ₂₇	90	1460 (1438)	21.0 (21.0)	2.9 (2.8)	136–523	75–972
saturated cyclic hydrocarbons C ₃ to C ₂₇ Luria-Benson	78	1251 (1220)	21.4 (21.3) 24.0 (23.8)	3.0 (2.9) 3.4 (3.3)	136–523	75–972
unsaturated cyclic hydrocarbons C ₅ to C ₈	10	132 (132)	2.3 (2.3)	0.9 (0.9)	141–328	99–222
aromatic hydrocarbons C ₆ to C ₃₆	64	928 (845)	8.8 (8.9)	1.5 (1.5)	162–671	134–970
aromatic hydrocarbons C ₆ to C ₂₄ Luria-Benson	25	427 (354) 427 (354)	9.0 (9.4) 24.4 (20.6)	1.8 (1.7) 3.7 (2.9)	162–589	134–671

^aStandard deviation is calculated as

$$SD = \sqrt{\frac{1}{n_c} \sum \frac{1}{n_p} \sum (C^{\text{rec}} - C^{\text{estd}})^2}$$

where n_c is the number of compounds and n_p is the number of data points for each compound (usually 10 K apart).

^bAverage absolute percent deviation is calculated as

$$APD = 100 \cdot \frac{1}{n_c} \sum \frac{1}{n_p} \sum \left| \frac{C^{\text{rec}} - C^{\text{estd}}}{C^{\text{rec}}} \right|$$

TABLE 15. Summary deviations between observed heat capacities and those estimated by the Lee-Kesler method (75LEE/KES). Values in parentheses apply to data up to the normal boiling temperature only.

Family	No. cmpds.	No. data points	Std. dev. ^a J·K ⁻¹ mol ⁻¹	Avg. dev. ^b %	Temp. range, K	Heat capacity range, J K ⁻¹ mol ⁻¹
<i>n</i> -alkanes C ₂ to C ₃₀ Lee-Kesler	22 22	369 (290) 356 (290)	17.1 (11.5) 11.3 (12.7)	3.1 (1.8) 2.7 (3.2)	81–520	68–1008
branched alkanes C ₄ to C ₁₀ Lee-Kesler	25 25	406 (383) 403 (383)	4.7 (3.0) 13.6 (14.0)	1.5 (1.2) 5.0 (5.2)	85–385	100–312
alkenes C ₂ to C ₁₂ Lee-Kesler	13 13	236 (191) 233 (191)	8.0 (3.8) 13.4 (14.5)	3.3 (1.9) 6.2 (6.7)	90–366	67–365
dienes C ₄ to C ₅ Lee-Kesler	2 2	35 (30) 35 (30)	0.2 (0.2) 11.2.2 (12.0)	0.1 (0.1) 5.1 (5.8)	130–304	103–153
saturated cyclic hydrocarbons C ₃ to C ₁₀ Lee-Kesler	23 23	341 (318) 336 (318)	6.7 (2.8) 18.7 (19.4)	1.6 (1.2) 6.5 (6.9)	136–523	75–320
unsaturated cyclic hydrocarbons C ₅ to C ₆ Lee-Kesler	2 2	33 (33) 33 (33)	2.4 (2.4) 13.6 (13.6)	1.3 (1.3) 7.8 (7.8)	99–149	141–301
aromatic hydrocarbons C ₆ to C ₁₂ Lee-Kesler	15	325 (254) 321 (254)	4.3 (3.3) 21.0 (23.6)	1.3 (1.1) 5.2 (6.2)	162–589	134–386

^aStandard deviation and average absolute percent deviation defined in Table 14.

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Appendix

Sample calculation for the estimation of the heat capacity of *n*-heptane at 300 K

- (1) Kind and number of additive groups.
The structural formula for *n*-heptane is:



The following groups are needed for the calculation of adjustable parameters necessary to estimate the heat capacity of *n*-heptane in the liquid phase at an arbitrary temperature in the range from the melting to the boiling temperature; let us choose 300 K.

Molecular fragment	Group	No. of groups
CH ₃ -	C-(H) ₃ (C)	2
C-CH ₂ -C	C-(H) ₂ (C) ₂	5

- (2) Group additivity representation for *n*-heptane.

$$(2 \times \text{C}-(\text{H})_3(\text{C})) + (5 \times \text{C}-(\text{H})_2(\text{C})_2)$$

- (3) Equations (1) and (2) are used to perform the calculation.

$$C/R = \sum n_i \Delta c_i, \text{ and } \Delta c_i = a_i + b_i(T/100) + d_i(T/100)^2, \text{ respectively, where } R = 8.31451 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1} \text{ and } T \text{ is in kelvin.}$$

- (4) Selection of groups and adjustable parameters. Adjustable parameters for C-(H)₃(C) and C-(H)₂(C)₂ are obtained from Table 5.

Group	<i>a_i</i>	<i>b_i</i>	<i>d_i</i>	Temp. range, K
C-(H) ₃ (C)	3.8452	-3.3997E-1	1.9489E-1	80-490
C-(H) ₂ (C) ₂	2.7972	-5.4967E-2	1.0679E-1	80-490

- (5) Calculation of the estimated value and comparison with the recommended value.

$$C/R = 27.126 \text{ and } C = 225.5 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$$

This result may be compared with the recommended value for the heat capacity of liquid *n*-heptane at 300 K given in 91RUZ/ZAB equal to 225.40 J·mol⁻¹·K⁻¹. The estimated value differs by 0.10 J·mol⁻¹·K⁻¹ or by 0.04%.