160 *J. Chem. Eng. Data* **1995,** *40,* 160−166

Additivity of Thermodynamic Properties of Organic Compounds in the Crystalline State. 1. Additive Calculations for Thermodynamic Properties of Alkanes, Alkenes, Alkanols, and Alkanones

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Additive constants to estimate thermodynamic properties of the crystals of alkanes, alkenes, alkanols, and alkanones in the range of $T = 10-160$ K have been derived. A classification of effective atoms and effective bonds was used. The average discrepancy between calculated and experimental thermodynamic values for the crystals of organic compounds at temperatures from 30 K to the first solid-to-solid transition temperature does not exceed 3−5 times the estimated experimental error.

Introduction

Additive calculation methods (*1−3*) based on the classical theory of molecule structure are often used for determining the energetic properties of substances. The application of similar additive calculations schemes for values of $C_p(T)$, $S°(T)$ and $G°(T) - H°(0)$ can be justified from statistical thermodynamics. According to Tatevsky (*1*), the partition function Q may be represented as

$$Q = \sum_i e^{-(\epsilon_i/kT)\sum_f \gamma_{if}} = \prod_f Q_f \tag{1}$$

where $\gamma_{if} = \epsilon_{if}/\epsilon_i$ is a fraction, related to the effective atom (effective bond, structure fragment) under the condition $\sum_f \gamma_{if} = 1$.

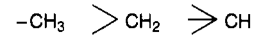
According to ref 1, for translation $\gamma_{ik} = m_k/m$, where m is a total molecule (particle) mass and m_k is a structure fragment mass.

In a number of compounds with the same structure group (effective atom) the value γ_{ik} is not constant. For example, for propane $\gamma_{i,CH_2} = 14.027/44.097 = 0.318$, but for decane $\gamma_{i,CH_2} = 14.027/142.2 = 0.0986$.

The same conclusions are also valid for the rotational partition function $Q_r = \prod Q_{r\alpha} = \prod Q_r^{\gamma_{r\alpha}}$, because $\gamma_{r\alpha} = I_\alpha/I_\beta$, where I_α is an inertia moment of a structure fragment and I_β is a principal inertia moment of a molecule. So, $\gamma_{r\alpha}$ for the same structure fragment, effective atom, and effective bond can change substantially in different molecules.

It is more difficult to analyze the possibilities of distribution of vibrational partition functions by separate fragments, conserving a relative constancy in different molecules. Although the incorporation of additive properties of vibrational contributions into predictive schemes for thermodynamic properties is possible, it is necessary to note that C_p and $H°(T) - H°(0)$ functions for ideal gases do not depend on the masses and moments of inertia of molecules at all temperatures (e.g., classical approximation). Hence, there is unadditive behavior of the various contributions to the thermodynamic functions.

In spite of difficulties in justifying the correctness of an additive scheme from the partition function by separate fragments, corresponding to certain structure groups, one can state (*2, 3*) the existence of a rather good constancy of contributions for ΔC_{pi} (298 K) and $\Delta S_i°$ (298 K) corresponding to various structure fragments such as



groups for various ideal gas species. The constancy of the group contributions in the calculations of C_p and $S°(T)$ is probably attributed to mutual compensation of unadditive parts in the translational, rotational, and vibrational contributions. In addition, only the unadditive entropy part, caused by differences in the symmetry of the molecules, by differences of tops, and by the mixing of stereoisomers for chiral molecules, has to be specially taken into account in additive calculations of the entropy of an ideal gas.

The theoretical bases of the additive methods to calculate thermodynamic properties of crystals are more complicated. Simirsky, Kabo, and Frenkel (*4*) established that additive calculations of enthalpies of formation for alkyl derivatives of urea were not satisfactory for tetrasubstituted ureas.

A comprehensive analysis of possibilities of additive calculations was made by Domalski and Hearing (*5, 6*) for more than 1500 compounds from various classes containing C−H−N−O−S−halogen atoms at 298.15 K. However, the choice of 298.15 K restricted substantially the number of organic compounds in the crystalline state for which reliable values of C_p (cr, 298.15 K) and $S°$ (cr, 298.15 K) are available. Hence, a detailed study on the additivity of these functions was not possible.

Bondi (*7*) proposed a theoretical basis for the calculation of entropies and enthalpies of fusion of organic crystals. However, the absence of a rigorous theory for fusion and the dependence of the fusion mechanism on the crystal structure permitted him (*7*) to calculate $\Delta_{fus} S$ only for a series of crystals with very similar molecular structures. The methods proposed in ref 7 are not universal, and they require detailed information concerning the molecular structure and crystal structure. Hence, it is difficult to predict the thermodynamic properties of crystals through the prediction of the phase change behavior.

Additive Calculations of the Thermodynamic Properties of Crystals

Additive methods to predict the thermodynamic functions of crystals are studied in this work. These methods classify the effective atoms, bonds, and structure fragments in organic molecules (*1−3*).

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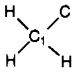
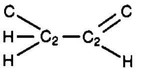
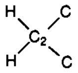
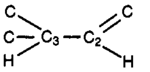
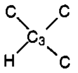
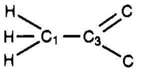
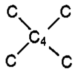
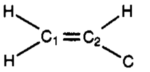
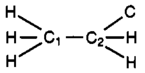
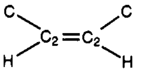
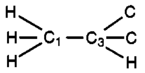
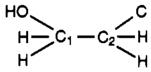
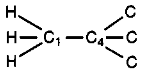
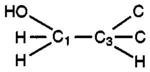
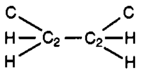
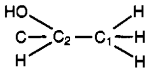
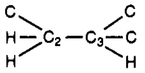
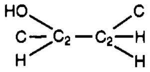
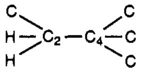
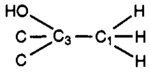
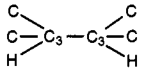
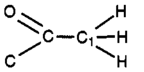
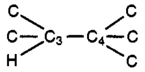
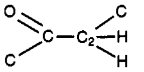
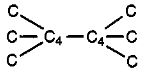
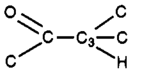
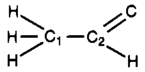
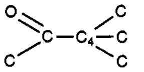
Table 1. Effective Atom, Effective Bond Types, and Designation of Additive Constants Used in Calculations of Thermodynamic Properties for Crystalline Alkanes, Alkenes, Alkanols, and Alkanones[a]

effective atom or bond type	additive constant designation for thermodynamic functions				effective atom or bond type	additive constant designation for thermodynamic functions			
	C_p	$S°(T)$	$\{G°(T) - H°(0)\}/T$	$\{H°(T) - H°(0)\}/T$		C_p	$S°(T)$	$\{G°(T) - H°(0)\}/T$	$\{H°(T) - H°(0)\}/T$
	C_1	S_1	G_1	H_1		$C_{2\bar{2}}$	$S_{2\bar{2}}$	$G_{2\bar{2}}$	$H_{2\bar{2}}$
	C_2	S_2	G_2	H_2		$C_{3\bar{2}}$	$S_{3\bar{2}}$	$G_{3\bar{2}}$	$H_{3\bar{2}}$
	C_3	S_3	G_3	H_3		$C_{1\bar{3}}$	$S_{1\bar{3}}$	$G_{1\bar{3}}$	$H_{1\bar{3}}$
	C_4	S_4	G_4	H_4		$C_{\bar{1}\bar{2}}$	$S_{\bar{1}\bar{2}}$	$G_{\bar{1}\bar{2}}$	$H_{\bar{1}\bar{2}}$
	C_{12}	S_{12}	G_{12}	H_{12}		$C_{\bar{2}\bar{2}}^{cis}$	$S_{\bar{2}\bar{2}}^{cis}$	$G_{\bar{2}\bar{2}}^{cis}$	$H_{\bar{2}\bar{2}}^{cis}$
	C_{13}	S_{13}	G_{13}	H_{13}		C_{12}^{OH}	S_{12}^{OH}	G_{12}^{OH}	H_{12}^{OH}
	C_{14}	S_{14}	G_{14}	H_{14}		C_{13}^{OH}	S_{13}^{OH}	G_{13}^{OH}	H_{13}^{OH}
	C_{22}	S_{22}	G_{22}	H_{22}		C_{21}^{OH}	S_{21}^{OH}	G_{21}^{OH}	H_{21}^{OH}
	C_{23}	S_{23}	G_{23}	H_{23}		C_{22}^{OH}	S_{22}^{OH}	G_{22}^{OH}	H_{22}^{OH}
	C_{24}	S_{24}	G_{24}	H_{24}		C_{31}^{OH}	S_{31}^{OH}	G_{31}^{OH}	H_{31}^{OH}
	C_{33}	S_{33}	G_{33}	H_{33}		C_{CO1}	S_{CO1}	G_{CO1}	H_{CO1}
	C_{34}	S_{34}	G_{34}	H_{34}		C_{CO2}	S_{CO2}	G_{CO2}	H_{CO2}
	C_{44}	S_{44}	G_{44}	H_{44}		C_{CO3}	S_{CO3}	G_{CO3}	H_{CO3}
	$C_{1\bar{2}}$	$S_{1\bar{2}}$	$G_{1\bar{2}}$	$H_{1\bar{2}}$		C_{CO4}	S_{CO4}	G_{CO4}	H_{CO4}

[a] Note: only those types of bonds are given for which it is possible to calculate additive constant values on the basis of the data available for this work.

Translation and rotation are absent in normal (nonplastic) crystals. Hence, it is not necessary to make corrections concerning molecular symmetry in any additive calculations for $S°(T)$ and $G°(T) - H°(0)$. These corrections should be considered only when there are rotational movements of molecules. Also corrections for the mixing of chiral isomers should not be taken into consideration.

To verify the possibility to use simple additive methods for C_p, $S°(T)$, $\{G°(T) - H°(0)\}/T$ and $\{H°(T) - H°(0)\}/T$, we made a number of calculations under the following conditions.

Initial Data for the Additive Calculations

Calculations were made for alkanes, alkenes, alkanols, and alkanones in the crystalline state. The thermodynamic property values of crystals were taken from the *TRC Thermodynamic Tables* (*8*, *9*), where smoothed values of thermodynamic functions based on the comprehensive analysis of literature are given, after corrections of some errors. We used the values from 10 K to the temperatures of the first phase transition T_{trs}. The T_{trs} values are peculiar to each compound. The thermodynamic properties of crystals at $T > T_{trs}$ were not used. As each substance has an individual temperature of the first phase transition, the number of compounds involved in our additive calculations (hence, the number of equations) decreases with increasing temperature at $T > 100$ K. Hence, we decided to limit ourselves to $T = 150$ K, at which the number of equations provides still a reasonable reliability of additive constants, taking into consideration their statistical nature.

Procedures of Compiling Equations for Additive Calculation

Our calculations were carried out on the basis of the equation

$$P = \sum_i n_i P_i \tag{2}$$

which is analogous with Benson's classification (*2*), and of the equation proposed in ref 10

$$P = \sum_{ij} n_{ij} P_{ij} \tag{3}$$

where P is a thermodynamic property, P_i and P_{ij} are property fractions related to an effective atom and a bond, respectively, and n_i and n_{ij} are the numbers of corresponding atoms and bonds, respectively.

Table 2. Matrix of Coefficients n_i for Additive Constants P_i, Used in the Classification of Effective Atoms in Alkanes

compound	P_1	P_2	P_3	P_4
hexane	2	4	0	0
2-methylpentane	3	2	1	0
3-methylpentane	3	2	1	0
2,2-dimethylbutane	4	1	0	1
2,3-dimethylbutane	4	0	2	0
heptane	2	5	0	0
2-methylhexane	3	3	1	0
3-ethylpentane	3	3	1	0
2,2-dimethylpentane	4	2	0	1
2,4-dimethylpentane	4	1	2	0
3,3-dimethylpentane	4	2	0	1
2,2,3-trimethylbutane	5	0	1	1
octane	2	6	0	0
2-methylheptane	3	4	1	0
3-methylheptane	3	4	1	0
2,2,4-trimethylpentane	5	1	1	1
2,3,4-trimethylpentane	5	0	3	0
2,2,3,3-tetramethylbutane	6	0	0	2
nonane	2	7	0	0
3,3-diethylpentane	4	4	0	1
2,2,3,3−tetramethylpentane	6	1	0	2
2,2,4,4-tetramethylpentane	6	1	0	2
decane	2	8	0	0

Table 3. Matrix of Coefficients n_{ij} for Additive Constants P_{ij}, Used in the Classification of Effective Bonds in Alkanes

compound	P_{12}	P_{13}	P_{14}	P_{22}	P_{23}	P_{24}	P_{33}	P_{34}	P_{44}
hexane	2	0	0	3	0	0	0	0	0
2-methylpentane	1	2	0	1	1	0	0	0	0
3-methylpentane	2	1	0	0	2	0	0	0	0
2,2-dimethylbutane	1	0	3	0	0	1	0	0	0
2,3-dimethylbutane	0	4	0	0	0	0	1	0	0
heptane	2	0	0	4	0	0	0	0	0
2-methylhexane	1	2	0	2	1	0	0	0	0
3-ethylpentane	3	0	0	0	3	0	0	0	0
2,2-dimethylpentane	1	0	3	1	0	1	0	0	0
2,4-dimethylpentane	0	4	0	0	2	0	0	0	0
3,3-dimethylpentane	2	0	2	0	0	2	0	0	0
2,2,3-trimethylbutane	0	2	3	0	0	0	0	1	0
octane	2	0	0	5	0	0	0	0	0
2-methylheptane	1	2	0	3	1	0	0	0	0
3-methylheptane	2	1	0	2	2	0	0	0	0
2,2,4-trimethylpentane	0	2	3	0	1	1	0	0	0
2,3,4-trimethylpentane	0	5	0	0	0	0	2	0	0
2,2,3,3-tetramethylbutane	0	0	6	0	0	0	0	0	1
nonane	2	0	0	6	0	0	0	0	0
3,3-diethylpentane	4	0	0	0	0	4	0	0	0
2,2,3,3-tetramethylpentane	1	0	5	0	0	1	0	0	1
2,2,4,4-tetramethylpentane	0	0	6	0	0	2	0	0	0
decane	2	0	0	7	0	0	0	0	0

Table 4. Matrices of Coefficients n_{ij} for Additive Constants P_{ij}, Used in the Classification of Effective Bonds C_i−C_j in Alkenes, Alkanols, and Alkanones

compound	P_{12}	P_{13}	P_{22}	$P_{1\bar{2}}$	$P_{2\bar{2}}$	$P_{3\bar{2}}$	$P_{1\bar{3}}$	$P_{\bar{1}\bar{2}}$	$P_{\bar{2}\bar{2}}^{cis}$
propene	0	0	0	1	0	0	0	1	0
1-butene	1	0	0	0	1	0	0	1	0
cis-2-butene	0	0	0	2	0	0	0	0	1
trans-2-butene	0	0	0	2	0	0	0	0	0
1-pentene	1	0	1	0	1	0	0	1	0
cis-2-pentene	1	0	0	1	1	0	0	0	1
trans-2-pentene	1	0	0	1	1	0	0	0	0
3-methyl-1-butene	0	2	0	0	0	1	0	1	0
2-methyl-2-butene	0	0	0	1	0	0	2	0	0

compound	P_{12}	P_{13}	P_{22}	P_{12}^{OH}	P_{13}^{OH}	P_{21}^{OH}	P_{22}^{OH}	P_{31}^{OH}
1-propanol	1	0	0	1	0	0	0	0
2-propanol	0	0	0	0	0	2	0	0
1-butanol	1	0	1	1	0	0	0	0
D-2-butanol	1	0	0	0	0	1	1	0
DL-2-butanol	1	0	0	0	0	1	1	0
2-methyl-1-propanol	0	2	0	0	1	0	0	0
2-methyl-2-propanol	0	0	0	0	0	0	0	3
1-pentanol	1	0	2	1	0	0	0	0

compound	P_{12}	P_{13}	P_{14}	P_{22}	P_{co1}	P_{co2}	P_{co3}	P_{co4}
2-propanone	0	0	0	0	2	0	0	0
2-butanone	1	0	0	0	1	1	0	0
2-pentanone	1	0	0	1	1	1	0	0
3-pentanone	2	0	0	0	0	2	0	0
3-methyl-2-butanone	0	2	0	0	1	0	1	0
2-hexanone	1	0	0	2	1	1	0	0
3-hexanone	2	0	0	1	0	2	0	0
3,3-dimethyl-2-butanone	0	0	3	0	1	0	0	1
2,4-dimethyl-3-pentanone	0	4	0	0	0	0	2	0
5-nonanone	2	0	0	4	0	2	0	0

Table 5. Additive Constant C_i, S_i, G_i, and H_i Values (All $J \cdot K^{-1} \cdot mol^{-1}$) for Heat Capacity, Entropy, Gibbs Energy Function [$\{G^\circ(T) - H^\circ(0)\}/T$], and Reduced Enthalpy [$\{H^\circ(T) - H^\circ(0)\}/T$] of Crystalline Alkanes According to Classification of Effective Atoms

T/K	C_1	C_2	C_3	C_4	S_1	S_2	S_3	S_4
10	0.66	0.11	0.06	−0.21	0.20	0.04	0.09	0.03
20	5.5	0.3	−3.7	−7.4	2.1	0.1	−1.2	−2.5
30	9.2	1.4	−4.8	−11.5	5.1	0.4	−2.9	−6.2
40	12.8	2.6	−7.0	−17.5	8.6	1.0	−4.6	−10.4
50	15.5	4.0	−8.1	−21.7	11.4	1.7	−6.3	−14.8
60	17.8	5.1	−8.9	−24.7	14.3	2.7	−7.6	−18.6
70	19.8	6.2	−9.4	−26.3	17.4	3.4	−9.3	−23.1
80	20.7	7.4	−7.7	−25.3	20.3	4.3	−10.8	−27.0
90	23.0	8.1	−8.4	−27.1	23.1	5.1	−12.1	−30.7
100	24.7	8.7	−8.2	−27.4	25.6	6.0	−13.0	−33.5
110	25.4	9.7	−7.1	−25.9	27.6	7.1	−13.4	−35.4
120	27.2	10.2	−7.4	−26.8	31.4	7.4	−16.0	−42.0
130	29.8	10.4	−9.1	−29.6	32.3	8.7	−14.8	−40.2
140	34.0	10.0	−13.5	−37.1	36.9	8.7	−19.1	−49.4
150	34.9	10.8	−11.8	−36.2	36.1	10.4	−14.3	−43.7

T/K	G_1	G_2	G_3	G_4	H_1	H_2	H_3	H_4
10	−0.05	−0.01	−0.03	−0.03	0.15	0.03	0.05	0.01
20	−0.4	−0.1	−0.3	−0.1	1.7	0.0	−1.5	−2.6
30	−1.5	−0.1	0.5	1.5	3.6	0.3	−2.4	−4.8
40	−2.8	−0.2	1.3	3.1	5.5	0.7	−3.3	−7.3
50	−4.2	−0.5	2.1	5.0	7.2	1.2	−4.2	−9.8
60	−5.6	−0.7	3.0	7.0	8.8	1.8	−4.8	−11.9
70	−7.1	−1.1	3.8	9.0	10.3	2.4	−5.5	−14.1
80	−8.6	−1.4	4.6	11.0	11.7	2.9	−6.2	−16.0
90	−10.0	−1.8	5.3	13.0	13.0	3.3	−6.8	−17.7
100	−11.5	−2.1	6.1	14.9	14.1	3.8	−6.9	−18.6
110	−12.7	−2.6	6.5	16.3	14.9	4.4	−6.9	−19.1
120	−15.0	−2.7	8.5	21.1	16.3	4.7	−7.5	−21.0
130	−15.6	−3.3	8.2	20.6	16.9	5.3	−7.0	−20.4
140	−18.0	−3.4	10.2	25.6	18.9	5.3	−8.9	−23.8
150	−17.5	−4.3	7.6	22.5	18.6	6.1	−6.7	−21.2

According to ref 1, the term "effective atom" (EA) means an atom transformed, in comparison with the free one, as a result of interactions in the molecules. As was shown (*1*, *10*), there are some constant linear relationships between the numbers of EAs of certain kinds in the molecules. This fact allows the number of EAs used in additive calculations to be reduced. As a rule, polyvalent atoms are selected as basic EAs. EAs are classified by their chemical individuality, by valence state, by nearest surroundings (*1*, *10*), and by belonging to a cycle (*3*). The principles of selecting EAs in additive calculations for various classes of organic compounds were described (*1*, *3*, *10*). EAs form effective bonds, which are classified by the principles noted above. The types of effective atoms and bonds in alkanes, alkenes, alkanols, and ketones used in our additive calculations are given in the first column of Table 1.

The available saturated heat capacity C_s data for the crystalline state for alkenes did not allow the determination of the constants for the system of equations obtained according to the effective bond classification scheme by Tatevsky (*1*). We used an alternate classification which contained a reduced number of parameters. The contribu-

Table 6. Additive Constant C_{ij}, S_{ij}, G_{ij}, and H_{ij} Values (All $J \cdot K^{-1} \cdot mol^{-1}$) for Heat Capacity, Entropy, Gibbs Energy Function [$\{G°(T) - H°(0)\}/T$], and Reduced Enthalpy [$\{H°(T) - H°(0)\}/T$] of Crystalline Alkanes

T/K	C_{12}	C_{13}	C_{14}	C_{22}	C_{23}	C_{24}	C_{33}	C_{34}	C_{44}
10	0.57	0.80	0.54	0.15	0.15	0.12	−0.64	0.38	0.47
20	5.1	4.4	3.6	0.4	−0.8	−1.1	−3.8	−1.6	−4.2
30	9.3	7.7	6.2	1.6	−0.4	−1.4	−4.4	−1.5	−6.4
40	13.5	10.5	8.3	2.8	−0.5	−2.2	−5.6	−4.0	−9.7
50	17.0	12.8	10.0	4.1	−0.2	−2.7	−6.1	−6.1	−11.8
60	20.0	14.8	11.6	5.3	0.1	−3.0	−6.5	−7.3	−13.1
70	22.5	16.4	13.2	6.3	0.6	−3.0	−5.9	−7.5	−14.3
80	23.9	17.9	14.0	7.6	1.9	−2.0	−5.4	−3.8	−11.2
90	26.2	19.7	15.8	8.4	2.2	−2.1	−5.4	1.2	−12.9
100	27.9	21.2	17.2	9.2	2.9	−1.5	−5.2	9.4	−12.0
110	29.6	22.8	18.8	9.9	3.4	−1.2	−5.2		−12.0
120	31.6	24.8	20.5	10.4	3.4	−1.3	−6.2		−12.6
130	34.3	27.1	22.4	10.6	2.8	−2.1	−8.2		−14.1
140	37.7	29.9	24.5	10.5	1.6	−3.3	−11.8		−16.3
150	37.4	31.1	24.8	11.7	4.1	−1.1	−11.7		−12.1

T/K	S_{12}	S_{13}	S_{14}	S_{22}	S_{23}	S_{24}	S_{33}	S_{34}	S_{44}
10	0.18	0.27	0.18	0.06	0.07	0.05	−0.18	0.14	0.26
20	1.9	1.9	1.4	0.2	−0.2	−0.3	−1.8	−0.4	−0.9
30	4.8	4.4	3.4	0.6	−0.5	−0.8	−3.5	−1.0	−3.0
40	8.1	7.0	5.5	1.2	−0.6	−1.3	−4.9	−1.8	−5.3
50	11.5	9.6	7.5	1.9	−0.7	−1.9	−6.3	−3.0	−7.8
60	14.7	12.0	9.5	2.9	−0.6	−2.3	−7.2	−4.0	−9.9
70	18.1	14.5	11.4	3.7	−0.6	−2.9	−8.5	−5.4	−12.2
80	21.4	16.9	13.3	4.6	−0.6	−3.4	−9.5	−6.6	−14.3
90	24.5	19.2	15.2	5.5	−0.5	−3.8	−10.3	−5.8	−16.3
100	27.3	21.4	16.9	6.4	−0.3	−4.0	−10.8	−5.3	−17.6
110	30.1	23.5	18.6	7.3	0.0	−4.1	−11.4		−18.8
120	34.4	26.9	20.8	7.6	−1.7	−5.9	−14.4		−22.2
130	35.7	28.0	22.1	9.0	0.1	−4.7	−13.4		−21.4
140	40.4	31.4	24.3	9.0	−2.0	−6.3	−16.6		−29.0
150	39.8	32.2	24.4	10.8	1.2	−3.3	−13.9		−21.9

T/K	G_{12}	G_{13}	G_{14}	G_{22}	G_{23}	G_{24}	G_{33}	G_{34}	G_{44}
10	−0.04	−0.07	−0.05	−0.01	−0.02	−0.01	0.04	−0.04	−0.09
20	−0.4	−0.6	−0.5	−0.1	0.0	0.1	0.0	0.4	−0.1
30	−1.4	−1.4	−1.1	−0.1	0.1	0.2	0.9	0.5	0.6
40	−2.7	−2.5	−1.9	−0.3	0.2	0.5	1.7	0.7	1.5
50	−4.1	−3.6	−2.9	−0.6	0.3	0.7	2.5	1.1	2.5
60	−5.6	−4.8	−3.8	−0.9	0.4	0.9	3.2	1.5	3.6
70	−7.2	−6.1	−4.8	−1.2	0.4	1.2	3.9	1.9	4.7
80	−8.7	−7.3	−5.7	−1.6	0.4	1.4	4.5	2.5	5.7
90	−10.3	−8.5	−6.7	−2.0	0.5	1.7	5.1	2.9	6.8
100	−11.9	−9.7	−7.6	−2.4	0.5	1.9	5.7	3.2	7.8
110	−13.3	−10.8	−8.5	−2.8	0.4	2.0	6.1		8.6
120	−16.0	−12.9	−9.7	−2.8	1.8	3.4	8.3		11.2
130	−16.7	−13.4	−10.4	−3.5	0.7	2.8	7.9		10.9
140	−19.2	−15.3	−11.5	−3.5	1.9	3.5	9.5		16.8
150	−19.0	−15.7	−11.5	−4.5	0.3	1.9	8.2		13.3

T/K	H_{12}	H_{13}	H_{14}	H_{22}	H_{23}	H_{24}	H_{33}	H_{34}	H_{44}
10	0.13	0.20	0.14	0.04	0.05	0.04	−0.14	0.10	0.17
20	1.5	1.3	1.0	0.1	−0.2	−0.3	−1.8	0.0	−0.9
30	3.4	2.9	2.3	0.4	−0.3	−0.6	−2.6	−0.5	−2.4
40	5.4	4.5	3.5	0.9	−0.4	−0.9	−3.2	−1.0	−3.8
50	7.4	5.9	4.7	1.4	−0.4	−1.2	−3.7	−1.9	−5.3
60	9.2	7.4	5.7	1.9	−0.5	−1.4	−4.5	−2.9	−6.4
70	11.0	8.5	6.6	2.5	−0.2	−1.7	−4.6	−3.5	−7.5
80	12.6	9.7	7.6	3.0	−0.2	−1.9	−5.0	−4.2	−8.5
90	14.2	10.7	8.5	3.5	−0.1	−2.1	−5.1	−2.9	−9.5
100	15.4	11.7	9.3	4.1	0.2	−2.1	−5.1	−2.1	−9.8
110	16.7	12.7	10.1	4.5	0.4	−2.1	−5.2		−10.2
120	18.4	14.0	11.1	4.8	0.0	−2.5	−6.1		−11.1
130	19.1	14.7	11.8	5.4	0.7	−2.1	−5.7		−10.8
140	21.2	16.1	12.9	5.5	−0.1	−2.9	−7.0		−12.1
150	20.8	16.5	12.9	6.3	1.5	−1.4	−5.8		−8.7

Table 7. Additive Constant C_{ij}, S_{ij}, G_{ij}, and H_{ij} Values (All $J \cdot K^{-1} \cdot mol^{-1}$) for Heat Capacity, Entropy, Gibbs Energy Function [$\{G°(T) - H°(0)\}/T$], and Reduced Enthalpy [$\{H°(T) - H°(0)\}/T$] of Crystalline Alkenes

T/K	$C_{1\bar{2}}$	$C_{2\bar{2}}$	$C_{3\bar{2}}$	$C_{1\bar{3}}$	$C_{\bar{1}\bar{2}}$	$C_{\bar{2}\bar{2}}^{cis}$
10	0.51	0.00	−0.85	0.55	1.12	0.21
20	3.4	−0.6	−3.7	3.1	5.2	0.4
30	7.9	0.8	−4.4	6.3	10.3	0.8
40	12.3	2.1	−5.0	9.3	14.7	1.6
50	16.2	3.6	−4.7	11.9	17.6	2.3
60	19.8	4.8	−4.2	14.2	19.9	2.7
70	23.0	6.1	−3.6	16.3	22.2	2.9
80	26.2	7.6	−3.5	18.1	24.6	2.9

T/K	$S_{1\bar{2}}$	$S_{2\bar{2}}$	$S_{3\bar{2}}$	$S_{1\bar{3}}$	$S_{\bar{1}\bar{2}}$	$S_{\bar{2}\bar{2}}^{cis}$
10	0.18	0.01	−0.28	0.19	0.41	0.08
20	1.2	−0.3	−2.0	1.2	2.3	0.3
30	3.5	−0.3	−3.6	3.1	5.4	0.6
40	6.3	0.1	−5.0	5.3	9.0	0.9
50	9.5	0.7	−6.1	7.7	12.6	1.3
60	12.8	1.6	−6.7	10.0	16.0	1.8
70	16.1	2.3	−7.5	12.4	19.3	2.2
80	19.4	3.0	−8.2	14.7	22.4	2.6

T/K	$G_{1\bar{2}}$	$G_{2\bar{2}}$	$G_{3\bar{2}}$	$G_{1\bar{3}}$	$G_{\bar{1}\bar{2}}$	$G_{\bar{2}\bar{2}}^{cis}$
10	−0.04	−0.01	0.08	−0.05	−0.11	−0.03
20	−0.3	0.1	0.7	−0.3	−0.7	−0.1
30	−1.0	0.2	1.4	−0.9	−1.7	−0.2
40	−1.9	0.2	2.1	−1.7	−3.1	−0.3
50	−3.1	0.1	2.8	−2.7	−4.6	−0.5
60	−4.5	−0.1	3.4	−3.7	−6.2	−0.7
70	−5.9	−0.4	4.0	−4.8	−7.9	−0.9
80	−7.4	−0.7	4.5	−5.9	−9.5	−1.1

T/K	$H_{1\bar{2}}$	$H_{2\bar{2}}$	$H_{3\bar{2}}$	$H_{1\bar{3}}$	$H_{\bar{1}\bar{2}}$	$H_{\bar{2}\bar{2}}^{cis}$
10	0.13	0.01	−0.22	0.15	0.31	0.06
20	0.9	−0.3	−1.3	0.9	1.6	0.2
30	2.5	−0.1	−2.2	2.1	3.7	0.3
40	4.4	0.2	−2.9	3.6	5.9	0.6
50	6.4	0.7	−3.3	5.0	8.0	0.8
60	8.3	1.3	−3.7	6.3	9.8	1.1
70	10.2	1.9	−3.6	7.6	11.4	1.4
80	12.0	2.5	−3.8	8.8	12.9	1.5

tions to the thermodynamic functions of the C=C bond were distributed by adjacent bonds (see Table 1). The C=C bond between two secondary C atoms is assumed to be in a trans configuration, and specific corrections P^{cis} are introduced for *cis*-alkenes.

We did not apply corrections for molecular symmetry and mixing of chiral isomers to calculate the entropies and Gibbs energies of crystals. Coefficients of equations for the whole set of compounds examined in this work are given in Tables 2–4 in a matrix form.

Using general expressions 2 and 3, one can obtain equations for the additive calculations of the thermodynamic properties of the investigated compounds. For example, equations to calculate the heat capacity of some alkanes using classification by effective atoms are the following:

$$C_s(\text{octane}) = 2C_1 + 6C_2$$

$$C_s(\text{2-methylheptane}) = 3C_1 + 4C_2 + C_3$$

$$C_s(\text{2,2,4-trimethylpentane}) = 5C_1 + C_2 + C_3 + C_4$$

Using classification by effective bonds, we obtain the following equations for C_s of compounds from different classes:

$$C_s(\text{octane}) = 2C_{12} + 5C_{22}$$

$$C_s(\text{2-methylheptane}) = C_{12} + 2C_{13} + 3C_{22} + C_{23}$$

$$C_s(\text{2,2,4-trimethylpentane}) = 2C_{13} + 3C_{14} + C_{23} + C_{24}$$

$$C_s(\textit{cis}\text{-2-pentene}) = C_{12} + C_{1\bar{2}} + C_{2\bar{2}} + C_{\bar{2}\bar{2}}^{cis}$$

$$C_s(\textit{trans}\text{-2-pentene}) = C_{12} + C_{1\bar{2}} + C_{2\bar{2}}$$

$$C_s(\text{1-pentene}) = C_{12} + C_{22} + C_{2\bar{2}} + C_{\bar{1}\bar{2}}$$

Table 8. Additive Constant C_{ij}, S_{ij}, G_{ij}, and H_{ij} Values (All J·K^{-1}·mol^{-1}) for Heat Capacity, Entropy, Gibbs Energy Function [$\{G°(T) - H°(0)\}/T$], and Reduced Enthalpy [$\{H°(T) - H°(0)\}/T$] of Crystalline Alkanols

T/K	C_{12}^{OH}	C_{13}^{OH}	C_{21}^{OH}	C_{22}^{OH}	C_{31}^{OH}
10	0.81	0.01	0.47	1.07	0.59
20	3.2	1.2	4.15	1.1	3.2
30	7.3	4.0	8.37	2.2	6.4
40	11.1	6.6	12.1	2.6	9.0
50	14.5	9.1	15.4	3.1	11.2
60	17.6	11.2	18.2	3.7	13.2
70	20.4	13.6	20.6	4.6	15.0
80	23.5	16.1	23.0	6.2	16.7
90	25.6	17.9	25.2	6.8	18.4
100	27.8	19.7	27.3	7.8	20.1
110	29.8	21.0	29.3	8.9	21.8
120	31.5	21.4	31.3	9.7	23.5
130	32.9	21.1	33.3	9.4	25.1
140	34.7	19.8	35.2	8.2	26.6
150	35.7	21.5	37.2	10.7	28.2

T/K	S_{12}^{OH}	S_{13}^{OH}	S_{21}^{OH}	S_{22}^{OH}	S_{31}^{OH}
10	0.30	0.01	0.14	0.45	0.21
20	1.4	0.1	1.4	1.2	1.3
30	3.5	1.1	3.9	1.8	3.3
40	6.1	2.6	6.8	2.5	5.5
50	8.9	4.3	9.9	3.1	7.7
60	11.9	6.3	13.0	3.9	10.0
70	14.9	8.0	16.0	4.4	12.1
80	17.6	9.8	18.9	5.0	14.2
90	20.4	11.6	21.7	5.6	16.3
100	23.3	13.5	24.5	6.4	18.3
110	25.9	15.4	27.2	7.1	20.3
120	27.6	14.6	29.8	6.3	22.3
130	31.0	18.3	32.4	8.4	24.2
140	32.2	17.2	34.9	7.0	26.1
150	36.9	21.3	37.4	10.9	28.0

T/K	G_{12}^{OH}	G_{13}^{OH}	G_{21}^{OH}	G_{22}^{OH}	G_{31}^{OH}
10	−0.09	0.00	−0.04	−0.13	−0.06
20	−0.4	0.1	−0.3	−0.5	−0.4
30	−1.1	−0.1	−1.1	−0.8	−1.0
40	−2.0	−0.5	−2.2	−1.2	−1.8
50	−3.1	−1.1	−3.4	−1.5	−2.8
60	−4.3	−1.8	−4.7	−1.8	−3.8
70	−5.6	−2.5	−6.1	−2.1	−4.8
80	−6.9	−3.3	−7.5	−2.5	−5.9
90	−8.3	−4.1	−9.0	−2.8	−6.9
100	−9.6	−5.0	−10.4	−3.1	−8.0
110	−11.1	−5.9	−11.8	−3.5	−9.0
120	−11.7	−4.8	−13.2	−2.7	−10.0
130	−13.5	−7.0	−14.6	−3.8	−11.0
140	−14.2	−6.3	−15.9	−3.1	−12.1
150	−17.1	−8.5	−17.3	−5.1	−13.1

T/K	H_{12}^{OH}	H_{13}^{OH}	H_{21}^{OH}	H_{22}^{OH}	H_{31}^{OH}
10	0.03	0.01	0.11	0.33	0.16
20	1.0	0.2	1.1	0.7	1.0
30	2.4	1.0	2.8	1.0	2.3
40	4.1	2.1	4.7	1.3	3.6
50	5.8	3.2	6.5	1.6	4.9
60	7.6	4.1	8.2	1.9	6.1
70	9.2	5.4	9.8	2.2	7.3
80	10.7	6.4	11.3	2.5	8.4
90	12.1	7.5	12.7	2.8	9.4
100	13.6	8.6	14.1	3.3	10.4
110	15.0	9.6	15.4	3.7	11.3
120	15.9	9.8	16.6	3.6	12.3
130	17.4	11.1	17.8	4.5	13.2
140	18.0	11.0	19.0	3.9	14.1
150	20.0	12.7	20.1	5.8	15.0

$$C_s(\text{1-pentanol}) = C_{12} + 2C_{22} + C_{12}^{\mathrm{OH}}$$

$$C_s(\text{2-pentanone}) = C_{12} + C_{22} + C_{\mathrm{CO1}} + C_{\mathrm{CO2}}$$

Similar equations also can be obtained for other thermodynamic properties such as $S°(T)$, $\{G°(T) - H°(0)\}/T$, and $\{H°(T) - H°(0)\}/T$.

Table 9. Additive Constant C_{ij}, S_{ij}, G_{ij}, and H_{ij} Values (All J·K^{-1}·mol^{-1}) for Heat Capacity, Entropy, Gibbs Energy Function [$\{G°(T) - H°(0)\}/T$], and Reduced Enthalpy [$\{H°(T) - H°(0)\}/T$] of Crystalline Alkanones

T/K	C_{CO1}	C_{CO2}	C_{CO3}	C_{CO4}	S_{CO1}	S_{CO2}	S_{CO3}	S_{CO4}
10	0.78	0.61	−0.03	0.95	0.27	0.24	0.03	0.42
20	4.8	1.4	−1.0	0.8	1.8	0.8	−0.5	1.0
30	10.4	3.1	−0.7	2.7	4.9	1.7	−0.8	1.6
40	15.2	4.6	−0.3	2.9	8.5	2.8	−1.0	2.5
50	19.3	5.9	0.3	0.9	12.4	3.9	−1.0	2.8
60	22.6	7.2	0.9	−0.4	16.2	5.2	−0.7	3.0
70	25.5	8.5	2.0	−1.5	19.9	6.4	−0.7	2.8
80	27.8	10.4	3.5	0.1	23.5	7.5	−0.5	2.4
90	29.9	11.4	4.4	−1.1	26.9	8.7	−0.2	1.9
100	32.0	12.7	5.8	−1.3	30.1	9.9	0.2	1.9
110	34.1	14.0	6.9	−2.0	33.3	11.4	0.8	1.8
120	36.2	15.7	6.9	−3.1	36.5	11.5	−1.3	−0.1
130	36.5	14.8	6.4	−3.3	38.8	14.0	1.3	1.5
140	37.7	15.0	4.5	−5.1	42.0	13.3	−0.9	−0.6
150	41.7	14.6	5.2	−4.5	43.1	18.5	2.3	5.5

T/K	G_{CO1}	G_{CO2}	G_{CO3}	G_{CO4}	H_{CO1}	H_{CO2}	H_{CO3}	H_{CO4}
10	−0.07	−0.07	−0.01	−0.10	0.20	0.18	0.02	0.28
20	−0.5	−0.3	0.2	−0.1	1.3	0.5	−0.3	0.8
30	−1.4	−0.6	0.4	−0.5	3.5	1.1	−0.4	1.1
40	−2.7	−1.0	0.5	−1.0	5.8	1.8	−0.5	1.6
50	−4.3	−1.5	0.6	−1.2	8.1	2.5	−0.4	1.6
60	−5.9	−2.0	0.7	−1.5	10.2	3.2	−0.4	1.4
70	−7.7	−2.5	0.7	−1.7	12.2	3.8	−0.1	1.0
80	−9.4	−3.1	0.7	−1.8	14.0	4.5	0.1	0.6
90	−11.2	−3.6	0.6	−1.8	15.7	5.0	0.5	0.2
100	−12.9	−4.2	0.6	−1.9	17.2	5.8	0.9	0.0
110	−14.6	−4.9	0.4	−2.0	18.7	6.7	1.3	−0.2
120	−16.3	−4.7	2.2	−1.0	20.2	6.8	1.0	−1.1
130	−17.8	−6.0	0.8	−1.8	21.1	7.9	1.9	−0.7
140	−19.6	−5.7	2.2	−0.9	22.4	7.6	1.3	−1.9
150	−20.1	−8.7	0.4	−4.7	23.0	9.7	2.8	0.8

Calculations of Additive Contributions of Effective Atoms and Bonds to the Thermodynamic Functions

The constants were calculated by the method of least squares for separate classes of compounds: alkanes, alkenes, alkanols, and alkanones. We used the necessary values of P_{ij} derived for the alkanes to calculate additive constants P_{ij} for alkenes, alkanols, and alkanones. The values of additive constants in the range from 10 to 150 K are summarized in Tables 5–9.

Values of additive constants obtained by the above method can be used for prediction of thermodynamic properties of crystalline compounds, molecules of which consist of effective atoms and bonds presented in Table 1. For example, the heat capacities of crystals at $T = 100$ K (for alkenes at $T = 50$ K) calculated from our constants C_i for effective atoms are

$$C_s(\text{cr, 100 K})(\text{octane}) = 2 \times 24.7 + 6 \times 8.7 = 101.6$$

$$C_s(\text{cr, 100 K})(\text{2-methylheptane}) = 3 \times 24.7 + 4 \times 8.7 + (-8.2) = 100.7$$

$$C_s(\text{cr, 100 K})(\text{2,2,4-trimethylpentane}) = 5 \times 24.7 + 8.7 + (-8.2) + (-27.4) = 96.6\ \mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$$

If we use the classification by effective bonds, we shall obtain the following results:

$$C_s(\text{cr, 100 K})(\text{octane}) = 2 \times 27.9 + 5 \times 9.2 = 101.8$$

$$C_s(\text{cr, 100 K})(\text{2-methylheptane}) = 27.9 + 2 \times 21.2 + 3 \times 9.2 + 2.9 = 100.8$$

Table 10. Experimental and Calculated by Contributions of Effective Atoms (in Braces) and of Effective Bonds (in Parentheses) Values of the Thermodynamic Functions for Some Crystalline Compounds at Different Temperatures

	$C_S(T)$/(J·K^{-1}·mol^{-1})			$S°(T)$/(J·K^{-1}·mol^{-1})			[$\{G°(T) - H°(0)\}/T$]/(J·K^{-1}·mol^{-1})			[$\{H°(T) - H°(0)\}/T$]/(J·K^{-1}·mol^{-1})		
compound	50 K	100 K	150 K	50 K	100 K	150 K	50 K	100 K	150 K	50 K	100 K	150 K
octane	53.80	100.85	131.99	32.36	85.64	132.69	−10.91	−35.14	−60.00	21.45	50.50	72.69
	(54.5)	(101.8)	(133.3)	(32.5)	(86.6)	(133.6)	(−11.2)	(−35.8)	(−60.5)	(21.8)	(51.3)	(73.1)
	{55.0}	{101.6}	{134.6}	{33.0}	{87.2}	{134.6}	{−11.4}	{−35.6}	{−60.8}	{21.6}	{51.0}	{73.8}
2-methylheptane	54.65	101.00	135.11	35.81	89.06	136.57	−12.76	−37.79	−62.95	23.04	51.26	73.61
	(54.7)	(100.8)	(138.8)	(35.7)	(89.0)	(137.8)	(−12.8)	(−38.0)	(−63.6)	(23.0)	(51.3)	(74.2)
	{54.4}	{100.7}	{136.1}	{34.7}	{87.8}	{135.6}	{−12.5}	{−36.8}	{−62.1}	{22.2}	{50.6}	{73.5}
2,2,4-trimethyl -pentane	52.92	97.30	140.57	38.40	88.44	136.22	−14.77	−39.27	−63.68	23.62	49.17	72.53
	(52.7)	(95.4)	(139.6)	(39.1)	(89.2)	(135.5)	(−14.9)	(−39.8)	(−63.7)	(24.3)	(49.4)	(71.8)
	{51.7}	{96.6}	{137.3}	{37.6}	{87.5}	{132.9}	{−14.4}	{−38.6}	{−61.7}	{23.2}	{48.8}	{71.2}
cis-2-pentene	39.88			24.18			−8.194			15.98		
	(39.1)			(23.0)			(−7.6)			(15.3)		
trans-2-pentene	38.00			22.80			−7.647			15.16		
	(36.8)			(21.7)			(−7.1)			(14.5)		
1-pentene	41.76			26.95			−9.403			17.54		
	(42.3)			(26.7)			(−9.2)			(17.5)		
1-pentanol	41.53	74.19	97.19	26.61	66.50	101.1	−9.333	−28.15	−46.83	17.27	38.35	54.23
	(39.7)	(74.1)	(96.5)	(24.2)	(63.4)	(98.3)	(−8.4)	(−26.3)	(−45.1)	(16.0)	(37.2)	(53.4)
2-pentanone	46.44	82.20	106.18	29.58	73.44	116.22	−10.33	−31.18	−52.27	19.25	42.26	61.05
	(46.3)	(81.8)	(105.4)	(29.7)	(73.7)	(112.2)	(−10.5)	(−31.4)	(−52.3)	(19.4)	(42.5)	(59.8)

$$C_s(\text{cr, 100 K})(\text{2,2,4-trimethylpentane}) = 2 \times 21.2 + 3 \times 17.2 + 2.9 + (-1.5) = 95.4$$

$$C_s(\text{cr, 50 K})(\textit{cis}\text{-2-pentene}) = 17.0 + 16.2 + 3.6 + 2.3 = 39.1$$

$$C_s(\text{cr, 50 K})(\textit{trans}\text{-2-pentene}) = 17.0 + 16.2 + 3.6 = 36.8$$

$$C_s(\text{cr, 50 K})(\text{1-pentene}) = 17.0 + 4.1 + 3.6 + 17.6 = 42.3$$

$$C_s(\text{cr, 100 K})(\text{1-pentanol}) = 27.9 + 2 \times 9.2 + 27.8 = 74.1$$

$$C_s(\text{cr, 100 K})(\text{2-pentanone}) = 27.9 + 9.2 + 32.0 + 12.7 = 81.8\ \text{J·K}^{-1}\text{·mol}^{-1}$$

We give the appropriate values for eight compounds in Table 10 to illustrate an agreement between the calculated and experimental (smoothed) values of the thermodynamic functions.

Main Results of the Additive Calculations

Our calculations allow us to make the following principal conclusion. Additive calculation methods for the thermodynamic properties of organic crystals based on the classical theory of molecular structure are sufficiently reliable in the range from 10 K to T_{trs} (Tables 11 and 12). From Table 12, the relative deviations of the calculated values of thermodynamic functions amount to no more than 10% at 10 and 20 K. The absolute values of the thermodynamic properties at T = 10 K are small. For example, C_p(10 K) < 4 J·mol^{-1}·K^{-1} and $S°$(10 K) < 2 J·mol^{-1}·K^{-1} for alkanes up to $C_{10}H_{22}$. The percent average deviations of the calculated values of thermodynamic properties for crystalline alkanes, alkenes, alkanols, and alkanones at T > 30 K do not exceed 3–5 times the probable experimental error. Further, the agreement between calculated values and values based on experiment becomes better with a more detailed classification of the structural fragments. This conclusion is confirmed for the alkanes with the use of additive schemes, which classify effective atoms (Table 11) and effective bonds (Table 12).

Table 11. Average Percentage Deviations of Thermodynamic Function Values, Calculated Using Atomic Additive Contributions P_i, from Those Based on Experiment for Crystalline Alkanes

T/K	C_S	$S°$	$\{G°(T) - H°(0)\}/T$	$\{H°(T) - H°(0)\}/T$
10	16.8	18.3	19.7	17.9
20	7.9	11.1	16.4	13.4
30	4.5	7.9	9.9	7.3
40	3.0	6.1	8.1	5.3
50	2.3	5.1	6.9	4.1
60	2.0	4.7	6.1	3.6
70	1.8	3.9	5.4	3.0
80	1.3	3.7	5.0	2.8
90	1.9	3.4	4.6	2.8
100	2.3	3.2	4.3	2.6
110	1.4	2.8	4.1	2.0
120	1.4	2.6	3.9	1.8
130	1.5	2.6	3.9	1.7
140	1.9	2.4	3.3	1.7
150	1.9	1.7	2.7	1.2

Additive constants P_{ij} for alkanes, alkenes, alkanols, and alkanones (Tables 6–9) can be used for estimation of thermodynamic properties of crystals of the named classes of substances with a probable error given in Table 12 (multiplied by the Student factor). It is possible to obtain high precision in the additive calculations using only the additive constants determined from the stable system of equations (*10*). Earlier, we had tested the above conclusion when developing an additive method to calculate the enthalpies of formation of derivatives of urea (*4*). It was shown (*4, 10*) that the probability of obtaining systems of equations with unstable solutions was less the higher the ratio of the number of equations to the number of constants. The number of equations in the systems to calculate the additive constants decreased as the temperature increased. This resulted from the fact that the compounds in which solid-to-solid transition had occurred had been excluded from the systems at temperatures above the transition value. Hence, a decrease in the accuracy of the additive calculations may result.

This conclusion also holds when the agreement between calculated and experimental values is very good, for example, in the case of alkenes in the range from 90 to 100 K. The good agreement was obtained as a result of a decrease of the number of equations and not as a result of an increase in the reliability of the additive constants. Complete agreement will be obtained in the limited case when the number of equations is equal to the number of constants. Then we can make no conclusion on the reliability of additive contribution values.

Table 12. Average Percentage Deviations of Thermodynamic Function Values, Calculated Using Additive Bond Contributions P_{ij}, from Those Based on Experiment for Crystalline Alkanes, Alkenes, Alkanols, and Alkanones[a]

	alkanes				alkenes			
T/K	C_p	$S°$	$G°/T$	$H°/T$	C_p	$S°$	$G°/T$	$H°/T$
10	14.5	16.2	17.6	15.8	15.0	16.5	19.0	16.5
20	6.6	9.7	14.4	9.9	7.0	11.2	13.6	10.3
30	3.4	6.6	9.1	5.7	4.4	7.5	9.8	6.5
40	2.2	5.0	6.9	4.1	3.2	5.8	7.8	5.0
50	1.8	4.1	5.8	3.2	2.5	4.8	6.5	3.9
60	1.6	3.8	5.0	2.7	2.4	4.1	5.6	3.4
70	1.4	3.1	4.5	2.3	2.4	3.7	5.0	3.1
80	0.8	2.9	4.1	2.2	2.9	3.5	4.6	2.9
90	1.1	2.7	3.8	2.0				
100	1.1	2.4	3.5	1.7				
110	1.2	2.4	3.5	1.6				
120	1.1	2.1	3.0	1.4				
130	1.0	2.1	3.2	1.4				
140	1.1	1.5	1.7	1.3				
150	0.7	0.7	0.8	0.7				

	alkanols				alkanones			
T/K	C_p	$S°$	$G°/T$	$H°/T$	C_p	$S°$	$G°/T$	$H°/T$
10	5.3	5.6	7.4	5.5	8.7	10.4	9.8	9.9
20	6.0	6.2	6.1	6.2	4.2	5.4	6.4	5.0
30	3.9	5.4	5.9	5.2	3.7	4.5	5.2	4.2
40	2.7	4.5	5.3	4.1	2.9	3.9	4.6	3.7
50	1.9	3.8	4.7	3.3	2.2	3.5	4.1	3.2
60	1.5	3.2	4.3	2.7	1.5	3.2	3.8	2.7
70	1.1	2.9	3.9	2.3	1.0	2.7	3.5	2.2
80	0.6	2.6	3.5	2.0	1.0	2.3	3.2	1.8
90	0.5	2.3	3.3	1.7	1.0	2.1	2.9	1.5
100	0.4	2.1	3.0	1.4	1.3	1.9	2.7	1.3
110	0.4	1.9	2.6	1.2	2.2	1.5	2.5	1.2
120	0.3	2.0	3.0	1.2	3.0	1.5	2.2	1.5
130	0.5	1.7	2.6	0.9	2.0	1.5	2.2	1.3
140	1.1	1.8	2.7	1.0	2.7	1.3	2.1	1.0
150	0.4	1.5	2.2	0.9	1.9	0.4	1.1	1.0

[a] $G°/T$ and $H°/T$ mean $\{G°(T) - H°(0)\}/T$ and $\{H°(T) - H°(0)\}/T$, respectively.

The order of magnitude of the percent average deviations between the calculated and the experimental values of thermodynamic properties is approximately the same for alkanes, alkenes, alkanols, and alkanones (Table 12). This proves a rather general character of the conclusion concerning applicability of additive calculations to estimate thermodynamic properties of crystals of organic compounds. The experimental values published in reference books (*8*, *9*) do not cover classes of compounds which have phase transitions at high temperatures required to test additivity relationships. That is why it is important to measure thermodynamic properties of crystals within systematically selected groups of organic compounds with a regularly changing structure which do not undergo phase changes except at higher temperatures compared with alkanes and their derivatives.

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Received for review April 29, 1994. Accepted October 9, 1994.[®] We express our gratitude to the Thermodynamics Research Center (The Texas A & M University System) for the permission to use data from the *TRC Thermodynamic Tables*.

JE940084P

[®] Abstract published in *Advance ACS Abstracts*, December 1, 1994.