sorbed from the unsaturated ethanol solution of BHT. Only a small amount of BHT was absorbed by polyethylene from the 50/50 ethanol/water mixture, yielding a partition coefficient of about 0.4. By applying the measured solubility of BHT in 50/50 ethanol/water mixture, the solubility of BHT in polyethylene should be on the order of 0.1% or less at 30 °C.

There are also other indications that the true solubility of BHT in either linear or branched polyethylene may be very low. In polyethylenes loaded with about 100 ppm of ^{14}C-labeled BHT and remolded several times by compression, we still find evidence, by means of autoradiography, that the distribution of the radioactivity is highly nonuniform and that the radioactivity seems to aggregate into small concentrated particulate forms in the molded polymer plaques. It is possible that even the distribution of BHT in the amorphous regions of the plaque is not necessarily uniform. In separate experiments (*12*), BHT was noticed to escape from thin sheets of polyolefins and ethylene–vinyl acetate copolymers at room temperature into air at a rate more rapid than by solvent extraction. It appears that the rapid rate of loss may be associated with the sublimation from a large surface area of finely divided BHT particles mixed in the loose polymer matrix.

Thus, the solubility of BHT in polyethylene from equilibrium partitioning studies is much less than that estimated from the upper and lower bounds of absorption as mentioned above, from vapor uptake studies (*10*), and from diffusion studies (*11*). These discrepancies between the observations of solubilities of BHT in polymers from equilibrium partition and those from diffusion or vapor absorption require further investigation.

Registry No. BHT, 128-37-0; heptane, 142-82-5; ethanol, 64-17-5; 1-octanol, 111-87-5; polyethylene, 9002-88-4; polypropylene, 9003-07-0.

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Bond–Bond Interactions in Alkanes and Their Heteroanalogues. Allen-Type Group Increments for Estimating Enthalpies of Formation of Alkanes and Their Oxygen, Sulfur, and Nitrogen Analogues and Aliphatic Ketones

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Experimental values for the enthalpies of formation of 21 alcohols, 17 ethers, 7 acetals, and 71 alkanes were used to derive the values of the different group increments for alkanes and their oxygen analogues. The average difference between the calculated and estimated values for these 116 compounds is ±1.1 kJ/mol. The bond–bond interaction scheme so obtained was extended to saturated sulfur and nitrogen containing compounds and to aliphatic ketones by using enthalpies of formation of 45 sulfur and 21 nitrogen compounds and 18 ketones. The average differences between the calculated and the experimental values are ±0.8 kJ mol^{-1} for the sulfur and nitrogen compounds and ±1.0 kJ mol^{-1} for the aliphatic ketones. The values of the necessary bond energies have been corrected in accordance with the latest recommended values for the enthalpies of formation of gaseous atoms and selected model compounds.

Table I. Bond Energies in the Gaseous State

bond	E_b(g)/ (kJ/mol)	compd	$-\Delta H_f°$(g)/ (kJ/mol)	ref
C–C	330.1	CH_3CH_3	83.8	*16*
C–H	415.85	CH_4	74.7	*16, 17*
C–O	327.95	CH_3OH	201.1	*2b*
O–H	463.5	H_2O	241.8	*9*
C–S	274.15	CH_3SH	22.8	*2a, 9*
S–H	366.8	H_2S	20.6	*8*
S–S	246.2	H_2S_2	−10.2	*2b*
C–N	273.05	CH_3NH_2	23.0	*9*
N–H	390.9	NH_3	45.9	*9*
N–N	158.6	H_2NNH_2	−95.2	*17*
C=O	678.8	CH_2O	108.6	*2b*

Introduction

An Allen-type (*1*) bond–bond interaction scheme can be used for many purposes like evaluation of enthalpies of formation, nonbonded interactions, and conformational energies (*2a*). Kalb

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Table II. Carbon and Oxygen Compounds Used in Calculations

	$-\Delta H_f°(g)/(\text{kJ mol}^{-1})$						
compd	obsd	calcd	diff	$S_{15}^{HH}(C)$	S_{16}^{HH}	S_L	ref
ethanol	235.3 ± 0.4	234.7	−0.6	0	0	0	*14*
1-propanol	255.2 ± 0.5	255.1	−0.1	0	0	0	*14*
2-propanol	272.5 ± 0.5	273.0	+0.5	0	0	0	*2b*
1-butanol	275.1 ± 0.8	275.2	+0.1	0	0	0	*9*
2-methyl-1-propanol	283.9 ± 0.9	283.1	−0.8	0	0	0	*2b*
2-butanol	292.9 ± 1.0	293.2	+0.3	0	0	0	*2b*
2-methyl-2-propanol	312.7 ± 0.9	312.5	−0.2	0	0	0	*2b*
1-pentanol	295.7 ± 1.0	295.5	−0.2	0	0	0	*14*
3-methyl-1-butanol	301.4 ± 1.5	301.4	±0.0	1	0	0	*2b*
2-methyl-2-butanol	330.9 ± 1.5	330.8	−0.1	1	0	0	*2b*
2-pentanol	314.7 ± 1.1	313.4	−1.3	0	0	0	*2b*
3-pentanol	314.8 ± 1.1	313.4	−1.4	0	0	0	*2b*
2-methyl-1-butanol	302.1 ± 1.5	301.4	−0.7	1	0	0	*2b*
3-methyl-2-butanol	315.8 ± 1.1	319.4	+3.6	1	0	0	*2b*
1-hexanol	315.8 ± 1.0	315.7	−0.1	0	0	0	*14*
1-heptanol	336.5 ± 1.2	336.0	−0.5	0	0	0	*14*
1-octanol	356.3 ± 1.5	356.3	±0.0	0	0	0	*14*
1-nonanol	376.4 ± 1.7	376.5	+0.1	0	0	0	*14*
1-decanol	396.6 ± 1.9	396.8	+0.2	0	0	0	*14*
1-dodecanol	436.7 ± 1.9	437.3	+0.6	0	0	0	*14*
1-tetradecanol	479.4 ± 2.9	477.8	−1.6	0	0	0	*14*
1-hexadecanol	517.4 ± 3.3	518.3	+0.9	0	0	0	*14*
dimethyl ether	184.1 ± 0.5	184.1	±0.0	0	0	0	*2b*
ethyl methyl ether	216.4 ± 0.7	217.2	+0.8	0	0	0	*2b*
diethyl ether	252.2 ± 0.8	250.3	−1.9	0	0	0	*2b, 19*
methyl propyl ether	237.7 ± 0.8	238.0	+0.3	0	0	0	*2b, 19*
isopropyl methyl ether	252.1 ± 1.0	252.7	+0.6	1^a	0	0	*2b*
butyl methyl ether	258.2 ± 1.3	258.8	+0.6	0	0	0	*2b, 19*
methyl *tert*-butyl ether	292.6 ± 5.4	290.2	−2.4	2^a	0	0	*2b, 19*
ethyl propyl ether	272.3 ± 1.2	271.1	−1.2	0	0	0	*19*
dipropyl ether	293.1 ± 1.7	292.0	−1.1	0	0	0	*19*
diisopropyl ether	319.4 ± 2.3	321.3	+1.9	2^a	0	0	*19*
dibutyl ether	333.0 ± 1.1	333.6	+0.6	0	0	0	*19*
di-*sec*-butyl ether	360.4 ± 1.7	361.0	+0.6	3^b	0	0	*2b, 19*
decyl methyl ether	381.2 ± 2.1	383.7	+2.5	0	0	0	*19*
3,7-dioxanonane	436.3 ± 1.5	437.5	+1.2	0	0	0	*20*
2,4-dioxapentane	348.4 ± 0.6	348.5	−0.1	0	0	0	*2b*
3-methyl-2,4-dioxapentane	390.2 ± 1.3	388.3	−1.9	1^c	0	0	*2b*
3,3-dimethyl-2,4-dioxapentane	426.3 ± 2.1	427.0	+0.7	2^c	0	0	*2b*
3,5-dioxaheptane	414.8 ± 0.8	414.5	−0.3	0	0	0	*9*
4-methyl-3,5-dioxaheptane	453.6 ± 3.1	454.5	+0.9	1^c	0	0	*21*
2,4,6-trimethyl-3,5-dioxaheptane	526.0 ± 4.8	525.5	−0.5	3^c	0	0	*22*
5,7-dioxaundecane	501.3 ± 3.3	497.7	−3.6	0	0	0	*2*
propane	104.7 ± 0.6	104.6	−0.1	0	0	0	*16*
butane	125.7 ± 0.7	125.4	−0.3	0	0	0	*16*
2-methylpropane	134.2 ± 0.6	133.9	−0.3	0	0	0	*16*
pentane	146.6 ± 1.1	146.2	−0.4	0	0	0	*14*
2-methylbutane	153.6 ± 1.1	152.7	−0.9	1	0	0	*14*
2,2-dimethylpropane	168.2 ± 0.9	168.3	+0.1	0	0	0	*2b, 23*
hexane	167.0 ± 1.1	167.0	±0.0	0	0	0	*14*
2-methylpentane	174.8 ± 1.2	173.6	−1.2	1	0	0	*14*
3-methylpentane	172.2 ± 1.0	171.6	−0.6	2	0	0	*2b*
2,2-dimethylbutane	186.2 ± 1.0	185.2	−1.0	2	0	0	*2b*
2,3-dimethylbutane	178.4 ± 1.0	180.1	+1.7	2	0	0	*2b*
heptane	187.9 ± 1.8	187.8	−0.1	0	0	0	*14*
2-methylhexane	194.8 ± 1.4	194.4	−0.4	1	0	0	*14*
3-methylhexane	191.4 ± 2.0	192.4	+1.0	2	0	0	*2b*
3-ethylpentane	189.4 ± 1.5	190.5	+1.1	3	0	0	*2b*
2,2-dimethylpentane	205.9 ± 1.0	206.0	+0.1	2	0	0	*2b*
2,3-dimethylpentane	198.1 ± 0.8	198.9	+0.8	3	0	0	*2b*
2,4-dimethylpentane	201.8 ± 1.2	200.9	−0.9	2	0	0	*2b*
3,3-dimethylpentane	201.3 ± 1.2	199.7	−1.6	4	0	1	*2b*
2,2,3-trimethylbutane	204.6 ± 1.4	205.8	+1.2	4	0	2	*2b*
octane	208.7 ± 1.8	208.7	−0.0	0	0	0	*14*
2-methylheptane	215.4 ± 1.8	215.2	−0.2	1	0	0	*14*
3-methylheptane	212.6 ± 1.4	213.2	+0.6	2	0	0	*2b*
4-methylheptane	212.1 ± 1.4	213.2	+1.1	2	0	0	*2b*
3-ethylhexane	210.8 ± 1.3	211.3	+0.5	3	0	0	*2b*
2,2-dimethylhexane	224.7 ± 1.3	226.8	+2.1	2	0	0	*2b*
2,4-dimethylhexane	219.4 ± 1.4	219.7	+0.3	3	0	0	*2b*
2,5-dimethylhexane	222.6 ± 1.7	221.7	−0.9	2	0	0	*2b*
3,3-dimethylhexane	220.1 ± 1.3	220.6	+0.5	4	0	1	*2b*
3,4-dimethylhexane	213.0 ± 1.7	213.0	±0.0	4	0	2	*2b*
2,2,3-trimethylpentane	220.1 ± 1.8	224.7	+4.6	5	0	2	*2b*
3-ethyl-2-methylpentane	211.2 ± 1.5	211.0	−0.2	5	0	2	*2b*

Table II (Continued)

	$-\Delta H_f°(g)/(kJ\ mol^{-1})$						
compd	obsd	calcd	diff	$S_{15}^{HH}(C)$	S_{16}^{HH}	S_L	ref
2,2,4-trimethylpentane	224.1 ± 1.5	222.8	−1.3	3	1	0	*2b*
2,3,4-trimethylpentane	217.4 ± 1.8	219.5	+2.1	5	0	2	*2b*
2,2,3,3-tetramethylbutane	225.6 ± 2.0	226.6	+1.0	6	0	6	*24*
nonane	228.8 ± 1.8	229.5	+0.7	0	0	0	*14*
2,2,3,3-tetramethylpentane	237.2 ± 1.8	238.7	+1.5	8	0	8	*2b*
2,2,3,4-tetramethylpentane	237.0 ± 1.5	241.4	+4.4	6	1	2	*2b*
2,3,3,4-tetramethylpentane	236.2 ± 1.9	233.6	−2.6	8	0	8	*2b*
decane	249.5 ± 1.6	250.3	+0.8	0	0	0	*14*
2-methylnonane	260.0 ± 2.5	256.8	−3.2	1	0	0	*2b*
5-methylnonane	258.6 ± 1.9	254.9	−3.7	2	0	0	*2b*
undecane	270.8 ± 3.0	271.1	+0.3	0	0	0	*14*
2,2,5,5-tetramethylheptane	302.4 ± 3.3	301.2	−1.2	6	0	1	*2b*
3,3,5,5-tetramethylheptane	276.7 ± 3.3	273.7	−3.0	8	2	2	*2b*
2,2,4,4,5-pentamethylhexane	281.2 ± 3.3	282.2	+1.0	8	2	2	*2b*
dodecane	289.1 ± 1.5	291.9	+2.8	0	0	0	*14*
3,3,6,6-tetramethyloctane	318.2 ± 3.8	315.7	−2.5	8	0	2	*2b*
4,4,6,6-tetramethylnonane	313.4 ± 3.8	315.3	+1.9	8	2	2	*2b*
3,5-diethyl-3,5-dimethylheptane	301.4 ± 3.8	302.7	+1.3	12	2	4	*2b*
4,6-diethyl-4,6-dimethylnonane	347.1 ± 5.0	344.4	−2.7	12	2	4	*2b*
hexadecane	375.0 ± 3.8	375.1	+0.1	0	0	0	*14*
octadecane	414.5 ± 7.1	416.8	+2.3	0	0	0	*2b*
5-butyldocosane	587.8 ± 7.5	585.9	−1.9	3	0	0	*2b*
cyclohexane	123.5 ± 0.6	124.9	+1.4	0	0	0	*2b*
methylcyclohexane	154.8 ± 1.0	154.1	−0.7	0	0	0	*2b*
ethylcyclohexane	171.8 ± 1.5	173.0	+1.2	1	0	0	*2b*
propylcyclohexane	193.3 ± 1.3	193.8	+0.5	1	0	0	*2b*
butylcyclohexane	213.2 ± 1.8	214.6	+1.4	1	0	0	*2b*
decylcyclohexane	339.7 ± 2.9	339.5	−0.2	1	0	0	*2b*
1,1-dimethylcyclohexane	181.0 ± 2.0	179.8	−1.2	2	0	2	*2b*
cis-1,2-dimethylcyclohexane	172.2 ± 1.8	172.7	+0.5	3	0	2	*2b*
trans-1,2-dimethylcyclohexane	180.0 ± 1.9	181.4	+1.4	1	0	0	*2b*
cis-1,3-dimethylcyclohexane	184.8 ± 1.8	183.4	−1.4	0	0	0	*2b*
trans-1,3-dimethylcyclohexane	176.6 ± 1.7	174.7	−1.9	2	0	2	*2b*
cis-1,4-dimethylcyclohexane	176.7 ± 1.8	174.7	−2.0	2	0	2	*2b*
trans-1,4-dimethylcyclohexane	184.6 ± 1.8	183.4	−1.2	0	0	0	*2b*
r-1,*cis*-3,*cis*-5-trimethylcyclohexane	212.1 ± 1.6	212.6	+0.5	0	0	0	*2b*
1-isopropyl-4-methylcyclohexane	230.6 ± 3.3	229.6	−1.0	2	0	0	*2b*
cis-decalin	169.3 ± 2.3	169.7	+0.4	3	0	2	*2b*
trans-decalin	182.2 ± 2.3	182.8	+0.6	0	0	0	*2b*
3,5,7-trioxanonane	581.2 ± 1.0	578.7	−2.5	0	0	0	*25*
3,5,7,9-tetroxaundecane	741.0 ± 1.4	742.9	+1.9	0	0	0	*25*
3,5,7,9,11-pentoxatridecane	906.0 ± 1.9	907.0	+1.0	0	0	0	*25*
			av diff ±1.1				

[a] $S_{15}^{HH}(O)$. [b] $S_{15}^{HH}(C) + 2S_{15}^{HH}(O)$. [c] $S_{15}^{HH}(O)$ because of special conformational requirements of acetals.

et al. (*3*) applied it to 56 alkanes and at the same time improved the scheme by inclusion of two new interaction parameters. In 1962 Skinner (*2a*, *4*) developed a set of steric correction terms for alkanes which, however, becomes tedious when applied to the heteroanalogues. Pihlaja (*5*, *6*) reported a bond–bond interaction scheme for saturated organic oxygen compounds. Because of the similarity of corresponding increments in both schemes it was decided to unite alkanes and oxygen compounds into one scheme (*7*). Since then new values have been reported for the enthalpies of formation of gaseous atoms (*8*) and of some compounds (cf. Tables I–V) (*9*).

There are also several reports (*10*–*12*) where the bonded and nonbonded interactions in saturated hydrocarbons have been described in terms of numerous buttressing and branching effects to allow accurate prediction of their standard enthalpies of formation. Kao and Chung-Phillips (*13*) treated similarly some alcohols, ethers, thioethers, and amines. Although all these approaches have their own merits, they are fairly tedious and hence an easy to apply method which allows accurate predictions of enthalpies of formation for a wide range of compounds would be preferable for practical purposes. An Allen-type correlation fulfills this requirement although it is not as accurate for some highly branched alkanes as the more elaborate schemes (*10*–*12*).

In the present work the best values for a minimum number of Allen-type group increments to evaluate the standard enthalpies of formation of different saturated compounds containing carbon, hydrogen, oxygen, sulfur, and nitrogen are computed by utilizing the latest thermochemical values and atomic weights. The second aim of this study is to get further information about steric interactions in the molecules. All experimental determinations which we have used were examined in much the same way as Sunner et al. did in their excellent report on the constancy of the CH_2 increments in homologous series (*14*) unless similarly treated data were available elsewhere. Even in the latter case they were, however, rechecked.

General Treatment

First we adjusted the coefficients (when X = O) in the equation (*1*, *2*, *6*)

$$\Delta H_a°(g) - \sum E_b(g) = n_1\Gamma_{CCC} + n_2\Gamma_{CCX} + n_3\Gamma_{CXC} + n_4\Gamma_{XCX} + n_5\Delta_{CCC} + n_6\Delta_{CCX} + n_7\Delta_{XCX} + n_8S_{15}^{HH}(C) + n_9S_{15}^{HH}(X) + n_{10}S_{16}^{HH}(C) + n_{11}S_L \quad (1)$$

where $\Delta H_a°(g)$ is the heat of atomization of the compound in question and $\sum E_b(g)$ the sum of the respective bond energies in the gaseous state. The structural parameters n_1, n_2, etc. correspond to the numbers of the different interactions in the molecule. The general term Γ_{ABC} illustrates the effect of the interaction A–B–C, and Δ_{ABC} means the trigonal interaction because of three nonbonded atoms A, B, and C attached to the same carbon atom. S_{15}^{HH}(C or O) are the contributions of the gauche-*n*-butane type nonbonded interactions between fifth-neighbor hydrogen atoms; S_{16}^{HH}(C) is the contribution of the nonbonded interactions between sixth-neighbor hydrogen atoms; finally, S_L is the so-called locking parameter in alkanes (*3*). The values of S_L(O) and $S_{15}^{HO:}$ were shown to be negligible. Of course, some additional terms are necessary in the case of sulfur and nitrogen compounds and aliphatic ketones as shown later.

It should be pointed out that the above S-type increments do not represent solely the nonbonded interactions but include also contributions from other gauche-*n*-butane type conformations (*15*). Our simplified treatment, however, is based on the concept of most stable conformations with the minimum number of S_{15}- or S_{16}-type arrangements, and hence we prefer to denote these group increments as stated. This helps also comparison with a part of earlier literature (*3*, *4*, *5–7*). It should also be mentioned that our S_{15}^{HH}(Z) and S_{16}^{HH}(Z) increments correspond to X^G_{CCZC} and X^V_{CCCZC} increments of Kao and Chung-Phillips (*12*, *13*). Similarly our $S_{15}^{HO:}$(C) increment corresponds to their X^G_{CCCO} increment (*13*).

The following values were used for the enthalpies of formation of the gaseous atoms (*8*): $\Delta H_f°$(C,g) 716.7 kJ/mol, $\Delta H_f°$(H,g) 218.0 kJ/mol, $\Delta H_f°$(O,g) 249.2 kJ/mol, $\Delta H_f°$(S,g) 277.0, and $\Delta H_f°$(N,g) 472.7 kJ mol^{-1}. The values of bond energies in the gaseous state used for the left-hand side of eq 1 are presented in Table I together with the enthalpies of formation of those compounds from which the bond energies in question have been calculated. Some of the bond energy values used in this work differ slightly from the previous ones (*2a*, *7*). This is because new values have been used for the enthalpies of formation of gaseous carbon and some molecules.

In order to calculate the C–H bond energy we used the mean (*16*, *17*) of the values of Rossini and Pittam and Pilcher for the enthalpy of formation of methane. In order to calculate the C–C bond energy we used the enthalpy of formation of ethane measured by Pittam and Pilcher (*16*). The preference of these values is based on the fact that the CH_2 increments calculated for the enthalpies of formation of *n*-alkanes, determined by Pittam and Pilcher for the first five members of the series, are all except that from CH_4 to CH_3CH_3 almost identical with (~21.0 kJ mol^{-1}) and very close to the value of 20.6 kJ/mol which is usually used for this increment (*14*).

The calculations were made on a UNIVAC 1108 computer using a linear regression programme with a least-squares criterion (*5*). Tables II–V list the numbers of the S-type interactions and the enthalpies of formation of all the compounds which have been used to estimate the increments in eq 1. Tables VI–IX show the increments obtained and their standard errors together with some comparable group increments from previous studies. The differences between the calculated and the experimental results are also shown in Tables II–V. All numerical results were recalculated to the 1975 table of atomic weights (*18*) using otherwise the reference data in ref 8, 9, and 14. The given $\Delta H_f°$ values refer to 298.15 K and 101.325 kPa.

Discussion

Alkanes and Their Oxygen Analogues. The standard enthalpies of formation of 71 hydrocarbons, 21 alcohols, 17 ethers, and 7 acetals were used to estimate the values of the different group increments for alkanes and their oxygen analogues from relation 1.

Table III. Enthalpies of Formation of Sulfur Compounds Used for Calculations

compd	$-\Delta H_f°$(g)/(kJ mol^{-1}) obsd	calcd	diff	S_{15}^{HH}-(C)	$S_{15}^{HS:}$	ref
ethanethiol	46.3 ± 0.6	46.5	+0.2	0	0	*9*
1-propanethiol	67.9 ± 0.6	67.3	−0.6	0	0	*9*
1-butanethiol	88.1 ± 1.2	88.1	±0.0	0	0	*9*
1-pentanethiol	110.1 ± 0.7	108.9	−1.2	0	0	*9*
1-hexanethiol	129.6 ± 0.9	129.7	+0.1	0	0	*9*
1-heptanethiol	149.8 ± 0.9	150.5	+0.7	0	0	*9*
1-decanethiol	212.4 ± 1.3	213.0	+0.6	0	0	*2a*, *9*
2-propanethiol	76.2 ± 0.6	76.4	+0.2	0	0	*9*
2-methyl-1-propanethiol	97.3 ± 0.8	96.6	−0.7	0	0	*9*
2-butanethiol	96.9 ± 0.8	97.3	+0.4	0	0	*9*
2-methyl-2-propanethiol	109.6 ± 0.8	109.4	−0.2	0	0	*9*
3-methyl-1-butanethiol	114.9 ± 1.2	115.4	+0.5	1	0	*9*
2-methyl-2-butanethiol	127.1 ± 0.9	126.7	−0.4	1	1	*9*
1,2-ethanedithiol	9.7 ± 1.2	9.2	−0.5	0	0	*9*
1,3-propanedithiol	29.7 ± 1.3	30.0	+0.3	0	0	*9*
1,4-butanedithiol	50.5 ± 1.9	50.8	+0.3	0	0	*2*, *9*
1,5-pentanedithiol	71.0 ± 1.5	71.6	+0.6	0	0	*9*
2-thiapropane	37.5 ± 0.5	36.2	−1.3	0	0	*9*
2-thiabutane	59.6 ± 1.1	59.9	+0.3	0	0	*9*
2-thiapentane	82.2 ± 0.9	80.7	−1.5	0	0	*9*
3-methyl-2-thiabutane	90.5 ± 0.7	89.8	−0.7	0	0	*9*
2-thiahexane	102.2 ± 0.7	101.5	−0.7	0	0	*9*
3,3-dimethyl-2-thiabutane	121.3 ± 0.7	122.8	+1.5	0	0	*9*
2-thiaheptane	122.0 ± 2.5	122.3	+0.3	0	0	*2a*, *9*
3-thiapentane	83.5 ± 0.8	83.6	+0.1	0	0	*2a*, *9*
3-thiahexane	104.7 ± 0.7	104.5	−0.2	0	0	*9*
3-thiaheptane	127.1 ± 2.3	125.2	−1.9	0	0	*9*
4-thiaheptane	125.3 ± 0.8	125.2	−0.1	0	0	*9*
5-thianonane	167.4 ± 1.1	166.8	−0.6	0	0	*2a*, *9*
2,6-dimethyl-4-thiaheptane	179.6 ± 2.3	180.7	+1.1	0	2	*2a*, *9*
2,8-dimethyl-5-thianonane	221.6 ± 2.7	221.5	0.1	2	0	*2a*, *9*
2,4-dimethyl-3-thiapentane	141.9 ± 0.9	143.5	+1.6	0	0	*9*
2-methyl-1-butanethiol	115.1 ± 0.9	113.9	−1.2	1	1	*9*
3-methyl-2-butanethiol	121.3 ± 0.9	123.1	+1.8	1	1	*9*
2,2-dimethyl-1-propanethiol	129.0 ± 0.9	128.0	−1.0	0	2	*9*
2,3-dimethyl-2-butanethiol	147.7 ± 0.8	147.7	±0.0	2[a]	2[a]	*9*, *27*
2-methyl-2-pentanethiol	148.4 ± 1.0	147.5	−0.9	1	1	*9*, *27*
2,3-dithiabutane	24.2 ± 1.0	26.8	+2.6	0	0	*9*
3,4-dithiahexane	74.7 ± 1.1	74.2	−0.5	0	0	*9*
4,5-dithiaoctane	117.3 ± 1.1	115.8	−1.5	0	0	*9*
5,6-dithiadecane	158.4 ± 2.6	157.4	−1.0	0	0	*2a*, *9*
2,7-dimethyl-4,5-dithiaoctane	170.9 ± 2.2	171.3	+0.4	0	2	*9*
2,2-dimethyl-3-thiapentane	148.0 ± 2.4	146.5	−1.5	0	0	*9*
6-thiaundecane	205.1 ± 2.7	208.5	+3.4	0	0	*2a*, *9*
3,6-dithiaoctane	83.3	83.4	+0.1	0	0	*28*

[a] Two of these interactions are locked. Hence $2S_L$ is also included.

Comparisons of the group increment values obtained in this work (Table VI) with those reported previously show that they are, in general, very similar. The magnitude of the carbon–oxygen increments for the united carbon–oxygen scheme is close to that of the increments calculated earlier separately for the oxygen containing compounds. The S_{16}^{HH}(C) value obtained in this study deviates from that of Kalb et al. (*3*) to such an extent that the difference is real. This may be due to the fact that Kalb had only one compound with the S_{16}^{HH}(C) interaction. The other greater deviation (Table VI) concerns the Δ_{OCO} increment of Cox and Pilcher (*2*). This is because they have not

Table IV. Enthalpies of Formation of Nitrogen Compounds Used for Calculations

compd	$-\Delta H_f^\circ(g)/(\mathrm{kJ\ mol^{-1}})$ obsd	calcd	diff	$S_{15}^{\mathrm{HN:}}(\mathrm{N})$	ref
ethylamine	47.5 ± 0.7	49.2	+1.7	0	*9*
dimethylamine	18.5 ± 0.4	19.9	+1.4	0	*9*
propylamine	70.2 ± 0.4	70.0	−0.2	0	*9*
isopropylamine	83.8 ± 0.5	83.3	−0.5	0	*9*
trimethylamine	23.7 ± 0.6	23.7	±0.0	0	*9*
butylamine[a]	91.9 ± 0.9	90.8	−0.8	0	*2b, 9, 29*
sec-butylamine[b]	104.8 ± 0.8	104.1	−0.3	0	*2b, 9, 29*
tert-butylamine	121.0 ± 0.4	122.1	+1.1	0	*2b, 9*
diethylamine	72.6 ± 1.3	72.2	+0.3	0	*2b, 9, 29*
isobutylamine	98.7 ± 0.5	99.3	+0.6	0	*9, 30*
dipropylamine	116.0 ± 1.4	113.8	−1.1	0	*9, 31*
dibutylamine	156.6 ± 1.3	155.4	−2.7	0	*9, 31*
1,2-ethanediamine	17.0 ± 0.6	16.4	−0.6	1	*30*
1,2-propanediamine	53.6 ± 0.5	54.2	+0.6	1	*30*
1,2-butanediamine	74.0 ± 0.8	75.0	+1.0	1	*9, 30*
2-methyl-1,2-propanediamine	90.3 ± 0.6	89.3	−1.0	1	*9, 30*
methylhydrazine	−94.6 ± 0.6	−93.8	+0.8	0	*9*
1,1-dimethylhydrazine	−83.8 ± 2.5	−83.8	0.0	0	*2b*
1,2-dimethylhydrazine	−92.0 ± 4.2	−92.4	−0.4	0	*9*
piperidine	49.2 ± 1.0	50.8	+1.6	0	*2b, 9*
2-methylpiperidine	84.6 ± 1.1	85.0	+0.4	0	*32*

[a] ΔH_v estimated at 36.1 ± 0.8 kJ mol^{-1} starting from the values for ethyl- and propylamines. [b] ΔH_v estimated at 33.2 ± 0.9 kJ mol^{-1} starting from the values for propyl-, isopropyl-, and butylamines.

Table V. Enthalpies of Formation of Aliphatic Ketones Used for Calculations

compd	$-\Delta H_f^\circ(g)/(\mathrm{kJ\ mol^{-1}})$ obsd	calcd	diff	$S_{15}^{\mathrm{H\Pi}}$	ref
propanone	217.2 ± 0.7	216.8	−0.5	0	*2b*
butanone	238.6 ± 1.2	238.1	−0.5	0	*33*
3-pentanone	258.0 ± 0.8	259.9	+1.9	0	*34*
2-pentanone	259.1 ± 1.1	258.9	−0.2	0	*34*
3-methyl-2-butanone	262.6 ± 0.9	264.1	+1.5	0	*34*
2-hexanone	279.8 ± 1.0	279.7	−0.1	0	*34*
3,3-dimethyl-2-butanone	290.7 ± 0.9	291.1	+0.4	0	*34*
3-hexanone	278.3 ± 0.9	280.7	+2.4	0	*34*
2-methyl-3-pentanone	286.2 ± 0.9	285.9	−0.3	0	*35*
2,2-dimethyl-3-pentanone	313.9 ± 1.4	312.9	−1.0	0	*35*
2,4-dimethyl-3-pentanone	311.4 ± 1.2	311.9	+0.5	0	*35*
2-nonanone	340.9 ± 1.7	342.1	+1.2	0	*36*
5-nonanone	345.0 ± 1.3	343.1	−1.9	0	*34*
2,2,5,5-tetramethyl-3-hexanone	394.1 ± 2.3	393.9	−0.2	2	*35*
2,6-dimethyl-4-heptanone	357.7 ± 1.2	356.6	−1.1	2	*35*
2,2,6,6-tetramethyl-4-heptanone	421.3 ± 3.5	422.0	+0.7	4	*37*
6-undecanone	387.5 ± 2.0	385.8	−2.7	0	*34*
2-dodecanone	404.4 ± 2.4	404.6	+0.2	0	*36*

Table VI. Optimum Values of Group Increments (kJ mol^{-1})

increments	this work	reference *7*[b]	*6*	*3*	*2b*
Γ_{CCC}	11.71 ± 0.03	11.23 ± 0.05	11.46 ± 0.10	11.49 ± 0.40	10.8
Γ_{CCC}(alcohols)	11.16 ± 0.09				
Γ_{CCO}	24.01 ± 0.45	23.62 ± 0.28	23.14 ± 0.10		23.7
Γ_{CCO}(alcohols)	24.49 ± 0.49				
Γ_{COC}	23.72 ± 0.77	24.40 ± 0.61	24.67 ± 0.56		24.7
Γ_{OCO}	54.75 ± 0.85	54.96 ± 0.78	55.92 ± 1.34		54.8
Δ_{CCC}	−3.27 ± 0.14	−3.05 ± 0.19	−2.59 ± 0.68	−3.39 ± 0.34	−2.3
Δ_{CCO}	−6.52 ± 0.56	−6.12 ± 0.39	−5.54 ± 0.38		−6.0
Δ_{OCO}	−14.30 ± 0.84	−12.94 ± 0.72	−12.28 ± 0.67		−15.4
$S_{15}^{\mathrm{HH}}(\mathrm{C})$	−1.94 ± 0.16	−2.66 ± 0.17	−3.20 ± 0.42	−2.28 ± 0.23	−2.5
$S_{15}^{\mathrm{HH}}(\mathrm{O})$	−2.79 ± 0.95				
$\mathrm{S}_{15}^{\mathrm{HO:}}$			−0.61 ± 0.54		
$S_{16}^{\mathrm{HH}}(\mathrm{C})$	−10.58 ± 0.50	−12.59 ± 1.68	−8.36 ± 1.71	−11.87 ± 2.09	
$S_{16}^{\mathrm{HH}}(\mathrm{O})$		−6.72 ± 1.81			
S_{L}	−2.42 ± 0.18	−1.44 ± 0.25		−1.64 ± 0.32	
RMS	±1.556	±1.522	±1.170	±0.077[a]	

[a] kJ mol^{-1} bond^{-1}. [b] Private communication by Pihlaja and Vainiotalo in ref 7.

taken into account the steric factors (*6*). As the oxygen scheme reported by Pihlaja (*6*) showed already, the $S_{15}^{\mathrm{HO:}}$ increment, i.e., the gauche interaction between a fifth-neighbor hydrogen atom and the lone-pair electrons of an oxygen atom, is negligible. This is why this increment has been excluded from the scheme. The $S_{16}^{\mathrm{HH}}(\mathrm{O})$ increment has been excluded since only one of the compounds studied, namely isopropyl *tert*-butyl ether, has this kind of interaction. The calculated scheme

Table VII. Optimum Values of Group Increments for Sulfur Compounds (kJ/mol)

		reference	
increments	this work	*7*[a]	*33*
Γ_{CCS}	14.62 ± 0.18	13.87 ± 0.13	13.8
Γ_{CSC}	11.18 ± 0.37	11.81 ± 0.26	12.4
Γ_{CSS}	16.29 ± 0.28		18.5
Δ_{CCS}	−5.49 ± 0.23	−4.95 ± 0.18	−5.0
$S_{15}^{\mathrm{HS:}}(\mathrm{C})$	−1.52 ± 0.28		
RMS	±1.121	±0.721	

[a] Private communication by Pihlaja and Vainiotalo in ref *7*.

Table VIII. Optimum Values of Group Increments for Nitrogen Compounds (kJ/mol)

		reference	
increments	this work	*7*[a]	*2b*
Γ_{CCN}	17.13 ± 0.35	17.46 ± 0.50	17.2
Γ_{CNC}	19.85 ± 0.78	16.33 ± 0.65	18.0
Γ_{CNN}	24.40 ± 0.55	24.64 ± 0.73	24.3
Δ_{CCN}	−3.79 ± 0.43	−4.70 ± 0.77	−4.2
${}^{\mathrm{N}}\Delta_{\mathrm{CCC}}$	−12.86 ± 2.64	−6.66 ± 1.83	−6.8
${}^{\mathrm{N}}\Delta_{\mathrm{CCN}}$	−11.25 ± 1.82	−7.79 ± 2.28	−9.8
$S_{15}^{\mathrm{HN:}}(\mathrm{N})$	1.67 ± 1.04		
RMS	±1.224	±1.632	

[a] Private communication by Pihlaja and Vainiotalo in ref *7*.

Table IX. Optimum Values of Group Increments for Ketones (kJ/mol)

$\Gamma_{\mathrm{CC(=O)C}}$	89.50 ± 0.88
$\Gamma_{\mathrm{CCC_d}}$	12.70 ± 0.55
$\Delta_{\mathrm{CCC_d}}$	−7.50 ± 0.54
S_{15}^{HH}	−1.71 ± 0.33
RMS	±1.425

includes only one new parameter: $S_{15}^{\mathrm{HH}}(\mathrm{O})$. This illustrates the gauche-*n*-butane type interaction in a CCOC system. The inclusion of this parameter is justified since the resulting reciprocal position of the hydrogen atoms is different from that of $S_{15}^{\mathrm{HH}}(\mathrm{C})$ due to the different covalent radii of carbon and oxygen. The present $S_{15}^{\mathrm{HH}}(\mathrm{C})$ value is very close to the value of 2.1 kJ/mol used by Allen for this increment (*1*). It is also within the error limits equal to the value calculated by Kalb et al. (*3*). The little larger values obtained in previous carbon–oxygen schemes can be explained by the influence of the $S_{15}^{\mathrm{HH}}(\mathrm{O})$ increment.

It is interesting to compare our $S_{15}^{\mathrm{HH}}(\mathrm{C})$, $S_{15}^{\mathrm{HH}}(\mathrm{O})$, and $S_{16}^{\mathrm{HH}}(\mathrm{C})$ increments with the $X^{\mathrm{G}}_{\mathrm{CCCC}}$ [−3.87 kJ mol^{-1} for alkanes (*12*) and −2.60 kJ mol^{-1} for alcohols and ethers (*13*)] and $X^{\mathrm{G}}_{\mathrm{CCOC}}$ (−5.80 kJ mol^{-1}) (*12*) and $X^{\mathrm{V}}_{\mathrm{CCCCC}}$ (7.66 kJ mol^{-1}) (*12*) increments of Kao and Chung-Phillips, respectively, since the latter are representative for distinct conformations whereas in our approach the S increments do not initiate from the butane gauche-type interactions only but include also contributions from other possible arrangements in which the various interactions are not necessarily only repulsive (*15*). It appears that the interrelation of the above quantities is exactly as stated by the latter authors (*12*, *13*); e.g. their X^{G} values are larger than our S_{15} values whereas their X^{V} value is clearly smaller than our S_{16} value. On the other hand $S_{15}^{\mathrm{HH}}(\mathrm{O}) > S_{15}^{\mathrm{HH}}(\mathrm{C})$ as $X^{\mathrm{G}}_{\mathrm{CCOC}} > X^{\mathrm{G}}_{\mathrm{CCCC}}$ (the ratios are 1.43 and 1.50, respectively). It should be also emphasized that in our case $S_{15}^{\mathrm{HH}}(\mathrm{C})$ (i.e., $X^{\mathrm{G}}_{\mathrm{CCCC}}$) has a common value for alkanes and their heteroanalogues. Our locking parameter S_{L} is higher than the X_{S} parameter by Kao and Chung-Phillips since part of the rigidity of the G form has already been accounted for in their X^{G} parameter (*12*).

In the case of alkanols both Γ_{CCC} and Γ_{CCO} group increments differ significantly from those for other compounds (cf. Table VI) which lends support to the special character of the OH group as well as to the finding of Sellers et al. (*14*) that the $\mathrm{CH_2}$ increment for 1-alkanols (20.18 ± 0.04 kJ mol^{-1}) differs significantly from its average value (20.75 ± 0.15 kJ mol^{-1}).

Table X. Standard Enthalpies of Compounds $(\mathrm{CH_3})_3\mathrm{CXC}(\mathrm{CH_3})_2\mathrm{R}$[a] and $S_{16}^{\mathrm{HH}}(\mathrm{X})$ Interactions in Them

R	X	$-\Delta H_{\mathrm{f}}°(\mathrm{g})$/ (kJ mol^{-1})	$S_{16}^{\mathrm{HH}}(\mathrm{X})$/ kJ mol^{-1}
H	C		10.6
H	O	357.6 ± 5.0[b]	7.6
H	N	165.0 ± 3.7[c]	10.3
$\mathrm{CH_3}$	C		13.0[d,e,f]
$\mathrm{CH_3}$	O	363.4 ± 1.6[g]	22.0[d]
$\mathrm{CH_3}$	N	171.9 ± 3.2[c]	23.2[d]
$\mathrm{CH_3}$	S	188.9 ± 0.7[h]	10.5[d]

[a] Cf. ref *7b*. [b] References *2* and *19*. [c] Suradi, S.; Hacking, J. M.; Pilcher, G.; Gümrückü, I.; Lappert, M. F. *J. Chem. Thermodyn.* **1981**, *13*, 857. [d] These compounds include two of these locked $S_{16}^{\mathrm{HH}}(\mathrm{X})$ interactions. [e] This has been taken equal to $S_{16}^{\mathrm{HH}}(\mathrm{C}) + S_{\mathrm{L}}$. [f] The corresponding value based on the standard enthalpy of formation (−241.8 ± 1.4 kJ mol^{-1}) of 2,2,4,4-tetramethylpentane (*9*, *12*) would be 12.0 kJ mol^{-1}. [g] Reference *19* and: Smutny, E. J.; Bondi, A. *J. Phys. Chem.* **1961**, *65*, 546. [h] References *9* and *32*.

Two ethers whose enthalpies of formation are known were excluded from the scheme. These are isopropyl *tert*-butyl ether (*2b*, *19*) and di-*tert*-butyl ether (*2b*). The former is the only compound with the $S_{16}^{\mathrm{HH}}(\mathrm{O})$ interaction. The latter has two interactions of this kind, but furthermore they are both locked.

In this context it is, however, interesting to derive the values of the $S_{16}^{\mathrm{HH}}(\mathrm{X})$ interactions (X = O, S, N) by using standard enthalpies of formation (Tables II and X) which are available for compounds $(\mathrm{CH_3})_3\mathrm{CXC}(\mathrm{CH_3})_2\mathrm{R}$ when R = H (except X = S) and when (R = $\mathrm{CH_3}$). The values of the derived parameters are shown in Table X together with those for X = $\mathrm{CH_2}$.

From the acetals the values for 4,4-dimethyl-3,5-dioxaheptane (*26*) and 6-ethyl-5,7-dioxaundecane (*22*) have been excluded. In the case of the latter the enthalpy of formation in the gaseous state has been derived by using the estimated enthalpy of vaporization (*22*) which is not very accurate for high-boiling acetals. In accordance with earlier statements (*10*–*13*) the Kalb–Allen–Chung (KCA) method does not fit for highly branched alkanes. Although our scheme does it better it still cannot predict the standard enthalpies of formation of highly branched alkanes as accurately as the Somayajulu–Zwolinski (*10*, *11*) and Kao–Chung-Phillips approaches (*12*). Obviously this can be done only by taking into account a great number of structural parameters (*10*, *11*) or conformationally defined factors (*12*, *13*). The merits of the present method are its simplicity, small number of necessary parameters, and reasonably accurate prediction of ΔH_{f} values especially in the case of lower and/or moderately branched alkanes and their O, S, and N analogues.

Sulfur Compounds. The group increments, Γ_{CCC}, Δ_{CCC}, $S_{15}^{\mathrm{HH}}(\mathrm{C})$ and S_{L} (Table VI), already calculated for alkanes and their oxygen analogues, are also applicable to their sulfur analogues. Consequently, the new group increments for sulfur compounds can be solved from the equation

$$\Delta H_{\mathrm{a}}°(\mathrm{g}) - \sum E_{\mathrm{b}}(\mathrm{g}) - n_1\Gamma_{\mathrm{CCC}} - n_5\Delta_{\mathrm{CCC}} - n_7 S_{15}^{\mathrm{HH}}(\mathrm{C}) - n_8 S_{\mathrm{L}} = n_2\Gamma_{\mathrm{CCS}} + n_3\Gamma_{\mathrm{CSC}} + n_4\Gamma_{\mathrm{CSS}} + n_6\Delta_{\mathrm{CCS}} + n_9 S_{15}^{\mathrm{HH}}(\mathrm{S}) + n_{10} S_{15}^{\mathrm{HS:}} \qquad (2)$$

where the notations are the same as in eq 1. Table III lists the sulfur compounds whose enthalpies of formation have been used to calculate values of the new increments in eq 2 (Table VII).

The enthalpy of formation of 3,5-dithiaheptane (*28*), −65.4 kJ mol^{-1}, leads to a value, 30.3 kJ mol^{-1} for the Γ_{SCS} increment. The stabilizing Γ_{OCO} increment is clearly larger, 54.7 kJ mol^{-1} (Table VI). In this context it is also worth noting that the O–C–C–O arrangement has a −7.8 kJ mol^{-1} destabilizing effect as can be seen from the difference of the observed (*25*)

(−408.2 kJ mol^{-1}) and calculated enthalpies of formation of 3,6-dioxaoctane whereas the corresponding S–C–C–S moiety has no effect (cf. 3,6-dithiaoctane in Table III).

Nitrogen Compounds. The principle of calculating the group increments for the nitrogen compounds (Table V) corresponds to that for the sulfur compounds. For amines and hydrazines the increments including heteroatom are Γ_{CCN}, Γ_{CNC}, Γ_{CNN}, Δ_{CCN}, ${}^{\mathrm{N}}\Delta_{\mathrm{CCC}}$, and ${}^{\mathrm{N}}\Delta_{\mathrm{CCN}}$. The notation ${}^{\mathrm{N}}\Delta_{\mathrm{ABC}}$ stands for the interaction caused by the atom trio ABC attached to a nitrogen atom. Only two amines whose enthalpies of formation are known have S_{15}^{HH}(N)-type interactions. These compounds will be discussed separately. Table VIII gives the group increments calculated for 13 amines, 3 hydrazines, and 4 diamines (*30*). All of the latter have two $S_{15}^{\mathrm{HN:}}$-type interactions, i.e., gauche-1,4 interactions where the free electron pair of the nitrogen atom gets close to a hydrogen atom. Depending on the case, the above-mentioned interaction can occur over a carbon, $\{S_{15}^{\mathrm{HN:}}(\mathrm{C})\}$ or a nitrogen atom, $\{S_{15}^{\mathrm{HN:}}(\mathrm{N})\}$. Like $S_{15}^{\mathrm{HO:}}$(C) for oxygen compounds, $S_{15}^{\mathrm{HN:}}$(C) proved to be negligible.

Triethylamine [$-\Delta H_f°$(g) 92.9 ± 0.8 kJ mol^{-1} (*2*, *9*)] has three S_{15}^{HH}(N)-type interactions and from the difference between the observed and calculated enthalpies of formation a value, −3.2 kJ/mol, can be obtained for this increment. Diisopropylamine ($-\Delta H_f°$(g) 144.2 ± 0.4 kJ mol^{-1}) (*9*) has two interactions of this kind. In this case the increment in question should have a positive value (+1.8 kJ mol^{-1}) which is hardly possible. Hence the experimental enthalpy of formation for diisopropylamine must be inaccurate.

Furthermore the Γ_{NCN} increment can be estimated manually from the standard enthalpy of formation (−17.6 ± 1.4 kJ mol^{-1}) (*9*) of gaseous *N*,*N*,*N*′,*N*′-tetramethylmethylenediamine at 44.9 kJ mol^{-1}, an intermediate value between those of Γ_{OCO} and Γ_{SCS}.

In general, a fairly accurate value can be calculated for an unknown enthalpy of formation by means of the group increments shown in Tables VII and VIII as can be concluded from the average differences between the observed and the calculated values: ±0.8 kJ/mol for both sulfur (Table III) and nitrogen compounds (Table IV).

The most interesting of the calculated increments are those of the *S*-type caused by steric interactions. These interactions can be qualitatively examined by means of the calculated increments. Let us first examine the gauche-1,4 interactions between two hydrogen atoms: S_{15}^{HH}(C), S_{15}^{HH}(O), S_{15}^{HH}(S), and S_{15}^{HH}(N). Significantly different values have been obtained for all the four S_{15}^{HH} increments. It seems natural to think that in CCYC-type systems where the gauche-1,4 interactions take place over the Y atom, the magnitude of the interaction depends on the length of the C–Y bond and, to some extent, on the CYC bond angle. For alkanes, ethers, thiaalkanes, and amines these lengths are r(C–O) ~ 143 pm, r(C–N) ~ 147 pm, r(C–C) ~ 154 pm, and r(C–S) ~ 182 pm. This should lead to $S_{15}^{\mathrm{HH}}(\mathrm{O}) > S_{15}^{\mathrm{HH}}(\mathrm{N}) > S_{15}^{\mathrm{HH}}(\mathrm{C}) > S_{15}^{\mathrm{HH}}(\mathrm{S})$. Only the value of S_{15}^{HH}(N) (−3.2 kJ mol^{-1}) does not seem to fit in the series. It is, however, based on the enthalpy of formation of triethylamine only and can hence be regarded as less accurate.

The size of the heteroatom is also important. From the gauche-1,4 interactions $S_{15}^{\mathrm{HO:}}$(C), $S_{15}^{\mathrm{HN:}}$(C), and $S_{15}^{\mathrm{HS:}}$(C) the first two are negligible whereas the value of $S_{15}^{\mathrm{HS:}}$(C) differs significantly from zero due to the voluminous sulfur atom (Table VII).

A notable positive value obtained for the $S_{15}^{\mathrm{HN:}}$(N) increment is in agreement with an attraction between the *N*-hydrogen atom and the lone-pair orbital of the other nitrogen atom (Table VIII). The $S_{15}^{\mathrm{HN:}}$(N) increment has been calculated by means of four diamines, all of which have one interaction of this kind. All of these compounds have, however, a pair of 1,4-nitrogen atoms. This kind of grouping like the 1,4-oxygen atoms may cause destabilization in the molecule (*25*, *39*). If this is the case, the actual stabilization caused by the $S_{15}^{\mathrm{HN:}}$(N) increment would be correspondingly greater than that obtained.

Ketones. When the interdependence of the structure and the enthalpy of formation of ketones was studied, the following interactions were supposed to be effective in addition to the normal carbon increments: $\Gamma_{\mathrm{CC(=O)C}}$, $\Gamma_{\mathrm{CCC_d}}$, $\Delta_{\mathrm{CCC_d}}$, S_{15}^{HH}(C=O), S_{16}^{HH}(C=O), and S_{15}^{HII}. Here $\mathrm{C_d}$ stands for a carbonyl carbon. S_{15}^{HH}(C=O) and S_{16}^{HH}(C=O) indicate the same steric interactions as S_{15}^{HH}(C) and S_{16}^{HH}(C) for hydrocarbons, but they take place over the carbonyl carbon. $S_{15}^{\mathrm{H\Pi}}$ corresponds to a gauche-1,4 interaction between a Π-orbital of the C=O bond and a hydrogen atom. Of the ketones whose enthalpies of formation are known, only 2,2,4-trimethyl-3-pentanone and 2,2,4,4-tetramethyl-3-pentanone have one and two S_{16}^{HH}(C=O) interactions, respectively. In addition, these interactions are locked in the latter. Hence they have been excluded from the correlation. Table V lists all the enthalpies of formation of the compounds which have been used to estimate the increments, and the number of *S*-type interactions for these compounds.

The number of different interactions was based on the eclipsed conformations to minimize the number of steric interactions. The S_{15}^{HH}(C=O) interaction was shown to be negligible. The values of the group increments for ketones are presented in Table IX.

Finally we discuss briefly the observed and calculated enthalpies of formation of 2,2,4-trimethyl- and 2,2,4,4-tetramethyl-3-pentanones (*35*):

	$-\Delta H_f°$(g)/(kJ/mol)		
	obsd	calcd	diff
2,2,4-trimethyl-3-pentanone	338.3	339.2	−0.4
2,2,4,4-tetramethyl-3-pentanone	345.8	366.3	−20.5

On the basis of these values it would seem that ketones had no normal S_{16}^{HH}(C=O) interaction. Instead, when being locked, this interaction would have such a high value as −10.3 kJ/mol. The real situation remains, however, somewhat unclear because of this minimum amount of experimental data.

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Activity Coefficients and Excess Gibbs Free Energies for the Systems Isobutyl Methyl Ketone (1)–1-Pentanol (2) and Isobutyl Methyl Ketone (1)–1-Hexanol (2)

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Isobaric boiling point data for the systems isobutyl methyl ketone (1)–1-pentanol (2) and isobutyl methyl ketone (1)–1-hexanol (2) were obtained by the indirect method over the entire range of composition by using a standard Swietoslawski type ebulliometer. The measurements were made at 200 and 700 mmHg. The experimental *t–x* data were used to estimate Wilson parameters and then used to calculate the equilibrium vapor compositions and the theoretical points for these binary mixtures. These Wilson parameters are useful to calculate activity coefficients, and these in turn are useful to calculate excess Gibbs free energy. Excess Gibbs free energies are positive over the entire range of composition in both the binary systems.

Introduction

Evaporation has been used as an effective means of separation in chemical processing. Evidently an accurate and complete knowledge of vapor–liquid equilibrium data on the mixture under consideration is necessary for the design of distillation equipment. Generally vapor–liquid equilibrium data are obtainable under two fixed conditions, namely, isothermal and isobaric. Most distillation process are carried out at constant pressure rather than constant temperature, so that the temperature–composition curves are more practical in making engineering calculations such as the number of plates, although for theoretical considerations the pressure–composition curves are preferable. Here, an attempt has been made to calculate vapor compositions, activity coefficients, and excess Gibbs free energies for the systems isobutyl methyl ketone (1)–1-pentanol (2) and isobutyl methyl ketone (1)–1-hexanol (2) at 200 and 700 mmHg.

Experimental Section

The vapor–liquid equilibrium measurements were studied in a Swietoslawski ebulliometer (*1*). The ebulliometer was connected to a vacuum system. The pressures were measured with a mercury manometer with an accuracy of ±1 mmHg. The temperatures were measured with a PT100 thermometer with an accuracy of ±0.1 °C. The detailed procedure was described previously (*1*).

Isobaric Binary Systems. The boiling points of the systems isobutyl methyl ketone (1)–1-pentanol(2) and isobutyl methyl ketone (1)–1-hexanol (2) were determined over the entire range of composition. Mixtures of different compositions were prepared by taking quantities (by weight) of the pure materials. The boiling points for the known binary compositions were measured at 200 and 700 mmHg.

The boiling point of a specified composition was first measured at 200 mmHg. Then the pressure was raised to 700 mmHg and the boiling point was determined. The system was brought back to 200 mmHg, where the boiling point measurement was repeated, and finally the measurement was repeated at 700 mmHg thereby obtaining duplicate sets of boiling points at both the pressures of interest.

Purification of Materials. The alcohols were purified by the method described by Rao and Naidu (*2*). Isobutyl methyl ketone was purified by the method described by Reddy and Naidu (*3*). The purity of the samples was checked by measuring densities, refractive indices, and boiling points. The densities were measured with a standard bicapillary pycnometer which gave an accuracy of 5 parts in 10^5. Refractive indices were determined with an Abbe's refractometer which gave an accuracy of ±0.0002. The measured values are in good agreement with the literature values (*4*, *5*).

Results and Discussion

In the present work, isobaric *t–x* measurements are used for the data reduction. The model for expressing the compo-