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A Group Additivity Approach for the Estimation of Heat Capacities of Organic Liquids and Solids at 298 K

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A group additivity method is described which provides heat capacity estimates of the condensed phase. The data base consists of 810 liquids and 446 solids. Group values for carbon in various common substitution and hybridization states and for 47 functional groups are provided. The standard error of estimation using this approach on this data base is 19.5 (liquids) and 26.9 J/(mole K) (solids). This can be compared to typical experimental uncertainties of 8.12 and 23.4 J/(mole K) associated with these measurements, respectively. Experimental uncertainties were estimated from the numerical differences obtained for a given substance from multiple independent literature reports.

KEY WORDS: Group additivity; estimation of heat capacity.

The corrections of many thermochemical properties to a standard state often require a knowledge of the heat capacity of a substance. Heat capacity corrections are often small and comparable in magnitude to the uncertainties in other thermochemical measurements (e.g., vaporization, sublimation, and fusion enthalpies) and are frequently ignored. Since most thermochemical measurements are usually performed at temperatures somewhat above ambient, this introduces a systematic error in the measurement at 298 K if heat capacity corrections are neglected. The fact that these corrections for measurements near ambient are generally small suggests that estimation techniques would prove useful if the experimental information is not available. For measurements far from ambient, and for large molecules, these corrections become increasingly important.

Several group methods have been developed for the estimation of heat capacity of gases. These include the methods of Benson [1, 2], Rihani and Doraiswamy [3], Thinh *et al.* [4], Dobratz [5], and Meghreblian [6]. The group parameters available for gases are extensive and parameters are available for a broad spectrum of functional group types.

In contrast to gases, the available methods for estimating condensed phase heat capacities are more limited [7]. Kopp's law is one of the simplest methods to use and is applicable to both liquids and solids [8]. In this treatment, the heat capacity of a substance is expressed in terms of the heat capacities of its constituent atoms. For liquids, Johnson and Huang developed a method that allows estimations of $C_p(l)$ to within 10% of the experimental value [9]. A similar method based on the principle of group additivity has been developed by Chueh and Swanson [10]. The latter method is more complicated to use but gives a better correlation with experiment. Both methods suffer from the limited number of group values that have been evaluated.

The methods presently available to estimate heat capacities of solids are far more limited in scope. Application of Kopp's law to solids has already been mentioned. Another group additivity method for estimating heat capacities of solids has been developed by Domalski and Hearing [11]. The method has only been applied to hydrocarbons.

Other methods developed for correcting vaporization enthalpies with temperature include Watson's equation and various modified versions [12]. Most require

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some knowledge of critical parameters and other thermochemical properties, some of which are generally more difficult to measure than the heat capacities themselves.

Domalski, Evans, and Hearing have critically reviewed a variety of thermochemical data including experimental heat capacities [13], and this compendium has recently been updated by Domalski and Hearing [14]. Our interest in developing reliable approximation techniques for latent enthalpies, the need to correct our own experimental data to the standard state, and the availability of critically reviewed data [13, 14] (our source of data) have encouraged us to extend the existing methods of estimating heat capacities to the condensed phases. As noted, the estimation of gas-phase heat capacities has been addressed by Benson [1] and the more recent work of Domalski and Hearing [11]. We have therefore focused our attention on the condensed phases. Since gas-phase corrections are often needed in conjunction with their condensed-phase counterparts (for vaporization and sublimation enthalpy corrections), we have modeled our technique and our notation to resemble the method developed by Benson [1]. Some differences between the two methods do exist and are described here in detail.

The same philosophical guidelines have been followed as reported in our earlier work [15]. We have tried to provide the best possible correlation with the fewest number of parameters. This has generally been interpreted to mean agreement within about two standard deviations of literature uncertainties. Our previous conventions with regard to the definition of the terms primary, secondary, tertiary, and quaternary carbon have also been retained. The terms are defined with respect to the number of attached hydrogens at carbon, 3, 2, 1, 0, respectively. Group values based on limited experimental data are enclosed in brackets.

The most significant difference between our method and Benson's method concerns the use of correction terms. Heat capacity estimates of cyclic systems using the Benson convention are addressed by ring corrections that are applied separately to the calculation. In addition, some non-nearest-neighbor corrections are also included. In our method these corrections have been eliminated by using group values designed for cyclic compounds. These terms are identified by the subscript c in Tables I and II. The introduction of any other corrections to the estimation does not seem justified at this time. In addition to the Benson notation, we also identify groups on the basis of hybridization and substitution patterns. Some differences in notation are the result of the fewer parameters used in this treatment. This is discussed in detail.

The following protocol was used in deriving group parameters. Most group values for carbon and hydrogen were derived from existing data on hydrocarbons. Group values for primary and secondary sp^3 carbons were derived from the *n*-alkanes. A two-parameter weighted least-squares fit of the experimental heat capacities of 25 liquid *n*-alkanes and 14 solid *n*-alkanes gave a good fit to the data and resulted in the contributions for methyl and methylene groups listed in the first and second entries in columns 3 and 4 of Table I. (The line was fit by a least-squares procedure where the fractional difference between experimental and calculation was minimized; i.e., $(C_p\ (\text{expt}) - C_p\ (\text{calcd}))/C_p\ (\text{expt})$.)

The remaining solid and liquid hydrocarbons were arranged according to phase and structure type in order to derive meaningful statistics for as many carbon groups as possible. Once a group value was evaluated, it was then used in subsequent calculations whenever necessary. In all calculations, the group value was obtained by allowing its value to vary while minimizing the fractional difference between experiment and calculation by the method of least squares. In certain instances, two or more group values were allowed to vary simultaneously. A detailed listing of the individual compounds used to derive each group value and the sequence in which these values were evaluated are available in the supplementary tables along with a comparison of experimental and calculated values. All experimental data used in the correlations have been critically reviewed [13, 14], and the value with the highest rating was used whenever possible. With a few exceptions, only data at 298 K were used.

For a few liquid (l) and solid (c) hydrocarbon groups (secondary (c), tertiary (c), and quaternary sp^2 carbons (l, c); cyclic tertiary (c) and quaternary sp^2 carbons (l, c); and cyclic quaternary sp^3 (l, c)), not enough hydrocarbon data were available to generate reliable group values. The following protocol was used in these cases to improve the statistics. All compounds in our data base containing these groups (102 entries consisting of 65 liquids and 37 solids) were separated from the entire data base (1256 entries). The data base consisting of all the hydrocarbon derivatives (937 total entries consisting of 601 liquids and 347 solids) were grouped according to phase and functional group type and group values for all the functional groups listed in Table I were evaluated as described above. Once heat capacity contributions for each functional group were established, these functional group values were then used as appro-

Table I. Group Values for Estimating Heat Capacities of Liquids and Solids at 298 K.

Hydrocarbon groups	Benson notation[a]	Group values[b,c] C_p(l)	Group values[b,c] C_p(c)	Data points Liquids	Data points Solids
Primary sp^3 carbon	$C(H)_3-(C)$	34.9	36.6	25	14
Secondary sp^3 carbon	$C(H)_2-(C)_2$	31.9	26.9	24	14
Tertiary sp^3 carbon	$C(H)-(C)_3$	22.4	9.00	20	11
Quaternary sp^3 carbon	$C-(C)_4$	14.0	−4.98	17	7
Secondary sp^2 carbon	$C_d(H)_2$	25.8	[46.0]	18	3
Tertiary sp^2 carbon	$C_d(H)-(C)$	27.8	21.4	22	13
Quaternary sp^2 carbon	$C_d-(C)_2$	21.7	[6.86]	30	6
Tertiary sp carbon	$C_t(H)$	[34.3]	[37.1]	3	3
Quaternary sp carbon	$C_t-(C)$, and C_a	28.9	[15.5]	9	6
Tertiary aromatic sp^2 carbon	$C_B(H)$	21.8	17.5	32	27
Quaternary aromatic sp^2 carbon	$C_{BF}(C_B)_2(C_{BF})$, and $C_{BF}(C_B)(C_{BF})_2$, and $C_B-(C)$	15.3	8.49	32	27
Internal quaternary aromatic sp^2 carbon	$C_{BFi}(C_{BF})_3$		[4.44]		4
Cyclic secondary sp^3 carbon	$C_c(H)_2-(C_c)_2$	25.9	24.6	46	27
Cyclic tertiary sp^3 carbon	$C_c(H)-(C_c)_2(C)$	20.6	11.7	40	20
Cyclic quaternary sp^3 carbon	$C_c-(C_c)_2(C)_2$	18.0	6.11	12	11
Cyclic tertiary sp^2 carbon	$C_{cd}(H)-(C_c)$	21.8	15.9	17	7
Cyclic quaternary sp^2 carbon	$C_{cd}-(C_c)(C)$	21.2	[4.73]	12	5

[a] The subscripts used in this column follow the notation used by Benson and have the following meanings: d, double bond; t, triple bond; B, carbon atom in benzene and related heterocycles; a, allenic carbon; BF, a carbon atom in a fused ring system such as naphthalene and $C_{BFi}-(C_{BF})_3$ represents a carbon atom in a graphite environment such as found in the two internal carbons of perylene (see text); subscript c refers to ring atoms (not used by the Benson notation); unsubscripted carbon atoms may be C_d, C_B, C_t, C_c, C_{cd} or any one of the functional groups listed in Table II; C_{cd} and C_B groups may be substituted for the C_c group; groups that potentially can be varied are set off by a hyphen; see text for further discussion; all values are in J/(mole K); 1 cal = 4.184 J.

[b] Values in brackets are considered as tentative assignments only.

[c] There are no other corrections to be applied.

priate to evaluate the carbon group values for those listed above. These compounds (102 entries) were then returned to their appropriate functional group listings, and functional group values were again allowed to vary in order to minimize the error. Generally, functional group values were not significantly affected by this iterative procedure once a group value had been evaluated. The last two columns in Tables I and II indicate the number of compounds used in evaluation of each parameter. Molecules containing multiple functional groups are counted more than once in this entry only if the group values for the functional groups in the molecule were allowed to vary simultaneously. As noted, those parameters considered tentative are enclosed in brackets, and estimations using these values should be treated with due caution.

The procedure just described allowed the evaluation of the group values listed in Tables I and II. The hydrocarbon groups in Table I are identified by substitution and hybridization. As noted, a modified version of the Benson notation (sometimes abbreviated) is also provided for each group (column 2). The subscripts d, t, a, B, BF, and BFi refer to a double- and triple-bonded atom, an allenic carbon, a benzene carbon, a bridge carbon in a fused aromatic ring such as naphthalene, and a fused internal carbon atom, respectively. The subscript BFi is new and refers to a fused carbon such as found in graphite. The two internal carbons of perylene (**1**),

Table II. Functional Group Values for Estimating Heat Capacities of Liquids and Solids at 298 K.

Functional group	Benson notation[a]	Group values[b] C_p(l)	Group values[b] C_p(c)	Data points Liquids	Data points Solids
Hydroxyl (alcohols, phenols)	HO−(C)	53.1	23.5	73	33
Fluorine	F−(C)	16.2	[24.8]	46	4
Chlorine	Cl−(C)	30.8	28.7	37	17
Bromine	Br−(C)	34.6	32.4	26	9
Iodine	I−(C)	39.1	[27.9]	8	3
Nitrile	NC−(C)	47.7	[42.3]	17	8
Carboxylic acid	CO(OH)−(C)	87.4	53.1	13	35
Acid chloride	CO(Cl)−(C)	[62.8]	[60.2]	4	1
Aldehyde	CO(H)−(C)	57.7	[84.5]	19	2
Ketone	CO−$(C)_2$	51.5	[28.0]	23	5
Cyclic ketone	CO−$(C_c)_2$	[46.4]	34.3	3	8
Ester	CO_2−$(C)_2$	63.2	40.3	72	24
Lactone	CO_2−$(C_c)_2$	[67.4]	[45.2]	4	5
Cyclic carbonate	CO_3−$(C_c)_2$	[92.0]	[68.2]	5	1
Cyclic anhydride	CO_2CO−$(C_c)_2$		[80.3]		6
Ether	O−$(C)_2$	29.8	49.8	54	8
Cyclic ether	O−$(C_c)_2$	24.6	9.71	20	16
Isocyanate	OCN−(C)	[58.2]	[52.7]	5	3
Nitro group	O_2N−(C)	[58.6]	56.1	6	26
Thiol	HS−(C)	49.0	[51.9]	23	1
Primary sp^3 nitrogen	$N(H)_2$−(C)	59.4	21.6	21	38
Secondary sp^3 nitrogen	N(H)−$(C)_2$	[51.0]	[−0.29]	6	3
Tertiary sp^3 nitrogen	N−$(C)_3$	22.0	[31.5]	10	2
Tertiary sp^2 nitrogen	N_I(H)−(C_d), and N_A(H)−(C_d)	[44.4]	10.7	1	10
Cyclic secondary sp^3 nitrogen	N(H)−$(C_c)_2$	46.0	[23.9]	11	9
Cyclic tertiary sp^3 nitrogen	N−$(C_c)_2$(C)	[28.6]	1.21	6	7
Cyclic tertiary sp^2 nitrogen	N_d−$(C_{cd})(C_c)$, and N_d−$(C_B)_2$	20.7	13.9	12	9
Primary amide	$CO(NH_2)$−(C)	[41.0]	[54.4]	1	4
Secondary amide	CONH−$(C)_2$	79.9	44.4	9	13
Tertiary amide	CON−$(C)_3$	[82.4]		1	
Cyclic secondary amide	CONH−$(C_c)_2$	[92.0]	46.4	1	9
Cyclic tertiary amide	CON−$(C_c)_2$(C)	[170]	[52.7]	1	3
Carbamate	$NHCO_2$−$(C)_2$		[76.1]		4
Cyclic imide	$NH(CO)_2$−$(C_c)_2$		[74.1]		2
Monosubstituted urea	NH_2CONH−(C)		[82.8]		3
Cyclic urea	$CO(NH)_2$−$(C_c)_2$		[63.6]		1
Monosubstituted Guanidine group	$NH_2(C{=}NH)NH$−(C)		[59.4]		2
Sulfide	S−$(C)_2$	40.3	[116]	14	1
Cyclic sulfide	S−$(C_c)_2$	33.8	[20.3]	11	1
Disulfide	S_2−$(C)_2$	[74.5]	[41.0]	2	1
Sulfoxide	SO−$(C)_2$	[83.7]	[47.7]	1	1
Sulfone	SO_2−$(C)_2$		[88.7]		1
Sulfonamide	SO_2NH_2−(C)		[104]		2
Quaternary silicon	Si−$(C^*)_4$	30.9	32.4	24	16
Tertiary aluminum	Al−$(C^*)_3$	[46.9]		3	
Quaternary tin	Sn−$(C^*)_4$	[58.6]	[77.2]	1	2
Quaternary germanium	Ge−$(C^*)_4$	[48.1]	[18.9]	1	2
Phosphine oxide	PO−$(C^*)_3$		[28.5]		1

[a] N_I and N_A refer to imino and azo nitrogens, respectively; all values are in J/(mole K); 1 cal = 4.184 J.
[b] Values in brackets are considered as tentative assignments only.
[c] Due to insufficient experimental data, only the parameters listed in Table I can be substituted for a C*.

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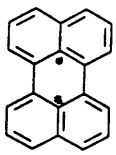

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identified by the asterisk, provide another illustration of this group. The subscripts c and cd are also new and refer to cyclic sp^3 and sp^2 carbons, respectively. Groups that are likely to vary are set off by a hyphen.

In deciding which carbon groups to use in the calculation of a complex molecule, the following guidelines may be useful. The terms in Table I containing an unsubscripted carbon group (C) can be used for calculations in any environment (i.e., they may be attached next to a C_d, C_B, C_t, C_c, C_{cd}, or any of the functional groups listed in Table II). Cyclic carbons (C_c) should be used in calculations with cyclic functional groups in estimating the contributions of the ring. Only the groups defined in Table I should be attached to those carbons in Table II identified by an asterisk (C*). This is due to the lack of relevant experimental data. Aromatic carbons that also form part of a saturated ring may also be attached to cyclic carbons, C_c. For additional details concerning the type of compounds successfully correlated by this approach, the reader is encouraged to consult the supplementary tables.

This method uses far fewer parameters than those developed by Benson. For example, the Benson terms for an aliphatic carboxylic acid, CO-(C)(O) and O-(H)(CO), have been replaced by the single term, CO(OH)-(C). Since C_B, C_d, C_c, etc., can be substituted for (C), this single term can be used for aromatic, α, β unsaturated and cyclic carboxylic acids. (Additionally, this method does not distinguish between *cis* and *trans*, *endo* vs. *exo* isomerism.) The use of fewer parameters generally leads to a less exact quantitative correlation. Benson notes that many estimations of gas-phase heat capacities are accurate within 4.2 J/(mole K) [1]. As will be shown, the uncertainty associated with condensed-phase experimental heat capacities is likely to be larger.

Table III illustrates the application of these group values in estimating heat capacities at 298 K for a variety of different classes of liquid (l) and solid (c) compounds. In the estimation of the heat capacity of thiazole (l), the molecule is treated as containing a cyclic sulfide linkage, a cyclic tertiary sp^2 hybridized nitrogen, and three cyclic sp^2 hybridized carbons. Despite the aromatic character of the molecule, the carbons are not treated as being benzenoid. Benzenoid carbons in this estimation are carbons in aromatic systems containing six-membered rings and the corresponding heterocyclic derivatives. The carbons in pyrimidine would be considered as aromatic, while those in pyrazole would be treated as cyclic tertiary sp^2 carbons. The sp^2 hybridized nitrogens in both pyrimidine and pyrazole would be considered as cyclic tertiary sp^2 nitrogens since there is no corresponding term, N_B, defined for nitrogen.

The estimations of bicyclo[2.2.2]octene (l) and indene (l) are relatively straightforward. The estimation

Table III. Estimations of Heat Capacity of Organic Compounds at 298 K.

	Group values	C_p Calcd (J/mole K)	Structure
Liquids			
C_3H_3NS thiazole (l)			
3 cyclic tertiary sp^2 carbons	$C_{cd}(H)-(C_c)_2$	65.4	
cyclic sulfide	$S-(C_c)_2$	33.8	
cyclic tertiary sp^2 nitrogen	$N_d-(C_{cd})(C_c)$	20.6	2
	total	119.8	
	expt	119.7	
C_8H_8 2-bicyclo[2.2.2]octene (l)			
2 cyclic tertiary sp^3 carbons	$C_c(H)-(C_c)_2(C)$	41.2	
4 cyclic secondary sp^3 carbons	$C_c(H)_2-(C_c)_2$	103.2	
2 cyclic tertiary sp^2 carbons	$C_{cd}(H)-(C_c)_2$	43.6	
	total	188.0	3
	expt	156.9	

Table III. Continued

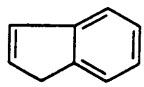
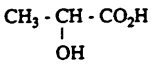
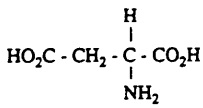
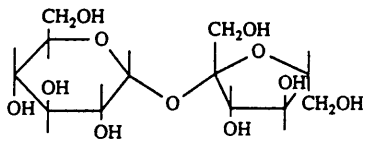
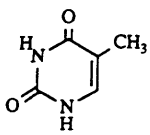
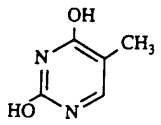
	Group values	C_p Calcd (J/mole K)	Structure
Liquids			
C_9H_8 indene (l)			
4 tertiary aromatic sp^2 carbons	$C_B-(H)$	87.2	
2 quaternary aromatic sp^2 carbons	$C_B-(C)$	30.6	
cyclic secondary sp^3 carbon	$C_c(H)_2-(C_c)_2$	25.9	
2 cyclic tertiary sp^2 carbons	$C_{cd}(H)-(C_c)_2$	43.6	4
	total	187.3	
	expt	187	
Solids			
$C_3H_6O_3$ D-lactic acid (c) L-lactic acid (c)			
carboxylic acid	$CO(OH)-(C)$	53.1	
hydroxyl group	$HO-(C)$	23.5	
primary sp^3 carbon	$C(H)_3-(C)$	36.6	
tertiary sp^3 carbon	$C(H)-(C)_3$	9.0	5
	total	122.2	
D-lactic acid	expt	127.6	
L-lactic acid	expt	128.4	
$C_4H_7NO_4$ L-aspartic acid (c)			
2 carboxylic acids	$CO(OH)-(C)$	106.2	
primary sp^3 nitrogen	$N(H)_2-(C)$	21.6	
secondary sp^3 carbon	$C(H)_2-(C)_2$	26.9	
tertiary sp^3 carbon	$C(H)-(C)_3$	9.0	
	total	163.7	6
	expt	155.2	
$C_{12}H_{22}O_{11}$ sucrose (c)			
8 cyclic tertiary sp^3 carbons	$C_c(H)-(C_c)_2(C)$	93.7	
cyclic quaternary sp^3 carbon	$C_c-(C_c)_2(C)_2$	6.11	
3 secondary sp^3 carbons	$C(H)_2-(C)_2$	80.8	
2 cyclic ethers	$O_c-(C_c)_2$	19.4	
ether	$O-(C)_2$	49.8	
8 hydroxyl groups	$HO-(C)$	187.8	7
	total	437.6	
	expt	425.5	
$C_5H_6N_2O_2$ thymine (c) Calculated as the diketo form			
primary sp^3 carbon	$C(H)_3-(C)$	36.6	
cyclic quaternary sp^2 carbon	$C_{cd}-(C_c)(C)$	4.73	
cyclic tertiary sp^3 carbon	$C_{cd}(H)-(C_c)$	15.9	
2 cyclic secondary amides	$CONH-(C_c)_2$	92.8	8
	total	150.0	
	expt	150.2	

Table III. Continued

	Group values	C_p Calcd (J/mole K)	Structure
$C_5H_6N_2O_2$ thymine (c)			
Calculated as the dienol form			
primary sp^3 carbon	$C(H)_3-(C)$	36.6	
3 quaternary aromatic			
sp^2 carbons	$C_B-(C)$	25.5	
tertiary aromatic			
sp^2 carbon	$C_B(H)$	17.5	
2 cyclic tertiary			
sp^2 nitrogen	$N_d-(C_B)_2$	27.8	
2 hydroxyl groups	$HO-(C)$	47.0	
	total	154.4	
	expt	150.2	
$(C_9H_{10})_n$ poly(α-methylstyrene) (c)			
5 tertiary aromatic			
sp^2 carbons	$C_B(H)$	87.5	
quaternary aromatic			
sp^2 carbon	$C_B-(C)$	8.49	
primary sp^3 carbon	$C(H)_3-(C)$	36.6	
quaternary sp^3 carbon	$C-(C)_4$	−4.98	
secondary sp^3 carbon	$C(H)_2-(C)_2$	26.9	
	total	154.5	
	expt	149.4	



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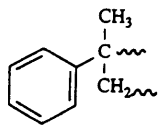

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for these compounds varies slightly from the Benson approach in that there are no additional correction factors necessary once the appropriate groups are identified.

In the estimation of lactic acid (c), a hydroxyl and a carboxylic acid functional group are substituted for two of the unsubscripted carbons of a tertiary carbon group. We do not distinguish between the racemic and optically active forms of chiral molecules, and the limited amount of available experimental heat capacity data seems to support this approximation. A similar estimation for aspartic acid (c) demonstrates that amino acids can also be successfully handled by this approach. Apparently, the zwitterionic nature of the solid α-amino acids does not significantly alter their heat capacities.

Calculation of the heat capacity of thymine is another example of an estimation of a compound with multiple functional groups that is capable of existing in tautomeric forms. In the diketo form, thymine (c) can be considered to possess two cyclic secondary amide groups. In the dienolic form, the calculation is of a dihydroxypyrimidine. It is reassuring that both calculations give reasonably good estimates of the heat capacity of thymine. Similar results were obtained for both the dienolic and diketo forms of uracil (dienol, 126.7; diketo, 125.1; expt. 120.5 J/(mole K)) and barbituric acid (trienol, 141.4; triketo, 144.3; expt. 141.0 J/(mole K); not shown). The success of this tautomeric approach with both amino acids and cyclic lactams suggests an indirect way of estimating heat capacities for some systems where group values may not be available. Some additional care in the proper identification of the functional group is necessary in this instance.

Estimation of the heat capacity of sucrose (c) illustrates the application of this technique for sugars. For the few liquid and solid polymers that have been examined by this approach, a reasonable estimation was obtained, provided the composition and structure of the polymer are reasonably well defined. The estimation of poly(α-methylstyrene) (c) illustrates the general procedure. The estimation provides the molar heat capacity per monomeric unit. A few amorphous polymers and polymers that form glasses have also been examined. In these instances, estimation of the heat capacity of the polymer using group values of solids gave the best correlation to experiment.

Some idea of the quality of the correlation obtained by this approach is shown in Figs. 1 and 2. Figure 1 compares experimental heat capacities to those calculated by the group values in Tables I and II for 812 liquids, and Fig. 2 contains a similar comparison for 451

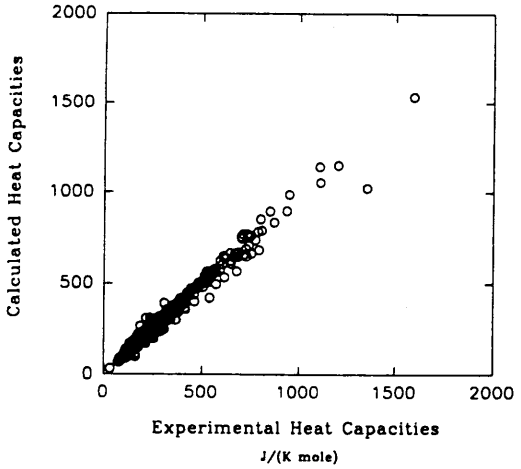

Fig. 1. A comparison of the calculated and experimental heat capacities of 812 liquids at 298 K.

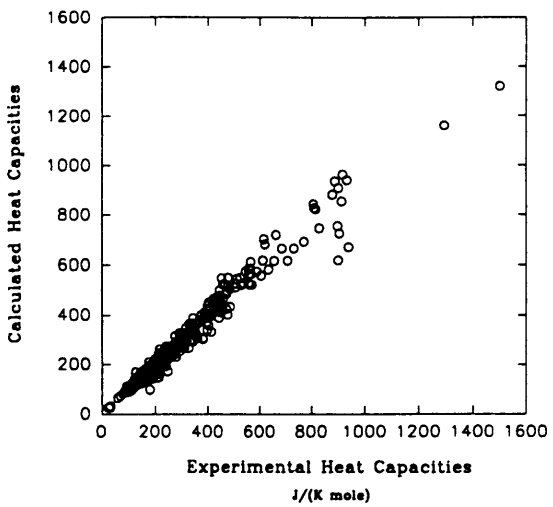

Fig. 2. A comparison of the calculated and experimental heat capacities of 451 solids at 298 K.

solids. Included in these figures are estimates for two liquids and five solids that were not used in the generation of group values. As illustrated, these compounds deviate sufficiently from the remainder of the compounds in their set that their inclusion would have caused a disproportionate effect on the value of the functional group being evaluated. The equations generated by a least-squares treatment of the experimental and calculated heat capacities are given here.

Liquids	
Equation of Fig. 1 for data used in correlation	$C_p(l)_{calcd} = 0.980\ C_p(l)_{expt} + 3.93$ $C_p(l)_{calcd} = 0.991\ C_p(l)_{expt}$
Number of entries	810
Correlation coefficient	0.9921, 0.9919
Std error	19.4, 19.5 J/(mole K)
All data	$C_p(l)_{calcd} = 0.964\ C_p(l)_{expt} + 7.5$
Number of entries	812
Correlation coefficient	0.9899
Std error	22.1 J/(mole K)
Solids	
Equation of Fig. 2 for data used in correlation	$C_p(c)_{calcd} = 0.964\ C_p(c)_{expt} + 7.54$ $C_p(c)_{calcd} = 0.988\ C_p(c)_{expt}$
Number of entries	446
Correlation coefficient	0.9882, 0.9879
Std error	26.4, 26.7 J/(mole K)
All data	$C_p(c)_{calcd} = 0.885\ C_p(c)_{expt} + 27.3$
Number of entries	451
Correlation Coefficient	0.9772
Std error	38.9 J/(mole K)

The first of the two equations listed under both liquids and solids describes the least-squares fit of the data used in the correlation. The second equation describes the fit when the intercept is forced to pass through the origin. The correlation coefficient and standard error associated with this second equation are included as the second term in their respective entry.

For purposes of comparison, some idea of the typical error associated with the experimental measurements would be useful. As a means of obtaining such an estimate, we have collected all multiple measurements reported in the literature on the same substance and have compared the results. A total of 877 and 284 independent measurements reported on 219 different liquids and 102 different solids resulted in standard errors of 8.1 and 23.4 J/(mole K), respectively. A comparison of standard errors between the experimental results and those estimated with the aid of Tables I and II shows the latter to be roughly within a factor of 2 for both solids and liquids. In view of this, the introduction of additional parameters to improve the correlation did not seem worthwhile at this time.

The error distributions obtained in these correlations are summarized in the histograms of Figs. 3 and 4. Intervals of 16 and 48 J/(mole K) used in these figures for liquids and solids, respectively, represent the distribution of calculated values that fall within ± 1 standard deviation of the experimental error. Slightly more than 50% of the calculated values fall within this error limit.

In summary, heat capacities can now be calculated for a wide variety of organic molecules in the gas, liquid, and solid phases. Group values evaluated at 298 K can now be used to correct thermochemical measurements obtained at slightly higher or lower temperatures.

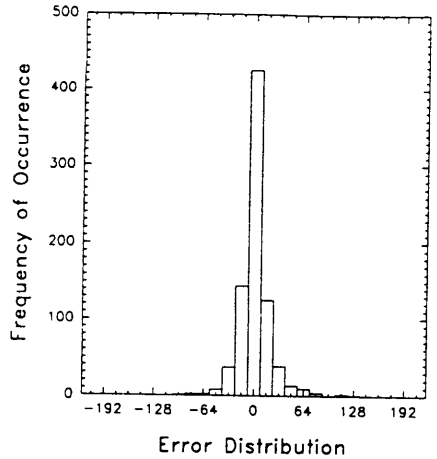

Fig. 3. The distribution of errors between experimental and calculated heat capacities of liquids at 298 K. Error intervals are at ± one standard deviation of the experimental uncertainty as defined in the text.

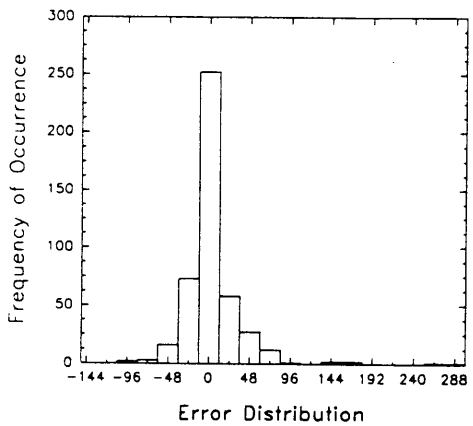

Fig. 4. The distribution of errors between experimental and calculated heat capacities of solids at 298 K. Error intervals are at ± one standard deviation of the experimental uncertainty as defined in the text.

The use of calculated heat capacity values to correct thermochemical measurements obtained at other temperatures is the subject of a future contribution.

SUPPLEMENTARY MATERIAL AVAILABLE

Tables containing the names and experimental heat capacities of 810 liquids and 446 solids used in this correlation as well as the values estimated by the group additivity parameters of Tables I and II are available (47 pages) from the authors upon request.

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