

# Estimating Phase Change Enthalpies and Entropies

James S. Chickos<sup>1</sup>, William E. Acree Jr.<sup>2</sup>, Joel F. Liebman<sup>3</sup>

<sup>1</sup>Department of Chemistry  
University of Missouri-St. Louis  
St. Louis MO 63121

<sup>2</sup>Department of Chemistry  
University of North Texas  
Denton TX 76203

<sup>3</sup>Department of Chemistry and Biochemistry  
University of Maryland Baltimore County  
Baltimore MD 21250

A group additivity method based on molecular structure is described that can be used to estimate total phase change entropies and enthalpies of organic molecules. Together with vaporization enthalpies which are estimated by a similar technique, this provides an indirect method to estimate sublimation enthalpies. The estimations of these phase changes are described and examples are provided to guide the user in evaluating these properties for a broad spectrum of organic structures.

Fusion, vaporization and sublimation enthalpies are important physical properties of the condensed phase. They are essential in studies referencing the gas phase as a standard state and are extremely useful in any investigation that requires information regarding the magnitude of molecular interactions in the condensed phase (1-4). The divergence in quantity between the many new organic compounds prepared and the few thermochemical measurements reported annually has encouraged the development of empirical relationships that can be used to estimate these properties.

We have found that techniques for estimating fusion, vaporization and sublimation enthalpies can play several useful roles (5-7). Perhaps most importantly, they provide a numerical value that can be used in cases when there are no experimental data. In addition we have used an estimated value to select the best experimental value in cases where two or more values are in significant disagreement and in cases where only one measurement is available, to assess whether the experimental value is reasonable. Given the choice between an estimated or experimental value, selection of the experimental value is clearly preferable. However, large discrepancies between estimated and calculated values can also identify experiments worth repeating. Finally, the parameters generated from such a treatment permit an investigation of inter and intramolecular interactions that are not well understood.

## Fusion Enthalpies

There are very few general techniques reported for directly estimating fusion enthalpies. Fusion enthalpies are most frequently calculated from fusion entropies and the experimental melting temperature of the solid,  $T_{fus}$ . One of the earliest applications of this is the use of Walden's Rule (8). The application of Walden's Rule provides a remarkably good approximation of  $\Delta_{fus}H_m$ , if one considers that the estimation is independent of molecular structure and based on only two parameters. Recent modifications of this rule have also been reported (9-10).

$$\text{Walden's Rule: } \Delta_{fus}H_m(T_{fus})/T_{fus} \sim 13 \text{ cal}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}; \quad 54.4 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}. \quad (1)$$

**Estimations of fusion entropies.** A general method has been reported recently for estimating fusion entropies and enthalpies based on the principles of group additivity (11,12). This method has been developed to estimate the total phase change entropy and enthalpy of a substance associated in going from a solid at 0 K to a liquid at the melting point,  $T_{fus}$ . Many solids undergo a variety of phase changes prior to melting, which affects the magnitude of the fusion entropy. The total phase change entropy and enthalpy,  $\Delta_0^{T_{fus}}S_{tpce}$  and  $\Delta_0^{T_{fus}}H_{tpce}$ , in most instances provide a good estimate of the entropy and enthalpy of fusion,  $\Delta_{fus}S_m(T_{fus})$  and  $\Delta_{fus}H_m(T_{fus})$ . If there are no additional solid phase transitions then  $\Delta_0^{T_{fus}}S_{tpce}$  and  $\Delta_0^{T_{fus}}H_{tpce}$  become numerically equivalent to  $\Delta_{fus}S_m(T_{fus})$  and  $\Delta_{fus}H_m(T_{fus})$ .

An abbreviated listing of the group parameters that can be used to estimate these phase change properties is included in Tables I and III. The group values in these tables have been updated from previous versions (11,12) by the inclusion of new experimental data in the parameterizations. Before describing the application of these parameters to the estimation of  $\Delta_0^{T_{fus}}S_{tpce}$  and  $\Delta_0^{T_{fus}}H_{tpce}$ , the conventions used to describe these group values need to be defined. Primary, secondary, tertiary and quaternary centers, as found on atoms of carbon and silicon and their congeners, are defined solely on the basis of the number of hydrogens attached to the central atom, 3, 2, 1, 0, respectively. This convention is used throughout this chapter. In addition, compounds whose liquid phase is not isotropic at the melting point are not modeled properly by these estimations. Those forming liquid crystal or cholesteric phases as well amphiphilic compounds are presently overestimated by these parameters and should also be excluded from these estimations. A large discrepancy between the estimated total phase change enthalpy and experimental fusion enthalpy is a good indication of undetected solid-solid phase transitions or non-isotropic liquid behavior. Finally, it should be pointed out that the experimental melting point along with an estimated value of  $\Delta_0^{T_{fus}}S_{tpce}$  is necessary to estimate the fusion enthalpy of a compound.

The parameters used for estimating  $\Delta_0^{T_{fus}}S_{tpce}$  of hydrocarbons and the hydrocarbon portions of more complex molecules are listed in Table I. The group value,

**Table I A. Contributions of the Hydrocarbon Portion of Acyclic and Aromatic Molecules**

Aliphatic and Aromatic Carbon Groups	Group Value $G_i, \text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$	Group Coefficients $C_i$
primary $\text{sp}^3$	$\text{CH}_3-$ 17.6	
secondary $\text{sp}^3$	$>\text{CH}_2$ 7.1	1.31 <sup>a</sup>
tertiary $\text{sp}^3$	$-\text{CH}<$ -16.4	0.60
quaternary $\text{sp}^3$	$>\text{C}<$ -34.8	0.66
secondary $\text{sp}^2$	$=\text{CH}_2$ 17.3	
tertiary $\text{sp}^2$	$=\text{CH}-$ 5.3	0.75
quaternary $\text{sp}^2$	$=\text{C}(\text{R})-$ -10.7	
tertiary $\text{sp}$	$\text{H}-\text{C}\equiv$ 14.9	
quaternary $\text{sp}$	$-\text{C}\equiv$ -2.8	
aromatic tertiary $\text{sp}^2$	$=\text{C}_a\text{H}-$ 7.4	
quaternary aromatic $\text{sp}^2$ carbon adjacent to an $\text{sp}^3$ atom	$=\text{C}_a(\text{R})-$ -9.6	
peripheral quaternary aromatic $\text{sp}^2$ carbon adjacent to an $\text{sp}^2$ atom	$=\text{C}_a(\text{R})-$ -7.5	
internal quaternary aromatic $\text{sp}^2$ carbon adjacent to an $\text{sp}^2$ atom	$=\text{C}_a(\text{R})-$ -0.7	

<sup>a</sup>The group coefficient of 1.31 for  $\text{C}_{\text{CH}_2}$  is applied only when the number of consecutive methylene groups exceeds the sum of the remaining groups; see equation 2 in text.

**Table I B. Contributions of the Cyclic Hydrocarbon Portions of the Molecule**

Contributions of Cyclic Carbons	Group Value ( $G_i$ ) $\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$	Group Coefficient $C_i$
cyclic tertiary $\text{sp}^3$	$>\text{C}_c\text{H}(\text{R})$ -14.7	
cyclic quaternary $\text{sp}^3$	$>\text{C}_c(\text{R})_2$ -34.6	
cyclic tertiary $\text{sp}^2$	$=\text{C}_c\text{H}-$ -1.6	1.92
cyclic quaternary $\text{sp}^2$	$=\text{C}_c(\text{R})-$ -12.3	
cyclic quaternary $\text{sp}$	$=\text{C}_c\equiv; \text{R}-\text{C}_c\equiv$ -4.7	

$G_i$ , associated with a molecular fragment is identified in the third column of the table. The group coefficients,  $C_i$ , are listed in column 4 of the table. These group coefficients are used to modify  $G_i$  whenever a functional group is attached to the carbon in question. Functional groups are defined in Table III. All values of  $C_i$  and  $C_k$  that are not specifically defined in both Tables I and III are to be assumed equal to 1.0. The group coefficient for a methylene group in Table I,  $\text{C}_{\text{CH}_2}$ , is applied differently from the rest. The group coefficient for a methylene group is used whenever the total number of consecutive methylene groups in a molecule,  $n_{\text{CH}_2}$ , equals or exceeds the sum of the other remaining groups,  $\Sigma n_i$ . This applies to both hydrocarbons and all derivatives. Introduction of this coefficient is new and differentiates this protocol from previous

versions (11, 12). The application of this group coefficient is illustrated below.

**Acyclic and Aromatic Hydrocarbons.** Estimation of  $\Delta_0^{T_{fus}} S_{tpce}$  for acyclic and aromatic hydrocarbons (*aah*) can be achieved by summing the group values consistent with the structure of the molecule as illustrated in the following equation:

$$\Delta_0^{T_{fus}} S_{tpce}(aah) = \sum_i n_i G_i + n_{CH_2} C_{CH_2} G_{CH_2}; \quad C_{CH_2} = 1.31 \text{ when } n_{CH_2} \geq \sum n_i; i \neq CH_2$$

$$\text{otherwise } C_{CH_2} = 1. \quad (2)$$

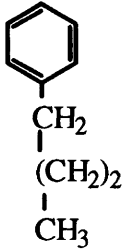
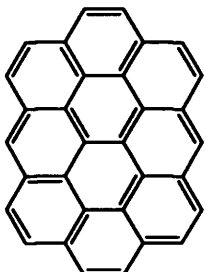
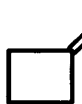
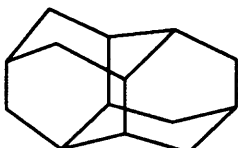
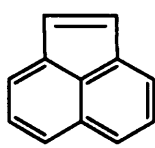
Some examples illustrating the use of both the groups in Table I A and equation 2 are given in Table II. Entries for each estimation include the melting point,  $T_{fus}$ , and all transition temperatures,  $T_t$ , for which there is a substantial enthalpy change. The estimated and experimental phase change entropy (in parenthesis) follows. Similarly, the total phase change enthalpy calculated as the product of  $\Delta_0^{T_{fus}} S_{tpce}$  and  $T_{fus}$  is followed by the experimental total phase change enthalpy (or fusion enthalpy). Finally, details in estimating  $\Delta_0^{T_{fus}} S_{tpce}$  for each compound are included as the last entry.

**n-Butylbenzene.** The estimation of the fusion entropy of n-butylbenzene is an example of an estimation of a typical aromatic hydrocarbon. Identification of the appropriate groups in Table I A results in an entropy of fusion of  $66.3 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$  and together with the experimental melting point, an enthalpy of fusion of  $12.3 \text{ kJ}\cdot\text{mol}^{-1}$  is estimated. This can be compared to the experimental value of  $11.3 \text{ kJ}\cdot\text{mol}^{-1}$ . It should be pointed out that the group values for aromatic molecules are purely additive while the group values for other cyclic  $sp^2$  atoms are treated as corrections to the ring equation. This will be discussed in more detail below.

**n-Heptacosane.** The fusion entropy of n-heptacosane is obtained in a similar fashion. In this case, the number of consecutive methylene groups in the molecule exceeds the sum of the remaining terms in the estimation and this necessitates the use of the group coefficient,  $C_{CH_2}$ , of 1.31. Heptacosane exhibits two additional phase transitions below its melting point. These are shown in parentheses for both  $\Delta_0^{T_{fus}} S_{tpce}$  and  $\Delta_0^{T_{fus}} H_{tpce}$  following the estimated value for each, respectively. For a molecule such as 4-methylhexacosane (estimation not shown), the group coefficient of 1.31 would be applied to the eleven consecutive methylene groups. The remaining two methylene groups would be treated normally ( $C_{CH_2} = 1.0$ ) but would not be counted in  $\sum n_i$ .

**Ovalene.** Estimation of the phase change entropy of ovalene provides an example of a molecule containing both peripheral and internal quaternary  $sp^2$  carbon atoms adjacent to an  $sp^2$  atom. The carbon atoms in graphite are another example of internal quaternary  $sp^2$  carbon atoms. In the application of these group values to obtain the phase change properties of other aromatic molecules, it is important to remember that aromatic molecules are defined in these estimations as molecules containing only benzenoid carbons and the corresponding nitrogen heterocycles. While a molecule like 1,2-benzacenaphthene (fluoranthene) would be considered aromatic, acenaphthylene, according to this definition is not. Estimation of  $\Delta_0^{T_{fus}} S_{tpce}$  for acenaphthylene will be illustrated below.

**Table II. Estimations of Total Phase Change Entropies and Enthalpies of Hydrocarbons<sup>a</sup>**

<b>C<sub>10</sub>H<sub>14</sub> n-butylbenzene</b> 		<b>C<sub>27</sub>H<sub>56</sub> n-heptacosane</b> CH <sub>3</sub>   (CH <sub>2</sub> ) <sub>25</sub>   CH <sub>3</sub>	
$T_{fus}:$ 185.3 K (13) $\Delta_0^{T_{fus}} S_{tpce}:$ 66.3 (60.6) $\Delta_0^{T_{fus}} H_{tpce}:$ 12.3 (11.3) $\Delta_0^{T_{fus}} S_{tpce}:$ {5[7.4]+3[7.1] +[-9.6]+[17.6]}	$T_f:$ 319; 325 K $T_{fus}:$ 332 K (14) $\Delta_0^{T_{fus}} S_{tpce}:$ 268 (7.1+80.8+177.8) $\Delta_0^{T_{fus}} H_{tpce}:$ 89 (2.3+26.3+59.1) $\Delta_0^{T_{fus}} S_{tpce}:$ {2[17.6]+25[1.31][7.1]}		
<b>C<sub>32</sub>H<sub>14</sub> ovalene</b> 		<b>C<sub>5</sub>H<sub>8</sub> methylenecyclobutane</b> 	
$T_f:$ 729 K $T_{fus}:$ 770 K (15) $\Delta_0^{T_{fus}} S_{tpce}:$ 36.6 (33.7) $\Delta_0^{T_{fus}} H_{tpce}:$ 28.2 (25.5) $\Delta_0^{T_{fus}} S_{tpce}:$ {14[7.4]+8[-7.5] +10[-0.7]}	$T_{fus}:$ 138 K (13) $\Delta_0^{T_{fus}} S_{tpce}:$ 42.1 (41.6) $\Delta_0^{T_{fus}} H_{tpce}:$ 5.8 (5.76) $\Delta_0^{T_{fus}} S_{tpce}:$ {[33.4]+[3.7] +[-12.3]+[17.3]}		
<b>C<sub>14</sub>H<sub>20</sub> congressane</b> 		<b>C<sub>12</sub>H<sub>8</sub> acenaphthylene</b> 	
$T_f:$ 407.2; 440.4 K $T_{fus}:$ 517.9 K (13) $\Delta_0^{T_{fus}} S_{tpce}:$ 45.7 (10.8+ 20.3+16.7) $\Delta_0^{T_{fus}} H_{tpce}:$ 23.7 (4.4+ 9.0+8.7) $\Delta_0^{T_{fus}} S_{tpce}:$ {[33.4]5- [3.7]+ 8[-14.7]}	$T_f:$ 116.6; 127.1 K $T_{fus}:$ 362.6 K (13,16) $\Delta_0^{T_{fus}} S_{tpce}:$ 37.6 (12.1+ 19.1) $\Delta_0^{T_{fus}} H_{tpce}:$ 13.6 (10.7) $\Delta_0^{T_{fus}} S_{tpce}:$ {[33.4]+2[3.7] +[-7.5]+6[7.4] +3[-12.3]+2[-1.6]}		

<sup>a</sup>Units for  $\Delta_0^{T_{fus}} S_{tpce}$  and  $\Delta_0^{T_{fus}} H_{tpce}$  are in J·mol<sup>-1</sup>·K<sup>-1</sup> and kJ·mol<sup>-1</sup>, respectively; experimental values are included in parentheses following the calculated value (in cases where additional solid-solid transitions are involved, the first term given is the total property associated with the transition and the second term represents the fusion property). A reference to the experimental data is included in parentheses following  $T_{fus}$ .

**Non-aromatic Cyclic and Polycyclic Hydrocarbons.** The protocol established for estimating  $\Delta_0^{T_{fus}} S_{tpce}$  of unsubstituted cyclic hydrocarbons uses equation 3 to

evaluate this term for the parent cycloalkane,  $\Delta_0^{T_{fus}} S_{tpce}(ring)$ . For substituted and polycyclic cycloalkanes, the results of equations 3 or 4, respectively, are then corrected

$$\Delta_0^{T_{fus}} S_{tpce}(ring) = [33.4] + [3.7][n-3]; \quad n = \text{number of ring atoms} \quad (3)$$

$$\Delta_0^{T_{fus}} S_{tpce}(ring) = [33.4]N + [3.7][R-3N]; \quad R = \text{total number of ring atoms}; \\ N = \text{number of rings} \quad (4)$$

for the presence of substitution and hybridization patterns in the ring that differ from the standard cyclic secondary  $sp^3$  pattern found in the parent monocyclic alkanes,  $\Delta_0^{T_{fus}} S_{tpce}(corr)$ . These correction terms can be found in Table I B. Once these corrections are included in the estimation, any additional acyclic groups present as substituents on the ring are added to the results of equations 3 or 4 and  $\Delta_0^{T_{fus}} S_{tpce}(corr)$ . These additional acyclic and/or aromatic terms ( $\Delta_0^{T_{fus}} S_{tpce}(aah)$ ) are added according to the protocol discussed above in the use of equation 2. The following examples of Table II illustrate the use of equations 3 and 4 according to equation 5 to estimate the total phase change entropy,  $\Delta_0^{T_{fus}} S_{tpce}(total)$ .

$$\Delta_0^{T_{fus}} S_{tpce}(total) = \Delta_0^{T_{fus}} S_{tpce}(ring) + \Delta_0^{T_{fus}} S_{tpce}(corr) + \Delta_0^{T_{fus}} S_{tpce}(aah). \quad (5)$$

**Methylenecyclobutane.** The estimation of  $\Delta_0^{T_{fus}} S_{tpce}$  for methylenecyclobutane illustrates the use of equation 5 for a monocyclic alkene. Once the cyclobutane ring is estimated ( $[33.4] + [3.7]$ ), the presence of a cyclic quaternary  $sp^2$  carbon in the ring is corrected ( $[-12.3]$ ) next. Addition of a term for the acyclic  $sp^2$  methylene group  $[17.3]$  completes this estimation.

**Congressane.** Congressane, a pentacyclic hydrocarbon, provides an example of how equation 4 is used in conjunction with equation 5. The usual criterion, the minimum number of bonds that need to be broken to form a completely acyclic molecule, is used to determine the number of rings. Application of equation 4 to congressane  $[33.4]5 + 3.7[14-15]$  provides  $\Delta_0^{T_{fus}} S_{tpce}(ring)$ . Addition of the contribution of the eight cyclic tertiary  $sp^3$  carbons to the results of equation 4,  $\Delta_0^{T_{fus}} S_{tpce}(corr)$ , completes the estimation.

**Acenaphthylene.** Estimation of  $\Delta_0^{T_{fus}} S_{tpce}$  and  $\Delta_0^{T_{fus}} H_{tpce}$  for acenaphthylene completes this section on cyclic hydrocarbons. Molecules that contain rings fused to aromatic rings but are not completely aromatic, according to the definition provided above, are estimated by first calculating  $\Delta_0^{T_{fus}} S_{tpce}(ring)$  for the contributions of the non-aromatic ring according to equations 3 or 4. This is then followed by adding the corrections and contributions of the remaining aromatic groups and any other acyclic substituents. The

five membered ring in acenaphthylene  $\{\Delta_0^{T_{fus}} S_{tpce}(ring): [33.4]+2[3.7]\}$  is first corrected for each non-secondary  $sp^3$  carbon atom  $\{\Delta_0^{T_{fus}} S_{tpce}(corr): +2[-1.6]+3[-12.3]\}$ , and then the remainder of the aromatic portion of the molecule  $(\Delta_0^{T_{fus}} S_{tpce}(aah): [-7.5]+6[7.4])$  is estimated as illustrated above.

**Hydrocarbon Derivatives.** Estimations involving derivatives of hydrocarbons are performed in a fashion similar to hydrocarbons. The estimation consists of three parts: the contribution of the hydrocarbon component, that of the carbon(s) bearing the functional group(s),  $\sum_i n_i C_i G_i$ , and the contribution of the functional group(s),  $\sum_k n_k C_j G_k$ . The terms  $n_i$ ,  $n_k$  refer to the number of groups of type  $i$  and  $k$ . Acyclic and cyclic compounds are treated separately as before. For acyclic and aromatic molecules, the hydrocarbon portion is estimated using equation 2; cyclic or polycyclic molecules are estimated using equations 3 and 4, respectively. Similarly, the contribution of the carbon(s) bearing the functional group(s) is evaluated from Table I A or Table I B modified by the appropriate group coefficient,  $C_j$ , as will be illustrated below. The group values of the functional groups,  $G_k$ , are listed in Table III A-C. The corresponding group coefficient,  $C_j$  is equal to one for all functional groups except those listed in Table III B. Selection of the appropriate value of  $C_j$  from Table III B is based on the total number of functional groups and is discussed below. Functional groups that make up a portion of a ring are listed in Table III C. The use of these values in estimations will be illustrated separately. Equations 6 and 7 summarize the protocol developed to estimate  $\Delta_0^{T_{fus}} S_{tpce}(total)$  for acyclic and aromatic derivatives and for cyclic and polycyclic hydrocarbon derivatives, respectively.

$$\Delta_0^{T_{fus}} S_{tpce}(total) = \Delta_0^{T_{fus}} S_{tpce}(aah) + \sum_i n_i C_i G_i + \sum_k n_k C_j G_k, \quad (6)$$

$$\Delta_0^{T_{fus}} S_{tpce}(total) = \Delta_0^{T_{fus}} S_{tpce}(ring) + \Delta_0^{T_{fus}} S_{tpce}(corr) + \sum_i n_i C_i G_i + \sum_k n_k C_j G_k, \quad (7)$$

$$\text{where: } C_j = \sum_k n_k.$$

In view of the large number of group values listed in Table III A-C, selection of the appropriate functional group(s) is particularly important. The four functional groups of Table III B are dependent on the total substitution pattern in the molecule. Coefficients for these four groups,  $C_j$ , are available for molecules containing up to six functional groups. Selection of the appropriate value of  $C_j$  for one of these four functional groups is based on the total number of functional groups in the molecule. All available evidence suggests that the group coefficient for  $C_6$  in Table III B, should be adequate for molecules containing more than a total of six functional groups (17).

**Acyclic and Aromatic Hydrocarbon Derivatives.** The estimations of 2,2',3,3',5,5'-hexachlorobiphenyl, 3-heptylamino-1,2-propanediol, trifluoromethanethiol

**Table III A. Functional Group Values<sup>a</sup>**

Functional Groups	Group Value ( $G_k$ ) $J \cdot mol^{-1} \cdot K^{-1}$	Functional Groups	Group Value ( $G_k$ ) $J \cdot mol^{-1} \cdot K^{-1}$		
bromine	-Br	17.5	tetrasubst. urea	>NC(=O)N<	[-19.3]
fluorine on an $sp^2$ carbon,	>CHF	19.5	1,1-disubst. urea	>NC(=O)NH <sub>2</sub>	[19.5]
aromatic			1,3-disubst. urea	-NHC(=O)NH-	[1.5]
fluorine	=C <sub>2</sub> F-	16.6	monosubst. urea	-NHC(=O)NH <sub>2</sub>	[22.5]
3-fluorines on			carbamate	-OC(=O)NH <sub>2</sub>	[27.9]
an $sp^3$ carbon	CF <sub>3</sub> -	13.3	N-subst. carbamate	-OC(=O)NH-	10.6
2-fluorines on			imide	>(C=O) <sub>2</sub> NH	[7.7]
an $sp^3$ carbon	>CF <sub>2</sub>	16.4	phosphine	-P<	[-20.7]
1-fluorine on			phosphate ester	-P(=O)(OR) <sub>3</sub>	[-10.0]
an $sp^3$ carbon	-CF<	12.7	phosphonyl halide	-P(=O)X <sub>2</sub>	[4.8]
fluorine on a			phosphorothioate ester	(RO) <sub>3</sub> P=S	1.1
ring carbon	>CHF; >CF <sub>2</sub>	[17.5]	phosphorodithioate ester	-S-P(=S)(OR) <sub>2</sub>	-9.6
iodine	-I	19.4	phosphonothioate ester	-P(=S)(OR) <sub>2</sub>	[5.2]
phenol	=C(OH)-	20.3	phosphoroamidothioate		
ether	>O	4.71	ester	-NHP(=S)(OR) <sub>2</sub>	[16.0]
aldehyde	-CH(=O)	21.5	sulfides	>S	2.1
ketone	>C(=O)	4.6	disulfides	-SS-	9.6
ester	-(C=O)O-	7.7	thiols	-SH	23.0
heterocyclic			sulfones	>S(O) <sub>2</sub>	0.3
aromatic amine	=N <sub>2</sub> -	10.9	sulfonate ester	-S(O) <sub>2</sub> O-	[7.9]
acyclic $sp^2$			N,N-disubst.		
nitrogen	=N-	[-1.8]	sulfonamide	-S(O) <sub>2</sub> N<	[-11.3]
tert. amine	-N<	-22.2	N-subst. sulfonamide	-S(O) <sub>2</sub> NH-	6.3
sec. amine	-NH-	-5.3	sulfonamide	-S(O) <sub>2</sub> NH <sub>2</sub>	[28.4]
primary amine	-NH <sub>2</sub>	21.4	aluminum	-Al<	[-24.7]
aliphatic tert.			arsenic	-As<	[-6.5]
nitramine	>N-NO <sub>2</sub>	5.39	boron	-B<	[-17.2]
nitro group	-NO <sub>2</sub>	17.7	gallium	-Ga<	[-11.9]
oxime	=N-OH	[13.6]	quat. germanium	>Ge<	[-35.2]
azoxy nitrogen	N=N(O)-	[6.8]	sec. germanium	>GeH <sub>2</sub>	[-14.7]
nitrile	-C≡N	17.7	quat. lead	>Pb<	[-30.2]
tert. amide	-C(=O)N<	-11.2	selenium	>Se	[6.0]
sec. amide	-C(=O)NH-	1.5	quat. silicon	>Si<	-27.1
primary amide	-CONH <sub>2</sub>	27.9	quat. tin	>Sn<	-24.2
			zinc	>Zn	[11.1]

<sup>a</sup>Values in brackets are tentative assignments; R refers to alkyl and aryl groups.



**Table III B. Functional Group Values Dependent on the Degree of Substitution<sup>a</sup>**

Functional Group	Group Value ( $G_k$ ) $J \cdot mol^{-1} \cdot K^{-1}$	Group Coefficient $C_j$					
		2	3	4	5	6	
chlorine	-Cl	10.8	1.5	1.5	1.5	1.5	1.5
hydroxyl group	-OH	1.7	10.4	9.7	13.1	12.1	13.1
carboxylic acid	-C(=O)OH	13.4	1.21	2.25	2.25	2.25	2.25
1,1,3-trisubst urea	>NC(=O)NH-	[0.2]	-12.8	-24	6		

<sup>a</sup>Values in brackets are tentative assignments

**Table III C. Heteroatoms and functional Groups Comprising a Portion of a Ring<sup>a</sup>**

Cyclic Functional Group	Group Value, $G_k$ $J \cdot mol^{-1} \cdot K^{-1}$	Cyclic Functional Group	Group Value, $G_k$ $J \cdot mol^{-1} \cdot K^{-1}$
cyclic ether	> $O_c$ 1.2	cyclic tert. amide	-C(=O)NR- -21.7
cyclic ketone	> $C_c(=O)$ -1.4	cyclic carbamate	-OC(=O)N- [-5.2]
cyclic ester	-C(=O)O- 3.1	cyclic anhydride	-C(=O)OC(=O)- 2.3
cyclic $sp^2$ nitrogen	= $N_c$ - 0.5	N-substituted	
cyclic tert. amine,	- $N_c$ < -19.3	cyclic imide	-C(=O)NRC(=O)- [1.1]
cyclic tert. amine		cyclic imide	-C(=O)NHC(=O)- [1.4]
-N-nitro	> $N_c(NO_2)$ -27.1	cyclic sulfide	> $S_c$ 2.9
cyclic tert. amine		cyclic disulfide	-SS- [-6.4]
-N-nitroso	> $N_c(N=O)$ -27.1	cyclic disulfide	
cyclic sec. amine	> $N_cH$ 2.2	S-oxide	-SS(O)- [1.9]
cyclic tert. amine		cyclic sulphone	> $S_c(O)_2$ [-10.4]
-N-oxide	> $N_c(O)$ - [-22.2]	cyclic	
cyclic azoxy group	N=N(O)- [2.9]	thiocarbonate	-OC(=O)S- [14.2]
cyclic sec. amide	-C(=O)NH- 2.7	cyclic quat. Si	> $Si_c$ < -34.7

<sup>a</sup>Values in brackets are tentative assignments; R refers to alkyl and aryl groups.

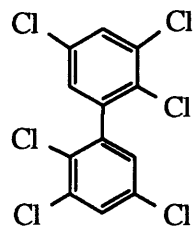
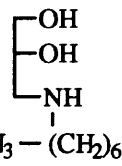
and 2,3-dimethylpyridine, shown in Table IV A, illustrate the estimations of substituted aromatic and acyclic hydrocarbon derivatives.

**2,2',3,3',5,5'-Hexachlorobiphenyl.** The estimation of 2,2',3,3',5,5'-hexachlorobiphenyl illustrates an estimation of a substituted aromatic molecule. Selection of the appropriate value for a quaternary aromatic  $sp^2$  carbon from Table IA depends on the nature of functional group. If the functional group at the point of attachment is  $sp^2$  hybridized or contains non-bonding electrons, the value for a "peripheral aromatic  $sp^2$  carbon adjacent to an  $sp^2$  atom" is selected. The remainder of the estimation follows the guidelines outlined above with the exception that chlorine is one of the four functional groups whose group coefficient,  $C_j$ , depends on the degree of substitution; in this case six.

**Table IV. Estimations of Total Phase Change Entropies and Enthalpies of :**

**A. Substituted Aromatic and Aliphatic Molecules<sup>a</sup>**

$C_{12}H_4Cl_6$  2,2',3,3',5,5'-hexachlorobiphenyl  $C_{10}H_{23}NO_2$  3-heptylamino-1,2-propanediol

	$T_{fus}:$ 424.9 K (18) $\Delta_0^{T_{fus}} S_{tpce}:$ 66.8 (68.7) $\Delta_0^{T_{fus}} H_{tpce}:$ 28.4 (28.2) $\Delta_0^{T_{fus}} S_{tpce}:$ {6[1.5][10.8] +8[-7.5]+4[7.4]}		$T_{fus}:$ 324.9 K (19) $\Delta_0^{T_{fus}} S_{tpce}:$ 105.4 (88.6) $\Delta_0^{T_{fus}} H_{tpce}:$ 34.2 (28.8) $\Delta_0^{T_{fus}} S_{tpce}:$ {2[9.7][1.7]+ [-5.3]+2[7.1]+[17.6]+ 6[1.31][7.1]+[-16.4][.6]}
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$CHF_3S$  trifluoromethanethiol

$T_{fus}:$  116.0 K (13)

$CF_3SH$

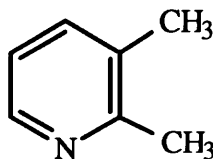
$\Delta_0^{T_{fus}} S_{tpce}:$  39.9 (42.4)

$\Delta_0^{T_{fus}} H_{tpce}:$  4.6 (4.9)

$\Delta_0^{T_{fus}} S_{tpce}:$  {[-34.8][.66]  
+3[13.3]+[23.0]}

$C_7H_9N$  2,3-dimethylpyridine

$T_{fus}:$  258.6 K (20)



$\Delta_0^{T_{fus}} S_{tpce}:$  49.1 (52.1)

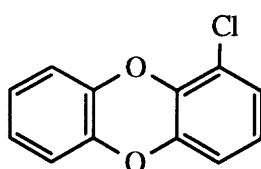
$\Delta_0^{T_{fus}} H_{tpce}:$  12.7 (13.5)

$\Delta_0^{T_{fus}} S_{tpce}:$  {2[17.6]+[10.9]  
+3[7.4]+2[-9.6]}

**B. Substituted Cyclic Molecules<sup>a</sup>**

$C_{12}H_7ClO_2$  1-chlorodibenzodioxin

$T_{fus}:$  378.2 K (21)



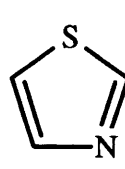
$\Delta_0^{T_{fus}} S_{tpce}:$  58.2 (61.3)

$\Delta_0^{T_{fus}} H_{tpce}:$  22.0 (23.2)

$\Delta_0^{T_{fus}} S_{tpce}:$  {[33.4]+3[3.7]  
+2[1.2]+4[-12.3]+7[7.4]+  
[-7.5]+[1.5][10.8]}

$C_3H_3NS$  thiazole

$T_{fus}:$  239.5 K (13)



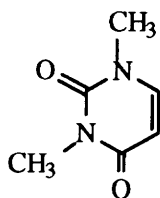
$\Delta_0^{T_{fus}} S_{tpce}:$  35.0 (40..0)

$\Delta_0^{T_{fus}} H_{tpce}:$  8.4 (9.6)

$\Delta_0^{T_{fus}} S_{tpce}:$  {[33.4]+2[3.7]  
+2[2.9]+[0.5]+  
3[-1.6][1.92]}

$C_6H_8N_2O_2$  1,3-dimethyluracil

$T_{fus}:$  398 K (13)



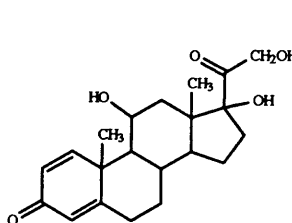
$\Delta_0^{T_{fus}} S_{tpce}:$  30.2 (36.7)

$\Delta_0^{T_{fus}} H_{tpce}:$  12.0 (14.6)

$\Delta_0^{T_{fus}} S_{tpce}:$  {[33.4]+  
3[3.7]+2[17.6]+  
2[-1.6][1.92]+  
2[-21.7]}

$C_{21}H_{28}O_5$  prednisolone

$T_{fus}:$  513 K (22)



$\Delta_0^{T_{fus}} S_{tpce}:$  76.7 (75.8)

$\Delta_0^{T_{fus}} H_{tpce}:$  39.3 (38.9)

$\Delta_0^{T_{fus}} S_{tpce}:$  {4[33.4]+[4.6]  
+5[3.7]+2[17.6]+[7.1]  
+2[-1.6][1.92]+[-1.6]+  
[-12.3]+4[-14.7]+[-1.4]  
3[-34.6]+3[1.7][12.1]}

<sup>a</sup>Units for  $\Delta_0^{T_{fus}} S_{tpce}$  and  $\Delta_0^{T_{fus}} H_{tpce}$  are in  $J \cdot mol^{-1} \cdot K^{-1}$  and  $kJ \cdot mol^{-1}$ , respectively; experimental values are given in parentheses and references are in italics.

**3-(n-Heptylamino)-1,2-propanediol.** The estimation of 3-(n-heptylamino)-1,2-propanediol illustrates another example of a molecule where the number of consecutive methylene groups exceeds the number of other functional groups. As noted previously, the group coefficient for a methylene group,  $C_{CH_2}$ , is only applied to the consecutive methylene groups. The remaining two methylene groups are treated normally and are not counted in  $\Sigma n_i$  (equation 2). One final comment about this estimation. The group coefficient for the hydroxyl group,  $C_3$ , was chosen despite the fact that the molecule contains two hydroxyl groups. In general, a  $C_j$  value is chosen based on the total number of functional groups present in the molecule and in this case  $j_{OH}(3)$  is used.

**Trifluoromethanethiol.** The estimation of  $\Delta_0^{T_{fus}} S_{tpce}$  for trifluoromethanethiol illustrates an example of a molecule containing fluorine. The group value for a fluorine on a trifluoromethyl group in Table III A is given per fluorine atom. The contribution of the quaternary carbon atom when attached to functional groups is attenuated by the group coefficient,  $C_i$ . Inclusion of the group value for a thiol completes this estimation.

**2,3-Dimethylpyridine.** The estimation of  $\Delta_0^{T_{fus}} S_{tpce}$  for 2,3-dimethylpyridine in Table IV provides an example of a calculation for a heterocyclic aromatic compound. Other aromatic heterocyclic molecules related to pyridine are estimated similarly, regardless of the number of nitrogens in the aromatic ring and their location. Molecules that can exist in two tautomeric forms such as dihydroxypyrimidine (uracil), should be calculated on the basis of the form which dominates the equilibrium.

**Cyclic and Polycyclic Hydrocarbon Derivatives.** The protocol for estimating the total phase change properties of cyclic and polycyclic molecules also follows from the procedure described above for the corresponding hydrocarbons. In cyclic molecules, the substituent or functional group may be attached to the ring or it may be part of the ring. If the functional group is part of the ring, the group values listed in Table III C are to be used. The procedure first involves estimating  $\Delta_0^{T_{fus}} S_{tpce}$  for the corresponding hydrocarbon ring, then correcting for the heterocyclic component(s), and if necessary, correcting the ring carbons attached to the cyclic functional group by the appropriate group coefficient. This is illustrated in Table IV B by the following examples.

**1-Chlorodibenzodioxin.** 1-Chlorodibenzodioxin is treated as being a derivative of cyclohexane. According to equation 7, the ring equation is first used to estimate the contributions of the dioxane ring. This ring contains two cyclic ether oxygens and four quaternary cyclic  $sp^2$  carbon atoms and must be modified accordingly. The remaining 8 carbon atoms are treated as aromatic carbons and values appropriate to their substitution pattern are chosen. The addition of the contribution of the chlorine completes the estimation.

**Thiazole.** Thiazole is estimated in a similar fashion. The ring equation (equation 3) is used first to generate the contribution of the five membered ring. In this instance the ring has been modified by the addition of a cyclic sulfur atom and a cyclic  $sp^2$  hybridized nitrogen atom. Both substitutions require appropriate corrections. The hybridization pattern of the remaining three ring carbon atoms have likewise been changed from the hybridization and substitution pattern found in cyclopentane and these changes must also be included in  $\Delta_0^{T_{fus}} S_{tpce}(corr)$ . Each cyclic  $sp^2$  hybridized carbon atom is attached

directly to one of the functional groups. The group coefficient, which in this case differs from 1.0, must also be included in evaluating the contributions of the ring carbons.

**1,3-Dimethyluracil** is an example of a molecule where some thought must be given to properly identify the functional groups in the molecule. The functional group that makes up a portion of the ring in this molecule can not be found directly in Table III C. It must therefore be simplified and this simplification can be accommodated in various ways. The functional group can be considered to be a combination of either an adjacent cyclic imide (-CONRCO-) and cyclic amide nitrogen (-NR-), a cyclic urea (-NRCONR-) and amide carbonyl (-CO-), or two cyclic tertiary amides. An examination of the available groups in Table III C will reveal that although a group value for a N-substituted cyclic imide is available, there is no appropriate group available for an N-substituted cyclic nitrogen of an amide. Similarly, group values for a cyclic urea and amide carbonyl are not available. The most appropriate group value that is available is for a cyclic tertiary amide. Once the appropriate group is identified, the procedure follows the same protocol established for thiazole.

**Prednisolone.** The estimation of the fusion enthalpy of prednisolone illustrates an example of an estimation of a complex polycyclic compound. This tetracyclic 17 atom ring system ( $4[33.4]+5[3.7]$ ) contains three cyclic quaternary centers ( $3[-34.6]$ ), four cyclic tertiary  $sp^3$  centers, ( $4[-14.7]$ ), three cyclic tertiary  $sp^2$  centers, two of which are attached to a functional group ( $2(1.92)+1[-1.6]$ ), a quaternary  $sp^2$  center ( $[-12.2]$ ) as well as a cyclic carbonyl group ( $[-1.4]$ ). Addition of these modifications to the ring equation estimates the contributions of the ring. Addition of the contributions of the substituents which include three hydroxyls ( $(3)(12.1)[1.7]$ ), two methyls ( $2[17.6]$ ), a methylene ( $[7.1]$ ) and a carbonyl group of an acyclic ketone ( $[4.6]$ ) completes the estimation. The molecule contains five functional groups, hence  $j_{OH}(5)$  is used.

**Polymers.** In addition to the estimation of  $\Delta_0^{T_{fus}} S_{tpce}$  of small molecules, the parameters of Tables I and III can be used to predict  $\Delta_0^{T_{fus}} S_{tpce}$  and  $\Delta_0^{T_{fus}} H_{tpce}$  of crystalline polymers when the experimental melting point is known. Since the parameters in Tables I and III differ somewhat from those reported previously, the predictions of equations 2-6 will likewise produce slightly different results than reported previously (17). However a similar overall correlation between experimental and calculated results should be obtained by these modified parameters. The protocol used to evaluate  $\Delta_0^{T_{fus}} S_{tpce}$  of polymers is exactly the same as outlined above with the exception that the enthalpic or entropic value is calculated on the basis of the structure of the repeat unit of the polymer. As examples, the calculated and experimental values (in brackets) of  $\Delta_0^{T_{fus}} S_{tpce}$  are provided for the following: polyethylene ( $CH_2$ ), 9.3 [9.9]; polytetramethylene terephthalate: 61.8 [58.6], nylon [6,12]: 152.2 [154]. Experimental values have been taken from the literature (23).

**Statistics of the Correlation.** The group values included in Tables I and III were generated from the fusion entropies of a total of 1862 compounds. The absolute average and fractional errors between experimental and calculated  $\Delta_0^{T_{fus}} S_{tpce}$  and  $\Delta_0^{T_{fus}} H_{tpce}$  values for these 1862 compounds were  $9.8 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$  and  $3.48 \text{ kJ}\cdot\text{mol}^{-1}$ ,

and 0.152 and 0.168, respectively. The standard deviations between experimental and calculated values for  $\Delta_0^{T_{fus}} S_{tpce}$  and  $\Delta_0^{T_{fus}} H_{tpce}$  were  $\pm 13.0 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$  and  $\pm 4.84 \text{ kJ}\cdot\text{mol}^{-1}$ , respectively. An additional 62 compounds with errors exceeding 3 standard deviations were excluded from the correlations and from the histogram of Figure 1. A similar histogram was obtained for  $\Delta_0^{T_{fus}} H_{tpce}$  (not shown). Values reported in brackets in Table III should be considered as tentative assignments.

### Distribution of Errors in $\Delta\Delta^{T_{fus}_0} S_{tpce}$

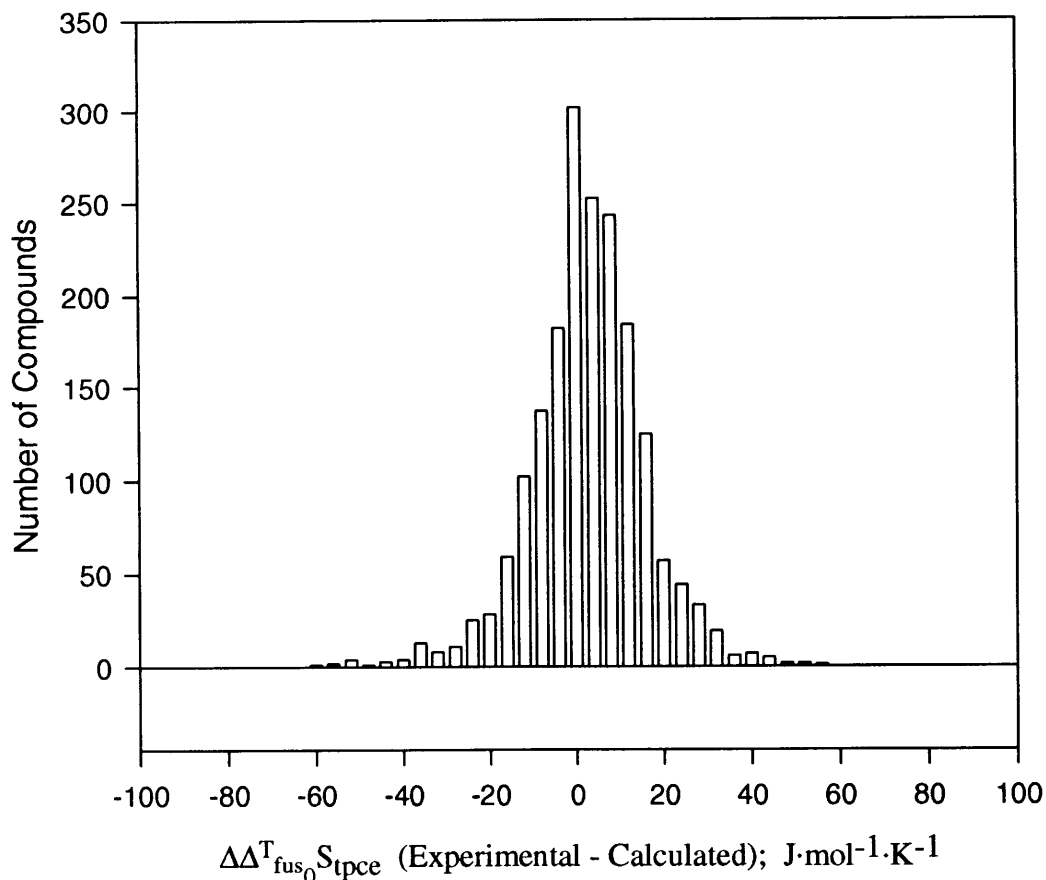


Figure 1. A histogram illustrating the distribution of errors in estimating  $\Delta_0^{T_{fus}} S_{tpce}$ .

### Vaporization Enthalpies

Vaporization enthalpy is a thermochemical property that can be estimated quite accurately. Many estimation methods in the chemical engineering literature, as reported by Rechsteiner, Jr. (24) and others (25), are reported accurate to a few %. Most require critical constants and other parameters which themselves may have to be estimated. In addition, many of these methods have been developed to provide vaporization enthalpies near or at the boiling point.

Numerous group additivity procedures have been reported for estimating the enthalpy of vaporization,  $\Delta_{vap}H_m^\circ$  (298.15 K) (24-37). Most group methods have been developed to provide vaporization enthalpies at 298.15 K although more recent work has focused on the development of group methods applicable to a wider range of temperatures (25, 26). A similar accuracy of a few % have been reported by their developers. While some vaporization enthalpies are known quite accurately, the n-alkanes from C<sub>5</sub>-C<sub>18</sub> for example (38), most  $\Delta_{vap}H_m^\circ$  (298.15 K) values in the literature are probably accurate to about 3-5% of the value reported. This 3-5% uncertainty reflects both experimental errors and errors introduced as a result of correcting the vaporization enthalpy from the mean temperature of measurement to 298.15 K. Consequently, any general estimation method which attempts to reproduce experimental data to better than a few % will obviously be affected by the limited amount of accurate experimental data available and the applicability of the method is likely to be highly focused. The 3-5% experimental uncertainty should serve as a useful lower limit of the typical error to be expected from an estimation technique developed to reproduce  $\Delta_{vap}H_m^\circ$  (298.15 K) of a wide range of substances using a reasonable number of parameters.

Selection of an estimation technique will generally be guided by a number of factors. The method of choice will depend on the temperature or temperature range of interest, the level of user sophistication necessary to perform the estimation, the required accuracy of the estimation and the availability of appropriate group values or other parameters. A major limitation to most group methods is the lack of a sufficient number of group values that can be applied to cover the broad spectrum of molecular structures that are of interest. For this reason, we decided to develop an alternative method to a group additivity approach (34-37). This method described below uses fewer parameters than most group methods and is quite flexible with regards to the carbon architecture that it can successfully model. Recently we compared the accuracy and applicability of this method to the methods reported by Guthrie and Taylor (29) and Ducros *et. al.* (30-32) to a series of hydrocarbon derivatives containing a single functional group (37) and also to more complex molecules (36).

A series of 48 monosubstituted hydrocarbons were randomly selected from a database of 433 (39-40). Group values for these compounds were unavailable for 9 of the 48 compounds using Guthrie's method and 23 of the 48 compounds using Ducros' method. When group values were available, the Ducros' method was generally the most accurate resulting in the best value 18 out of 25 times while Guthrie's method gave the best agreement for 8 of the 39 compounds. The method described below gave the best agreement 28 out of 48 times. Identical predictions were obtained in some instances for certain compounds after the values were rounded off to one significant figure after the decimal. The average absolute error of the 25 compounds estimated by the Ducros' method was 0.9 kJ·mol<sup>-1</sup>; 2.9 kJ·mol<sup>-1</sup> was the average absolute error for the 39 compounds estimated by Guthrie's method. This compares to an average absolute error of 1.76 kJ·mol<sup>-1</sup> for the 48 compounds estimated by the method to be described below.

A second set of 30 compounds containing two or more functional groups were also compared (39-40). We were not able to reproduce the precise values reported by Ducros for those compounds whose functional groups depended on the function  $\gamma$ .

Vaporization enthalpy predictions for these compounds were obtained from the tables provided. Ducros' method resulted in the best value 13 out of 25 times with a standard deviation between experimental and calculated values of  $\pm 2.9 \text{ kJ}\cdot\text{mol}^{-1}$  while Guthrie's method gave the best agreement for 9 of the 28 compounds with a standard deviation of  $\pm 5.0 \text{ kJ}\cdot\text{mol}^{-1}$ . The estimation method described below gave the best agreement 14 out of 30 times with a standard deviation of  $\pm 3.9 \text{ kJ}\cdot\text{mol}^{-1}$ .

**Hydrocarbons.** A number of simple equations have been developed for the estimation of the vaporization of hydrocarbons. Equation 8, originally reported by Morawetz (A, B values) (41) was derived from the vaporization enthalpies of the n-alkanes. The term  $n_{CH_2}$  refers to the number of methylene groups. This equation, recently modified to reflect both refinements and inclusion of additional vaporization data (A', B' values) (42), is capable of reproducing the known vaporization enthalpies of the n alkanes from pentane to triacontane with a standard error of  $\pm 2.1 \text{ kJ}\cdot\text{mol}^{-1}$ .

$$\Delta_{vap}H_m^\circ(298.15 \text{ K})/(\text{kJ}\cdot\text{mol}^{-1}) = A \cdot n_{CH_2} + B; \quad A = 4.97; B = 1.61; A' = 5.43; B' = -3.3. \quad (8)$$

A similar equation, equation 9, containing only three parameters was found to reproduce the vaporization enthalpies of any hydrocarbon with 20 or fewer carbons, regardless of structure, with an error of approximately  $\pm 4.2 \text{ kJ}\cdot\text{mol}^{-1}$ . The terms  $n_C$  and  $n_Q$  refer to the total number of carbons and the total number of quaternary  $sp^3$  hybridized carbon atoms where the definition of quaternary is based, as above, on the number of hydrogens attached to carbon. This equation can also be used on molecules containing more than 20 carbons but the error appears to be slightly larger (7, 42).

$$\Delta_{vap}H_m^\circ(298.15 \text{ K})/(\text{kJ}\cdot\text{mol}^{-1}) = (4.69 \pm 0.08) \cdot (n_C - n_Q) + (1.3 \pm 0.2) \cdot n_Q + (3.0 \pm 0.2) \quad (9)$$

**Simple Hydrocarbon Derivatives.** Vaporization enthalpies of compounds that contain a single functional group can be estimated by using the functional group values in Tables V A-C, the correction terms of Table V D and equation 10:

$$\Delta_{vap}H_m^\circ(298.15 \text{ K})/(\text{kJ}\cdot\text{mol}^{-1}) = 4.69 \cdot (n_C - n_Q) + 1.3 \cdot n_Q + (3.0) + n_M \cdot M + b + C. \quad (10)$$

Application of equation 10 to estimate  $\Delta_{vap}H_m^\circ(298.15 \text{ K})$  of a particular hydrocarbon derivative is quite straightforward. Once the number and type of carbon atoms are properly identified, the contribution of the functional group is included next. Consider as an example the value of a carbonyl group in a ketone. The value b of  $10.5 \text{ kJ}\cdot\text{mol}^{-1}$  represents the additional contribution of the carbonyl oxygen since the contribution of the carbon has already been accounted for by  $n_C$ . For compounds containing silicon, germanium and tin, the metal is treated like carbon but with a contribution, M, that depends on the number of atoms,  $n_M$ , and the substitution pattern as indicated in the lower portion of Table V A. For compounds containing a single fluorine substituent, the value of the fluorine is chosen on the basis of the hybridization of the atom to which it is

**Table V A. Functional Group Contributions to Vaporization Enthalpies**

Class of Compounds	Functional Group Class	b	Class of Compounds	Functional Group Class	b
acid	-C(=O)OH	I 38.8	iodide	-I	I 18.0
alcohol	-OH	I 29.4	ketone	>C=O	II 10.5
aldehyde	-CHO	I 12.9	nitrile	-CN	I 16.7
amide [mono-subst.]	-C(=O)NH-	II 42.5	nitro	-NO <sub>2</sub>	I 22.8
amine [pri.]	-NH <sub>2</sub>	I 14.8	heterocyclic aromatic nitrogen	=N-	II [12.2]
amine [sec.]	-NH-	II 8.9	sulfide	>S	II 13.4
amine [tert.]	>N-	II 6.6	disulfide	-SS-	II [22.3]
bromide	-Br	I 14.4	sulfoxide	>SO	II [42.4]
chloride	-Cl	I 10.8	sulfone	-SO <sub>2</sub> -	II [53.0]
ester	-C(=O)O-	II 10.5	thiolester	-C(=O)S-	II [16.9]
ether	>O	II 5.0	thiol	-SH	I 13.9
<b>Organometallics</b>			<b>M</b>		
prim. silane	-SiH <sub>3</sub>	I 7.8	prim. germane	-GeH <sub>3</sub>	I 10.8
sec. silane	>SiH <sub>2</sub>	II 3.9	sec. germane	>GeH <sub>2</sub>	II [9.8]
tert. silane	>SiH-	II 3.4	quat. germane	>Ge<	II 6.6
quat. silane	>Si<	II 1.8	quat. stannane	>Sn<	II [10.9]

**Table V B. Functional Group Contributions to Vaporization Enthalpies in Molecules with Multiple Functional Groups**

Substitution Pattern <sup>a</sup>	Substitution Factor, F <sub>i</sub>	Substitution Pattern	Substitution Factor, F <sub>i</sub>
single substitution on a primary sp <sup>3</sup> atom	1.62 <sup>b</sup>	1,1-disubstitution on a secondary sp <sup>3</sup> atom	0.94
secondary sp <sup>3</sup> atom	1.08	tertiary sp <sup>3</sup> atom	0.78
tertiary sp <sup>3</sup> atom	0.60	quaternary sp <sup>3</sup> atom	0.55
quaternary sp <sup>3</sup> atom	0.79	quaternary sp <sup>2</sup> atom	0.56
tertiary sp <sup>2</sup> atom	0.69		
quaternary sp <sup>2</sup> atom	0.85	1,1,1-trisubstitution	
quaternary sp atom	0.3	tertiary sp <sup>3</sup> atom	0.81
		quaternary sp <sup>3</sup> atom	0.62
		1,1,1,1-tetrasubstitution	
		quaternary sp <sup>3</sup> atom	0.59

<sup>a</sup>Primary, secondary, tertiary, and quaternary positions are defined by the number of hydrogens attached to the atom bearing the substituent, 3,2,1,0, respectively; <sup>b</sup>a value of 0.79 replaces 1.62 for compounds containing silicon, germanium and tin.



**Table V C. Fluorine Group Contributions to Vaporization Enthalpies**

Fluorine as a single substituent	b	Fluorine as one of several substituents	b
a single fluorine		single or multiple fluorine atoms	
on any $sp^2$ C (or Si)	1.2	on a 1,1-disubstituted $sp^3$ C (or Si)	3.1
on any $sp^3$ C (or Si)	7.1	on a 1,1,1-trisubstituted C (or Si)	1.9
		on a 1,1,1,1-tetrasubstituted C	1.1
		on a 1,1,1,1-tetrasubstituted Si	3.2

**Table V D. Correction Terms for Monosubstituted and Multisubstituted Hydrocarbons**

Nature of the Correction C	Correction (kJ·mol <sup>-1</sup> )	Nature of the Correction C	Correction (kJ·mol <sup>-1</sup> )
Ring correction for cyclic Class II functional groups including cyclic ethers, cyclic ketones, cyclic secondary amines, and cyclic sulfides	2.9 <sup>a</sup>	Alkyl branching on acyclic $sp^3$ carbons	-2.0 <sup>b</sup>
		<i>Ortho</i> and vicinal alkyl branching on $sp^2$ and $sp^3$ carbons on 5 and 6 membered rings	-2.0 <sup>b</sup>

**Table V E. Additional Corrections Term for Multisubstituted Compounds**

Nature of the Correction C	Correction (kJ·mol <sup>-1</sup> )	Nature of the Correction C	Correction (kJ·mol <sup>-1</sup> )
Intramolecular hydrogen bonding for alcohols (5-9 membered rings)	-7.6	Intramolecular hydrogen bonding for $\beta$ diketones	-18.0

<sup>a</sup>One correction per molecule; <sup>b</sup>branching and *ortho* alkyl branching corrections are applied for each carbon branch; branching due to an acyclic quaternary carbon center is counted as one branch; branching due to a cyclic quaternary carbon center is ignored; a branch resulting from attachment of a functional group is ignored.

attached. Values for fluorine attached to carbon and silicon are listed in Table V C.

**Additional Correction Terms.** The terms listed in Table V D were introduced primarily to correct for steric effects on the solvation of the functional group in the neat liquid. Carbon branching near the functional group generally increases steric interactions and reduces intermolecular solvation of the functional group as do *ortho* carbon branches on a ring. Carbon branching also decreases the solvent accessible surface area and this can result in a decrease in the magnitude of the vaporization

enthalpy (7). Inclusion of a functional group as part of a ring generally decreases the steric environment around the group thereby allowing better intermolecular interaction. This structural feature usually results in an increase in vaporization enthalpy. These factors, while small, should be taken into consideration when applying these correction terms to molecules of interest.

**Applications.** Some applications of equation 10 are illustrated in the examples of Table VI. Group values for tertiary amines, fluorine, and the organometallic compounds are new. Details concerning these values will be published elsewhere. Group values given in brackets are considered tentative assignments.

**Triisobutyl amine.** Estimation of the vaporization enthalpy of triisobutyl amine in Table VI illustrates the use of the group values and correction terms listed in Table VA and V C. Application of equation 10 without the correction term affords a vaporization enthalpy of  $65.9 \text{ kJ}\cdot\text{mol}^{-1}$  which would be the vaporization enthalpy calculated for tributyl amine (lit.  $66.5 \text{ kJ}\cdot\text{mol}^{-1}$  (43)). Application of the branching correction for each branch completes the estimation for triisobutyl amine.

**Bicyclo[3.3.0]octan-2-one.** The estimation of *cis* and *trans* bicyclo[3.3.0]octan-2-one illustrates an example of an estimation where the functional group is part of a ring. Application of equation 10 without the correction terms results in a value of  $51.0 \text{ kJ}\cdot\text{mol}^{-1}$ . Note that the carbonyl carbon according to our definition is quaternary but also  $\text{sp}^2$  hybridized and therefore is treated normally. The carbonyl group is also part of a ring. The ring correction increases the vaporization enthalpy to  $53.9 \text{ kJ}\cdot\text{mol}^{-1}$ . In addition, the carbonyl group is *ortho* to a five membered ring. Since this second ring is part of a fused ring system, the *ortho* correction is not applied. A molecule like 2-methylcyclopentanone however should have both the ring and *ortho* correction applied.

**2,4,6-Trimethylacetophenone.** The estimation of 2,4,6-trimethylacetophenone illustrates an example with two *ortho* interactions. In this estimation, once the contributions of the carbons atoms and the functional group is evaluated, the *ortho* interaction can be evaluated in a straightforward fashion.

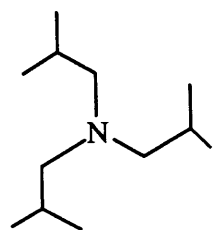
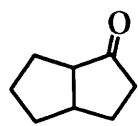
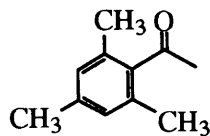
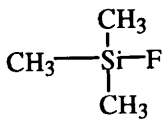
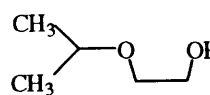
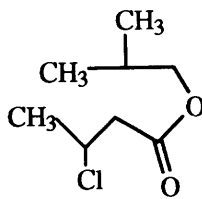
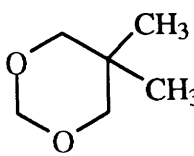
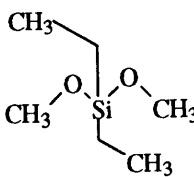
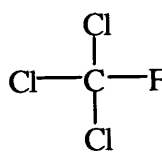
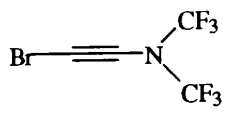
**Fluorotrimethylsilane.** The estimation of the organometallic compounds listed in the bottom of Table V A are estimated in the same manner as other organic molecules with one exception. The metals are not treated as functional groups but simply as replacements for carbon. Thus a molecule like fluorotrimethylsilane is treated like *t*-butyl fluoride, a molecule containing a single functional group. The branching correction has been incorporated into the group value for a quaternary silicon.

**Polysubstituted Hydrocarbon Derivatives.** The protocol established to estimate vaporization enthalpies of molecules containing two or more of the functional groups listed in Table V follows from the protocol established for hydrocarbons and singly substituted derivatives (36). Application of this protocol results in equation 11.

$$\Delta_{\text{vap}}H_m^\circ(298.15\text{K})/(\text{kJ}\cdot\text{mol}^{-1}) = 4.69\cdot(n_C - n_Q) + 1.3\cdot n_Q + n_M M + \sum_i n_i F_i b_i + (3.0) + C \quad (11)$$

The contribution of carbon and any metal components is estimated as previously described for singly substituted compounds. The contribution of a functional group to the vaporization enthalpy of a multifunctional compound depends on both the nature

**Table VI. Estimation of Vaporization Enthalpies (kJ·mol<sup>-1</sup>)**

C <sub>12</sub> H <sub>27</sub> N triisobutylamine	C <sub>8</sub> H <sub>12</sub> O bicyclo[3.3.0]octan-2-one
	
$\Delta_{vap}H_m^\circ(298.15\text{ K})$ lit: 56.4 (43) calcd: 59.9 {[4.69]12+[3.0]+ [6.6]-3[2]}	$\Delta_{vap}H_m^\circ(298.15\text{ K})$ cis lit: 54.4 (39) trans lit: 53.6 (39) calcd: 53.9 {[4.69]8+[3.0]+[10.5] +[2.9]}
C <sub>11</sub> H <sub>14</sub> O 2,4,6-trimethylacetophenone	C <sub>3</sub> H <sub>9</sub> FSi fluorotrimethylsilane
	
$\Delta_{vap}H_m^\circ(298.15\text{ K})$ lit: 62.3 (39) calcd: 61.1 {[4.69]11+[3.0]+ [10.5]-2[2.0]}	$\Delta_{vap}H_m^\circ(298.15\text{ K})$ lit: 25.7 (43) calcd: 26.0 {[4.69]3+[3.0]+[1.8]+ [7.1]}
C <sub>5</sub> H <sub>12</sub> O <sub>2</sub> 2-isopropoxyethanol	C <sub>8</sub> H <sub>15</sub> ClO <sub>2</sub> 2-methylpropyl 3-chlorobutanoate
	
$\Delta_{vap}H_m^\circ(298.15\text{ K})$ lit: 50.2 (43) calcd: 54.8 {[4.69]5+[3.0]+ [29.4](1.08)+[-7.6] +[5.0](1.08+0.6)/2}	$\Delta_{vap}H_m^\circ(298.15\text{ K})$ lit: 52.3 (43) calcd: 56.3 {[4.69]8+[3.0]+ [10.5]1.08+[-2.0] [10.8](0.6)}
C <sub>6</sub> H <sub>12</sub> O <sub>2</sub> 5,5-dimethyl-1,3-dioxane	C <sub>6</sub> H <sub>16</sub> O <sub>2</sub> Si diethyldimethoxysilane
	
$\Delta_{vap}H_m^\circ(298.15\text{ K})$ lit: 41.3 (43) calcd: 40.8 {[4.69]5+[3.0]+[1.3]+ 2[5.0](1.08+0.94)/2+[2.9]}	$\Delta_{vap}H_m^\circ(298.15\text{ K})$ lit: 39.3 (43) calcd: 39.6 {[4.69]6+[3.0]+[1.8] +2[5.0](0.79+0.55)/2}
CCl <sub>3</sub> F trichlorofluoromethane	C <sub>4</sub> BrF <sub>6</sub> N bromo-N,N-bis(trifluoromethyl)ethynylamine
	
$\Delta_{vap}H_m^\circ(298.15\text{ K})$ lit.: 26.2 (43) calcd: 24.1 {[3.0]+[1.3]+ 0.59([1.1]+3[10.8])}	$\Delta_{vap}H_m^\circ(298.15\text{ K})$ lit.: 31.9 (43) calcd: 26.5 {[4.69]2+2[1.3]+[3.0] +6[1.1](0.59)+ (0.3)[14.4]+ [6.6](0.3+2(0.59))/3}

(b) and location (F) of the functional group. The nature of a functional group, characterized by the constant  $b$ , has already been discussed. The substitution factors,  $F_j$ , reported in Table V B, take into account the location of the functional group in the molecule. Hybridization and substitution characteristics are used as identifiers of the steric environment of the functional group and its ability to interact intermolecularly. Most substitution factors attenuate the contribution of the functional group. Two classes of functional groups are identified in Table V A. Class I functional groups refer to monodentate ligands while class II groups refer to multidentate ligands. Substitution factors for class I functional groups depend solely on the hybridization and substitution of the carbon to which the functional group is attached. Substitution factors for class II functional groups are dependent on the hybridization and substitution pattern of two or more carbon atoms or their equivalent. The arithmetic mean of each of the substitution factors is used as the modifier to  $b$  in this case.

Most of the substitution factors reported in Table V B are identical to those reported previously (36) except in cases where a tentative value was reported. One substitution factor, the value for a primary  $sp^3$  atom, has a value that depends on the chemical composition of the molecule in question. The value typically used for a primary  $sp^3$  carbon atom, 1.62, is replaced by 0.79 for the same atom in any estimation of an organosilane. The same value, 0.79, also appears applicable to organogermanes and organostannanes, although this conclusion is based on far fewer experimental data.

The contribution of fluorine in organofluorine compounds containing multiple fluorines or other substituents can be obtained directly from the group values in Table V C. The contribution of fluorine to the vaporization enthalpy depends on the number of substituents attached to the same carbon or silicon atom. Once the appropriate  $b$  value is identified, the estimation of organofluorine compounds follows the same protocol as established for other functional groups. Values for fluorine substitution are new and some substitution factors that were tentatively assigned previously (36) have changed due to the inclusion of new data in the correlations.

**Additional Correction Terms.** In addition to the functional group values and substitution factors listed in Tables V A and B, additional correction terms applicable to polyfunctional compounds are also included in Table V D. An important correction applicable to polyfunctional molecules is for the formation of intramolecular hydrogen bonds. Two correction terms are available. One correction is applicable to any alcohol capable of forming an intramolecular hydrogen bond to oxygen by means of a 5-9 membered ring (including the hydrogen atom). A second correction is available specifically for intramolecular hydrogen bonds formed by the enolic form of  $\beta$ -diketones. Intramolecular hydrogen bonding corrections for other functional groups such as amines or thiols do not appear to be necessary. There is some evidence that suggests that this correction should be applied to hydroxyl groups intramolecularly hydrogen bonded to nitrogen in amines.

The inclusion of substituent factors in equation 11 reduces the instances where branching corrections are necessary. Branching and the *ortho* correction are necessary in multifunctional compounds only when the branch occurs at a carbon atom that is not directly attached to any functional group but clearly affects intermolecular interactions of the functional group. The examples in Table VI B illustrate the application of this

protocol.

**Applications.** Some applications using equation 11 are illustrated in the last six examples of Table VI.

**2-Isopropoxyethanol.** 2-Isopropoxyethanol is an example of a molecule containing two functional groups and one correction term, a correction for intramolecular hydrogen bonding. The contributions of the carbons and the constant account for the first two terms in the estimation. The hydroxyl group is a class I functional group, and in this instance, is connected to an secondary  $sp^3$  carbon. The contribution of the ether oxygen, a class II functional group, is obtained from the product of the group value for an ether and an averaged substitution factor based on the two carbon environments at the point the ether oxygen is attached. Correction for the intramolecular hydrogen bond completes the estimation. There is no branching correction applied because the branch is not remote but occurs at the point of substitution of a functional group and is corrected by the substitution factor for a tertiary  $sp^3$  carbon (0.6).

**2-Methylpropyl 3-chlorobutanoate.** Estimation of the vaporization enthalpy of 2-methylpropyl 3-chlorobutanoate follows a similar protocol. The first two terms in the estimation account for the contributions of the carbon backbone and the constant. The third term accounts for the contribution of the ester group. In this case the structural environment at the atoms to which the  $-C(=O)O-$  group is attached is the same, both are secondary  $sp^3$  carbons. The contribution of the chlorine is attenuated by its structural environment. Finally, this molecule contains a remote acyclic carbon branch which is not corrected by the substitution factor as in 2-isopropoxyethanol. This correction is included as the fourth term in the estimation. It should be pointed out that there are two functional groups that can be influenced by carbon branching. Based on the rationale presented earlier for justification of this correction term, it can be argued that this correction should be applied once for each functional group in the molecule. While the estimation would improve in this case if this correction were applied twice, there are not sufficient experimental data available at present to justify this argument. At present, we recommend applying this correction term once for each acyclic carbon branch in the molecule, regardless of the number of functional groups that are present.

**5,5-Dimethyl-1,3-dioxane.** The estimation of a cyclic molecule, 5,5-dimethyl-1,3-dioxane, follows the same protocol. In this instance the molecule contains a quaternary  $sp^3$  carbon atom. The "ortho or vicinal" branching correction for cyclic molecules is not applicable here since the methyl groups are remote from the ether oxygens. Neither is the branching correction (see footnote b, Table V). Once the carbon atoms are accounted for, the contributions of the ether oxygens can be evaluated. In this instance, both oxygens are equivalent but are attached to two different environments, singly substituted and geminally substituted secondary  $sp^3$  carbons. Finally, this molecule is a cyclic ether and requires a ring correction term. This correction term is applied once regardless of the number of oxygens in the ring.

**Diethyldimethoxysilane.** The first two terms in the estimation of diethyldimethoxysilane account for the contribution of the carbon atoms and the constant and the third term accounts for the quaternary silicon. This molecule is considered to contain two functional groups. The contributions of the two ether oxygens are attenuated by their position of attachment. Note that the substitution factor used for a primary  $sp^3$  carbon

in an organosilane (0.79) is different than the value used for estimations in other compounds (1.62). Branching is not remote but occurs at the center of substitution by the functional groups and is corrected by the geminal substitution factor, 0.55.

**Trichlorofluoromethane.** The estimation of trichlorofluoromethane illustrates the use of the various group values for fluorine. The estimation consists of the contributions of the quaternary carbon and the constant, and the contributions of the three chlorines and single fluorine. All halogens are in the same structural environment. The group value selected for fluorine is the one for a tetrasubstituted carbon atom.

**2-Bromo-N,N-bis(trifluoromethyl)ethynylamine.** The estimation of the vaporization enthalpy of 2-bromo-N,N-bis(trifluoromethyl)ethynylamine is the last example of the diversity of molecular structure that can be handled by this approach. While all carbon atoms in this molecule are quaternary atoms based on our definition, only two are both quaternary and  $sp^3$  hybridized. The contribution of the two pairs of carbon atoms to the vaporization enthalpy differ. The first two terms in the estimation are based on this distinction. The contributions of the functional groups, each attenuated by its location in the molecule as previously described, and the constant complete the estimation.

**Statistics of the Correlation.** The statistics of the correlation for hydrocarbons, monofunctional hydrocarbons and polyfunctional compounds have been reported previously (34-36). Typically, the vaporization enthalpies of hydrocarbons, monofunctional hydrocarbons, and polyfunctional compounds used in the data base (138, 433, 175 compounds, respectively) are reproduced to within 5% of the experimental data ( $\Delta\Delta_{vap}H_m^\circ(298.15\text{ K})$ ) (experimental - calculated) average deviation, hydrocarbons:  $\pm 2.5$ ; monofunctional compounds:  $\pm 1.6$ ; polyfunctional compounds:  $\pm 2.5$   $\text{kJ}\cdot\text{mol}^{-1}$ ). An additional group of compounds totaling 400 and containing the elements of Si, Ge, Sn, F and N (in the form of tertiary amines) have been used to generate the parameters of the additional groups included in this discussion. These parameters were able to reproduce the experimental values of this data base within 8% (standard deviation  $\pm 4.0$   $\text{kJ}\cdot\text{mol}^{-1}$ ). These estimations have not yet been compared to those available from the group additivity approach described by Myers and Danner for organometallic compounds (33). The reader is encouraged to compare the predictions of alternative estimation methods whenever possible.

## Sublimation Enthalpies

Several different empirical and theoretical approaches have been exploited in developing estimation techniques for sublimation enthalpies of solids. An optimized force field of general applicability for the calculation of crystal energies has been developed (44). Correlations have been found which allow an estimate of the sublimation enthalpy,  $\Delta_{sub}H_m(298.15\text{ K})$ , from molecular parameters like the number of valence electrons and the van der Waals surface (45). Quantitative structure-sublimation enthalpy relationships have also been studied by neural networks (46), linear free energy relationships (47), and conformational force field analysis (CoMFA, (48)). Earlier work in this area also included a group additivity method reported by Bondi and various other related group incremental methods applicable for a related series of molecules (49-51).

The development of reliable means of estimating sublimation enthalpies is an extremely important goal in thermochemistry. Enthalpies of combustion can presently be measured with a precision of a few tenths of a percent. This in turn results in very precise heats of formation for many organic solids. Sublimation enthalpies are added to these enthalpies of formation to convert them to gas phase values. An examination of the sublimation literature reveals a situation where sublimation enthalpies are rarely accurate beyond 5% and for molecules with low volatility, discrepancies in sublimation enthalpies of 10 kJ·mol<sup>-1</sup> or more are not uncommon. In fact a survey of the reproducibility of experimental sublimation enthalpies of 44 compounds in the literature resulted in a standard deviation of the mean of 7.3 kJ·mol<sup>-1</sup> (52).

One of the most flexible approaches to estimating sublimation enthalpies is to take advantage of the thermodynamic cycle that relates sublimation enthalpy to the enthalpies of vaporization and fusion, equation 12.  $\Delta_{fus}H_m(T_{fus})$  and  $\Delta_{vap}H_m(298.15\text{ K})$  refer to the molar enthalpy change in going from solid to liquid and from liquid to gas respectively. While this equation is an equality only for enthalpies measured at the same

$$\Delta_{sub}H_m(298.15\text{ K}) \approx \Delta_{fus}H_m(T_{fus}) + \Delta_{vap}H_m(298.15\text{ K}) \quad (12)$$

temperature, it generally serves as a good approximation when vaporization enthalpies at 298 K are used in conjunction with fusion enthalpies measured at the melting point. The ability to mix and match both experimental and estimated enthalpies, depending on availability, makes this approach particularly attractive. The application of equation 12 to estimate sublimation enthalpies of hydrocarbons has been documented previously (53). This section will attempt to illustrate various applications of equation 12 to estimate sublimation enthalpy.

**Vaporization Enthalpies at 298.15 K.** For many compounds that are solids at room temperature, experimental vaporization enthalpies or vapor pressures as a function of temperature, are available above the melting point of the solid (43). Vaporization enthalpies of these compounds are often evaluated from the temperature dependence of vapor pressure (P) and are obtained from the slope of a ln P vs 1/T plot according to the Clausius Clapeyron equation. These vaporization enthalpies are usually referenced to some mean temperature <T> evaluated either from the average value of the reciprocal of  $[1/T_1+1/T_2]/2$  or from  $(T_1+T_2)/2$  where  $T_1$  and  $T_2$  are the initial and final temperatures of the measurements, respectively. To use the vaporization enthalpy in equation 12, correction to 298 K may be necessary. Compendia of heat capacities for many organic liquids are available (54-57). However heat capacity data for the liquid state of the solid compound of interest at 298.15 K may be unavailable. Several estimation methods are available for estimating the heat capacities of the liquid and gas phase phases and these techniques can be used directly to arrive at a value for  $\Delta_{vap}H_m(298.15\text{ K})$ (58-60). An alternative and simpler method of correcting this data is through the use of equations 13 and 14.

$$\Delta_g^l C_p(<T>-298.15\text{ K})/\text{J}\cdot\text{mol}^{-1} = (10.58+0.26 C_{pl})(<T> - 298.15\text{ K}) \quad (13)$$

$$\Delta_{vap}H_m(298.15\text{ K})/\text{J}\cdot\text{mol}^{-1} = \Delta_{vap}H_m(<T>)+(10.58+0.26C_{pl})(<T>-298.15\text{ K}) \quad (14)$$

The term  $\Delta_g^l C_p$  in equation 13 refers to the difference in heat capacities between the liquid and gas phase and  $C_{pl}$  in equations 13 and 14 refers to the heat capacity of the liquid at 298.15 K which can be estimated by group additivity. An experimental value of  $C_{pl}$  can be used if available. The relationship between  $\Delta_g^l C_p$  and  $C_{pl}$  in equation 13 was obtained by correlating differences in experimental heat capacities between the liquid and gas phases at 298.15 K with the heat capacity of 289 organic liquids estimated by group additivity (60, 61). Equation 13 was the relationship obtained from this correlation. While heat capacities of both the liquid and gas phases are temperature dependent, equation 13 is based on the assumption that  $\Delta_g^l C_p$  will be independent of temperature. This assumption was tested by comparing the predictions of equation 14 to differences observed in experimental vaporization enthalpies of a series of compounds, each measured at temperature  $\langle T \rangle$ , and a reference temperature, usually 298.15 K. Vaporization enthalpies of a total of 126 organic compounds were examined. Vaporization enthalpies of these materials were reported over the temperature range, 260-370 K and included a temperature near or at 298.15 K. Excluding compounds that form hydrogen bonds (15 of 126), the standard error associated with using equation 14 to correct the vaporization enthalpy measured at temperature  $\langle T \rangle$  to the reference temperature, usually 298.15 K, was  $\pm 490 \text{ J}\cdot\text{mol}^{-1}$ . This increased to  $\pm 710 \text{ J}\cdot\text{mol}^{-1}$  if molecules capable of hydrogen bonding were included in the correlation.

**Sublimation enthalpies at 298.15 K.** Although sublimation enthalpies at 298.15 K are necessary for correcting solid state enthalpy of formation data, the vapor pressure of many solids necessitate the measurement of sublimation enthalpies at other temperatures. This necessitates correcting these data back to 298.15 K. A number of simple equations have been used to adjust sublimation enthalpies to 298.15 K (52). The term  $\Delta_{sub}H_m(\langle T \rangle)$  in equation 15 represents the sublimation enthalpy measured at some mean temperature  $\langle T \rangle$  and R is the gas constant ( $8.313 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ ). Values for n of 2-6 have been used by various research groups (52). An alternative approach to equation 15 and one which appears to give some improvement over equation 15 is equation 16. The term  $C_{pc}$  refers to the heat capacity of the solid at 298.15 K. Either experimental or estimated  $C_{pc}$  values can be used. The same assumption used in

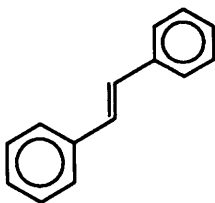
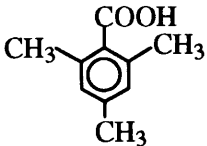
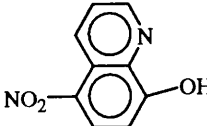
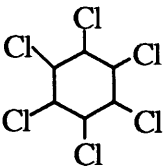
$$\Delta_{sub}H_m(298.15 \text{ K}) = \Delta_{sub}H_m(\langle T \rangle) + nR[\langle T \rangle - 298.15] \quad (15)$$

$$\Delta_{sub}H_m(298.15 \text{ K}) = \Delta_{sub}H_m(\langle T \rangle) + [0.75 + 0.15C_{pc}][\langle T \rangle - 298.15] \quad (16)$$

generating equation 13 was used here. Since the heat capacity of a liquid is usually larger than for the corresponding solid, which in turn is larger than for the gas, heat capacity adjustments applied to experimental measurements conducted above 298.15 K increase the enthalpy of the corresponding phase change when corrected back down to 298.15 K. For a given temperature difference, the adjustment to the sublimation enthalpy is usually smaller than the adjustment to the vaporization enthalpy.



**Table VII. Estimation of Sublimation Enthalpies<sup>a</sup>**

<b>C<sub>14</sub>H<sub>12</sub> <i>trans</i> 1,2-diphenylethene</b>			
	$T_{fus}:$	397.4 K	$\Delta_{vap}H_m$ (T/K)
	$\Delta_0^{T_{fus}} S_{tpce}$	calcd.: 69.6	exp: 65.5(434) (43)
		{10[7.4]+2[-7.5]+2[5.3]}	$C_{pl}(298.15\text{ K})/J\cdot\text{mol}^{-1}$
	$\Delta_0^{T_{fus}} H_{tpce}$	exp.: 27.4 (55)	102.1 (52)
		calcd.: 27.7	99.2 (52)
			$\Delta_{vap}H_m$ (T/K)
			99.6 (313) (43)
			103.8 (315) (64)
			calcd: {27.4+75.2}= 102.6
			(eq 14): 75.2(298.15 K) {27.7 + 75.2 = 102.9
		(eq 9): 68.7 (298.15 K) 27.7 + 68.7 = 96.4	
		{14[4.69]+[3.0]}	
<b>C<sub>10</sub>H<sub>12</sub>O<sub>2</sub> 2,4,6-trimethylbenzoic acid</b>			
	$T_{fus}:$	428.15 K	$\Delta_{vap}H_m$ (T/K)
	$\Delta_0^{T_{fus}} S_{tpce}$	calcd: 44.7	calcd: 84.7 (298.15)
		{3[17.6]+[-7.5]+2[7.4]+3[-9.6]+[13.4]}	{10[4.69]+[3.0]+[38.8]-2[2.0]}
	$\Delta_0^{T_{fus}} H_{tpce}$	calcd: 19.1	calcd: 19.1 + 84.7 = 103.8
<b>C<sub>9</sub>H<sub>6</sub>N<sub>2</sub>O<sub>3</sub> 8-hydroxy-5-nitroquinoline</b>			
	$T_{fus}:$	456.2 K	$\Delta_{vap}H_m$ (T/K)
	$\Delta_0^{T_{fus}} S_{tpce}$	calcd: 55.9	calcd: 91.4 (298.15)
		{5[7.4]+4[-7.5]+[17.7]+[20.3]+[10.9]}	{9[4.69]+[3.0]+([22.8]+[29.4])0.85+[12.2](0.69+0.85)/2+[-7.6]}
	$\Delta_0^{T_{fus}} H_{tpce}$	calcd: 25.5	calcd: 25.5 + 91.4 = 116.9
<b>C<sub>6</sub>H<sub>6</sub>Cl<sub>6</sub> <math>\gamma</math>-hexachlorocyclohexane (Lindane)</b>			
	$T_{fus}:$	386.8 K	$\Delta_{vap}H_m$ (T/K)
	$\Delta_0^{T_{fus}} S_{tpce}$	calcd.: 53.5	calcd: 70.0 (298.15)
		{[33.4]+3[3.7]+6[-14.7]+6[1.5][10.8]}	{6[4.69]+[3.0]+6[10.8]0.60}
	$\Delta_0^{T_{fus}} H_{tpce}$	calcd: 20.7	exp: 90.8 (298.15) (66)
		exp: 22.1 (65); 25.9(55)	106.6 (273) (67)
			99.2 (328) (43)
			88.9 (303) (68)
			115.5 (69)
		calcd: 20.7 + 70.0 = 90.7	
		24.0 + 70.0 = 94.0	

<sup>a</sup> $\Delta_0^{T_{fus}} H_{tpce}$ ,  $\Delta_{vap}H_m$  and  $\Delta_{sub}H_m$  enthalpies in kJ·mol<sup>-1</sup>;  $\Delta_0^{T_{fus}} S_{tpce}$  in Jmol<sup>-1</sup>K<sup>-1</sup>

**Applications.** Application of equation 12 to estimate sublimation enthalpies is shown in the examples in Table VII. Examples were chosen to illustrate the use of most of the equations discussed in this presentation.

***trans* 1,2-Diphenylethene.** The estimation of *trans* 1,2-diphenylethene illustrates the estimation of a hydrocarbon in a case where experimental fusion, vaporization and sublimation enthalpies are available. The vaporization enthalpy was obtained from the temperature dependence of vapor pressure at a mean temperature of 434 K and corrected back to 298.15 K using the experimental heat capacity of the liquid at 298.15 K and equation 14. The vaporization enthalpy was also estimated using equation 9. A direct measurement of the sublimation enthalpy of *trans* 1,2-diphenylethene has been reported by a number of workers and a partial list of available values is provided in Table VII. These values can be compared to the value obtained by addition of either the experimental or estimated latent enthalpies. Additional details describing the estimations of hydrocarbons have been reported previously (53).

**2,4,6-Trimethylbenzoic acid.** This estimation acid is an example of an estimation of a molecule containing a single functional group. An experimental fusion enthalpy for this material is not currently available. However it can easily be estimated using the experimental melting point and the total phase change entropy as summarized in Table VII. The vaporization enthalpy can be estimated using equation 10. In this estimation there are two *ortho* alkyl branches to correct. Addition of these two estimated enthalpies produces a value, 103.8 kJ·mol<sup>-1</sup>, which agrees favorably with the experimental value.

**8-Hydroxy-5-nitroquinoline.** The estimation of 8-hydroxy-5-nitroquinoline illustrates the use of equations 6 and 11 to estimate the fusion and vaporization enthalpies, respectively. While different values for the hydroxyl group in phenols and alcohols are used for estimating solid-liquid phase change properties, the same group value is used for estimating vaporization enthalpies. The quinoline structure is treated as an aromatic system and the group value for a heterocyclic aromatic amine is used for nitrogen. In the estimation of the vaporization enthalpy, the pyridine group value is used for nitrogen and this group is treated like any other class II functional group in a multisubstituted compound. The vaporization enthalpy is corrected for an intramolecular hydrogen bond.

**$\gamma$ -Hexachlorocyclohexane.** Lindane, is another example of a molecule containing multiple substitution. In this instance, equation 7 is used in the estimation of the total phase change entropy. Chlorine is a functional group that is influenced by the presence of multiple substitutions in the evaluation of  $\Delta_0^{T_{fus}} S_{tpce}$ . Estimation of the vaporization enthalpy is accomplished using equation 11. An examination of the literature, reveals a number of reports of the sublimation enthalpy of Lindane. The scatter in the experimental values observed here is not uncommon. The estimated value in this case illustrates how it can be used to select the most probable experimental value from a series of discordant measurements.

**Statistics of the Correlation.** Statistics to determine how well sublimation enthalpies can be estimated by this technique for functionalized molecules are not currently available. Statistics describing the correlation obtained when using equation 12 to estimate the sublimation enthalpies of hydrocarbons has been reported (53). A

standard error of  $\pm 10.6 \text{ kJ}\cdot\text{mol}^{-1}$  has been reported in the estimation of the sublimation enthalpies of 137 different hydrocarbons. We would expect this uncertainty to rise somewhat with increasing molecular complexity, but the magnitude of this number should serve as a useful guide in various applications.

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