Thermochimica Acta 495 (2009) 5–13

Contents lists available at ScienceDirect

Thermochimica Acta

journal homepage: www.elsevier.com/locate/tca

Total phase change entropies and enthalpies. An update on fusion enthalpies and their estimation

James S. Chickos [a,*], William E. Acree Jr. [b]

[a] Department of Chemistry, University of Missouri-St. Louis, 1 Univ Blvd, Saint Louis, MO 63121, United States
[b] Department of Chemistry, University of North Texas, Denton, TX 76203, United States

ARTICLE INFO

Article history:
Received 25 February 2009
Received in revised form 12 May 2009
Accepted 14 May 2009
Available online 23 May 2009

Keywords:
Fusion enthalpy
Total phase change enthalpy
Total phase change entropy
Fusion entropy

ABSTRACT

This compendium summarizes the fusion enthalpies of approximately 1000 new measurements. A group additivity method developed to estimate the total phase change entropies and enthalpies of organic solids is updated, applied to the new data and the results are compared. The uncertainties associated with the 1016 new measurements, ±18.5 J mol^{-1} K^{-1} and ±7.6 kJ mol^{-1} for total phase change entropies and enthalpies, respectively, are similar in magnitude to those reported previously. Experimental and estimated fusion entropies and fusion enthalpies along with references are available as supplementary material.

1. Introduction

Fusion enthalpy is an important physical property of the solid state. The magnitude of the fusion enthalpy influences solute solubility in both an absolute sense and in its temperature dependence. This property is an important consequence of molecular packing in crystals and can be useful in correcting thermochemical data to a standard state when combined with other thermodynamic properties. Techniques for estimating fusion enthalpies can play several useful roles. Perhaps most importantly, they provide a numerical value that can be used in cases when there are no experimental data. Estimations are also useful in selecting the most probable experimental value in cases where two or more values are in significant disagreement.

It is precisely because of the unpredictability of various phase changes that can occur in the solid state that the direct estimation of fusion enthalpy has had only limited success. An alternative approach that we have selected has been to model the total entropy change associated with all phase transitions from a rigid crystal at $T = 0$ K to an isotropic liquid at the melting point, $T = T_{\text{fus}}$. It has been previously shown that the total phase change entropy is a more reliable group property than fusion entropy [1]. Once the total phase change entropy is calculated and the fusion temperature measured, the total phase change enthalpy can be calculated [2].

Large positive differences between estimated and experimental values ($\Delta_0^{T_{\text{fus}}} H_{\text{tpce calc}} - \Delta H_{\text{fus}}$) are useful in identifying systems exhibiting either dynamic or complex phase behavior in the solid state. Plastic crystals exhibit molecular motion in the solid state while those forming liquid crystals can exhibit non-isotropic molecular motion in the liquid phase. Both have associated with these phenomena, additional phase transitions or unusually large heat capacities that can attenuate the enthalpy and entropy associated with fusion [2]. Large negative differences between estimated and experimental values on the other hand can often be an indicator of decomposition occurring during the fusion process.

Since the publication of our last report [2], we have continued to search the chemical and pharmaceutical literature for recently measured enthalpy of fusion data and the older literature for published experimental data that were overlooked during our earlier searches. These efforts have led to the retrieval of enthalpy of fusion data for approximately 1000 new measurements mostly on new compounds. At the time of our previous publication, approximately 160 group values had been defined. The additional enthalpy of fusion data has enabled us to provide group parameters for several new functional groups and to modify group values for a few functional groups tentatively assigned previously. In order to avoid a plethora of new functional groups, this work has made an effort to use existing group values in estimations whenever possible and to maintain the protocol used in estimations as constant as possible. Tables 1 and 2 list the group values for hydrocarbons and the hydrocarbon portion of the molecule, most of which have not changed. New group values are listed in bold in both columns 1 and 3 of Tables 3 and 4 . Values that have changed since our previous

---

* Corresponding author. Tel.: +1 314 516 5377; fax: +1 314 516 5342.
E-mail address: jsc@umsl.edu (J.S. Chickos).

0040-6031/$ – see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.tca.2009.05.008

Table 1

Contributions of the hydrocarbon portion of the molecule.

Aliphatic and aromatic carbon groups	Group value (G_i)[a] (J/(mol K))			Group coefficient (C)[a]	
Primary sp^3 C	$\mathbf{CH_3}$–R	17.6	(A1)		
Secondary sp^3 C	$R_2>\mathbf{CH_2}$	7.1	(A2)	1.31[b]	(B2)
Tertiary sp^3 C	$R_2>\mathbf{CH}$–R	−16.4	(A3)	0.60	(B3)
Quaternary sp^3 C	$R_2>\mathbf{C}<R_2$	−34.8	(A4)	0.66	(B4)
Secondary sp^2 C	$=\mathbf{CH_2}$	17.3	(A5)		
Tertiary sp^2 C	$=\mathbf{CH}$–	5.3	(A6)	0.75	(B5)
Quaternary sp^2 C	$=\mathbf{C}$(R)–	−10.7	(A7)		
Tertiary sp C	$\mathbf{H}$–$\mathbf{C}\equiv$	**17.5**	(A8)		
Quaternary sp C	R–$\mathbf{C}\equiv$	−**4.3**	(A9)		
Tertiary benzenoid sp^2 C	$=\mathbf{CH}$–	7.4	(A10)		
Quaternary benzenoid sp^2 C adjacent to an sp^3 atom[c]	$=\mathbf{C}$(R)–	−9.6	(A11)		
Quaternary benzenoid sp^2 C adjacent to an sp^2 atom[d]	$=\mathbf{C}$(R)–	−7.5	(A12)		
Internal benzenoid quaternary sp^2 C adjacent to an sp^2 atom[e]	$=\mathbf{C}$(R)–	−0.7	(A13)		

[a] The alphanumerical terms, A1, A2, B2, . . . are a device used to identify each carbon group value in the estimations provided in Table 5 and Table 1A (appendix); carbon groups are not considered functional groups; group values in bold reflect changes from previous reports; R refers to any group or heteroatom.

[b] The group coefficient of 1.31 for C_{CH_2} is applied only when the number of consecutive methylene groups exceeds the sum of the remaining groups (both carbon and other functional groups); see text for additional details.

[c] This group applies to any quaternary benzenoid carbon adjacent to an sp^3 hybridized atom with no lone pair of electrons.

[d] This group applies to any quaternary benzenoid carbon adjacent to any sp^2 hybridized atom and to sp^3 hybridized atoms with non-bonding electrons with the exception of internal quaternary carbon atoms (see footnote e).

[e] Any internal quaternary benzenoid carbon that is not at the periphery of a molecule; for example the six internal quaternary benzenoid carbon atoms of coronene.

publication are also listed in bold but only in column 3. These values were adjusted taking into account both new data and data previously in our database. Tentative assignments are reported in column 3 of Tables 3 and 4 in brackets and are based on the number of entries reported in parenthesis in column 1 for each functional group considered as such. It should also be noted that in the discussions that follows and as in earlier publications, primary, secondary, tertiary, and quaternary carbons atoms are defined by the number of hydrogens attached to carbon, 3, 2, 1, and 0, respectively. This convention also applies to other central atoms as well.

2. Method description

2.1. *Aliphatic and benzenoid aromatic hydrocarbons (aah)*

The estimation of the fusion entropy of hydrocarbons is based solely on the groups present in the molecule according to the following equation:

$$\Delta_0^{T_{\mathrm{fus}}}S_{\mathrm{tpce}}(aah)=\sum_i n_iG_i+n_{\mathrm{CH_2}}C_{\mathrm{CH_2}}G_{\mathrm{CH_2}};\qquad C_{\mathrm{CH_2}}=1.31$$

$$\text{when } n_{\mathrm{CH_2}}\geq\Sigma n_i;\quad i\neq \mathrm{CH_2}\ \text{ otherwise } C_{\mathrm{CH_2}}=1.0 \tag{1}$$

Groups are defined by substitution and hybridization patterns of the carbon atom. The term n_iG_i refers to the number of G_i type groups defined in Table 1. The term $n_{\mathrm{CH_2}}$ refers to the number of methylene groups in the molecule, $G_{\mathrm{CH_2}}$ refers to the group value associated with a CH_2 group and $C_{\mathrm{CH_2}}$ is normally equal to one unless the number of consecutive CH_2 groups equals or exceeds the total sum of other groups present in the molecule, Σn_i where $i\neq CH_{2,}$ as defined in Tables 1–4, in which case $C_{\mathrm{CH_2}}$ is equal to 1.31. This coefficient does not apply to any other non-consecutive aliphatic CH_2 groups that may also be present. These additional CH_2 groups are treated normally but are not included in the total sum of other groups present. The other group coefficients reported in Table 2 are used for hydrocarbon derivatives and will be discussed in more detail below. Groups values reported in bold in Table 1 reflect values that have been changed from previous versions [1,2].

Table 2

Adjustments to contributions of the cyclic hydrocarbon portions of the molecule.

Contributions of cyclic carbons	Group value (G_i)[a] (J/(mol K))			Group coefficient (C)	
cyclic tertiary sp^3 carbon	–$\mathbf{CH}$(R)–	−14.7	(A16)		
cyclic quaternary sp^3 carbon	–$\mathbf{C}<(R)_2$–	−34.6	(A17)		
cyclic tertiary sp^2 carbon	$=\mathbf{C}$H–	−1.6	(A18)	1.92	(B18)
cyclic quaternary sp^2 carbon	$=\mathbf{C}$(R)–	−12.3	(A19)		
cyclic quaternary sp carbon	$=\mathbf{C}=$; R–$\mathbf{C}\equiv$	−4.7	(A20)		

[a] R refers to any organic fragment including other functional groups or heteroatom.

Table 3A

Contributions of the functional group portion of the molecule. Acyclic functional groups dependent on the substitution pattern.

Functional groups[a]	Group value (G_k)[a] (J/(mol K))		Group coefficient (C_k)[a], k		
Total number of functional groups=			2	3	k_n[b]
Chlorine	R–$\mathbf{Cl}$	10.8 (A22)			1.5 (D22)
2-Fluorines on an acyclic sp^3 carbon	$R_2>\mathbf{CF_2}$	13.2 (A26)	1.06 (B26)	1.06 (C26)	1.15[c] (D26)
Hydroxyl group	R–$\mathbf{OH}$	1.7 (A30)	10.4 (B30)	9.7 (C30)	13.1 (D30)
Carboxylic acid	R–$\mathbf{C(=O)OH}$	13.4 (A36)	1.21 (B36)		2.25 (D36)

[a] The alphanumerical terms, A1, A2, B2, . . . are a device used to identify each group value in the estimations provided in Table 5 and Table 1A (appendix); the group value refers to the atoms in bold; the group coefficient refers to the total number of functional groups; R refers to any organic fragment including other functional groups.

[b] To be used in all cases of multiple substitutions unless noted otherwise in the preceding two columns.

[c] To be used in acyclic perfluorinated hydrocarbons.

Table 3B

Contributions of the functional group portion of the molecule. Remaining acyclic functional groups.

Functional groups[a]		Group value (G_k)[b] J/(mol K)	
Bromine	R–**Br**	17.5	(A21)
Fluorine on an sp^2 carbon	R$_2$ > CH**F**	19.5	(A23)
Fluorine on an aromatic carbon	**=CF–**	16.6	(A24)
3-Fluorines on an sp^3 carbon	**CF$_3$**–R	13.2	(A25)
1-Fluorine on an sp^3 carbon	R$_2$ > **CF**–R	12.7	(A27)
1 Fluorine on a ring carbon (15)	–CH**F**–	[17.5]	(A28)
2 Fluorines on a ring carbon (9)	–C**F$_2$**–	[17.5]	(A28)
Iodine	R–**I**	19.4	(A29)
Phenol	=C–(**OH**)–	20.3	(A31)
Hydroperoxide (2)	R–**OOH**	[31.8]	(A158)
Ether	R–**O**–R	4.71	(A32)
Peroxide (2)	R–**O**–**O**–R	[10.6]	(A33)
Aldehyde	R–**CH(=O)**	21.5	(A34)
Ketone	R–**C(=O)**–R	4.6	(A35)
Formate ester (3)	R–**O(C=O)H**	[**22.3**]	(A37)
Ester	R–**C(=O)O**–R	7.7	(A38)
Carbonate (10)	R–**OC(=O)O**–R	[**7.1**]	(A149)
Anhydride (2)	R–(**C=O)O(C=O)**–R	[10.0]	(A39)
Acyl chloride (1)	R–(**C=O**)Cl	[25.8]	(A40)
Aromatic heterocyclic nitrogen	**=N**–	10.9	(A41)
Acyclic sp^2 nitrogen	**=N**–	−1.8	(A42)
Tertiary amine	R$_2$ > **N**–R	−22.2	(A43)
Secondary amine	R–**NH**–R	−5.3	(A44)
Primary amine	R–**NH$_2$**	21.4	(A45)
Azide (2)	R–**N$_3$**	[−23]	(A46)
Tertiary amine N-nitro (19)	R$_2$ > **N**–(NO$_2$)	[**−21**]	(A47)
Fluorine on a ring nitrogen (1)	–N–**F**	[**39.3**]	(A48)
Fluorine on a nitrogen (2)	-N-**F$_2$**	[**39.3**]	(A48)
Diazo nitrogen (1)	**C=N$_2$**	[**9.2**]	(A49)
Nitro group	R–**NO$_2$**	17.7	(A50)
N-nitro (32)	>N–(**NO$_2$**)	**31.3**	(A51)
N-nitroso (3)	>N–**N=O**	[**25.6**]	(A52)
Oxime	**=N–OH**	13.6	(A53)
Azoxy nitrogen (6)	R–N=**N**(→**O**)–R	[6.8]	(A54)
Nitrate ester (16)	R–**ONO$_2$**	[24.4]	(A55)
Nitrile	R–**C≡N**	17.7	(A56)
Isocyanide (1)	R–**NC**	[17.5]	(A57)
Isocyanate (4)	R–**N=C=O**	[23.1]	(A58)
Tertiary amides	R–**C(=O)N** < R$_2$	−11.2	(A59)
Secondary amides	R–**C(=O)NH**–R	1.5	(A60)
Primary amide	R–**CONH$_2$**	27.9	(A61)
N,N-dialkylformamide (3)	**HC(=O)N** < R$_2$	[6.9]	(A62)
N-alkylformamide (3)	**HC(=O)NH**R	[**27.0**]	(A162)
hydrazide (4)	R–**C(=O)NHNH$_2$**	[**26.0**]	(A147)
Iminohydrazide (4)	R–**C(=O)NHN**=CHR	[18.6]	(A159)
Tetra substituted urea (2)	R$_2$ > **NC(=O)N** > R$_2$	[−19.3]	(A63)
1,1,3-Trisubstituted urea (16)	R$_2$ > **NC(=O)NH**–R	**(0)**	(A64)
1,1-Disubstituted urea (2)	R$_2$ > **NC(=O)NH$_2$**	[19.5]	(A65)
1,3-Disubstituted urea (12)	R**NHC(=O)NH**–R	[**−8.1**]	(A66)
Mono substituted urea (24)	R–**NHC(=O)NH$_2$**	**14.1**	(A67)
N,N-disubstituted carbamate (1)	R–**OC(=O)N** < R$_2$	[−23]	(A68)
N-substituted carbamate	R–**OC(=O)NH**–R	7.8	(A69)
Carbamate (3)	R–**OC(=O)NH$_2$**	[**27.1**]	(A70)
Carbamic acid (1)	R–**NHCO$_2$H**	[**11**]	(A178)
Imide (7)	R–**C(=O)NHC(=O)**–R	[10.4]	(A71)
Phosphine (6)	R$_2$ > **P**–R	[−20.7]	(A72)
Phosphine oxide (1)	R$_3$**P=O**	[−32.7]	(A73)
Phosphate ester (3)	(R–**O**)$_4$**P(=O)**	[−10.0]	(A74)
Phosphonate ester	R–**P(=O)**(**O**–R)$_2$	[**−11.4**]	(A75)
Phosphonic acid (1)	R–(**P=O**)(**OH**)$_2$	[−12.1]	(A76)
Phosphinic acid (1)	R$_2$ > (**P=O**)**OH**	[**−12**]	(A173)
Phosphonyl halide (4)	R–**P(=O)**X$_2$,	[4.8]	(A77)
Phosphoramidate ester (1)	(R–**O**)$_2$**P(=O)NH**–R	[−0.7]	(A78)
Phosphorothioate ester (12)	(R–**O**)$_3$**P(=S)**	1.1	(A79)
Phosphorodithioate ester (7)	R–**S**–**P(=S)**(**O**–R)$_2$	−9.6	(A80)
Phosphonothioate ester (3)	R–**P(=S)**(**O**–R)$_2$	[5.2]	(A81)
Phosphoroamidothioate ester (1)	R–**NHP(=S)**(**O**–R)$_2$	[16.0]	(A82)
Phosphoroamidodithioate ester (1)	**NH$_2$P(=S)(S–R)**(**O**–R)	[6.9]	(A83)
Sulfides	R–**S**–R	2.1	(A84)
Disulfides (4)	R–**SS**–R	[9.6]	(A85)
Thiols	R–**SH**	23.0	(A86)
Sulfoxide (5)	R–**S(=O)**–R	[**8.0**]	(A87)
Sulfones (20)	R–**S(=O)$_2$**–R	**0.6**	(A88)
Sulfonate ester (3)	R–**S(=O)$_2$O**–R	[7.3]	(A89)
1,3-Disubstituted thiourea	R–**NHC(=S)NH**–R	**7.8**	(A90)

Table 3B (*Continued*)

Functional groups[a]		Group value (G_k)[b] J/(mol K)	
Tetrasubstituted thiourea (1)	$R_2>\mathbf{NC(=S)N}<R_2$	[−7.2]	(A148)
Isothiourea (1)	$R-\mathbf{S-(C=NH)NH}R$	**[23.8]**	(A160)
S,N,N′-trisubstituted isothiourea (8)	$R-\mathbf{S-(C=NR)NH}R$	**[0.7]**	(A161)
Monosubst thiourea (4)	$R-\mathbf{NHC(=S)NH_2}$	**[30.1]**	(A91)
Thioamide (3)	$R-\mathbf{C(=S)NH_2}$	**[15.0]**	(A92)
N-substituted thioamide (2)	$R-\mathbf{C(=S)NH}R$	**[4.07]**	(A174)
N,N-disubstituted thioamide (4)	$R-\mathbf{C(=S)N}R_2$	[−**13.5**]	(A175)
N,N disubstituted thiocarbamate (1)	$R-\mathbf{S(C=O)N}<R_2$	[5.6]	(A93)
Thiocarbamic ester (5)	$R-\mathbf{(C=O)NH(C=S)O}-R$	**[4.8]**	(A176)
Sulfonic acid (1)	$R-\mathbf{S(=O)_2OH}$	[1.8]	(A145)
N,N-disubstituted sulfonamide (2)	$R-\mathbf{S(=O)_2N}-R_2$	[−11.3]	(A94)
N-substituted sulfonamide (7)	$R-\mathbf{S(=O)_2NH}-R$	**[6.6]**	(A95)
Sulfonamide (10)	$R-\mathbf{S(=O)_2NH_2}$	**[25.2]**	(A96)
N-acyl sulfonamide (1)	$R-\mathbf{S(=O)_2NH(C=O)}-R$	**[11.9]**	(A177)
Sulfonyl chloride (2)	$R-\mathbf{S(=O)_2}Cl$	**[23.4]**	(A157)
Trisubstituted aluminum (2)	$R_3\mathbf{Al}$	[−24.7]	(A97)
Trisubstituted arsenic (6)	$R_3\mathbf{As}$	**[3.1]**	(A98)
Trisubstituted boron (2)	$R_3\mathbf{B}$	[−17.2]	(A99)
Trisubstituted bismuth (1)	$R_3\mathbf{Bi}$	[−14.5]	(A100)
Aryltricarbonyl chromium (2)	$R-\mathbf{Cr(C=O)_3}$	**[20.8]**	(A182)
Trisubstituted gallium (2)	$R_3\mathbf{Ga}$	[−11.3]	(A101)
Tetrasubstituted germanium (12)	$R_4\mathbf{Ge}$	[−35.2]	(A102)
Disubstituted germanium (1)	$R_2\mathbf{GeH_2}$	[−14.7]	(A103)
Disubstituted mercury (1)	$R_2\mathbf{Hg}$	[8.4]	(A104)
Trisubstituted indium (2)	$R_3-\mathbf{In}$	[−19.3]	(A105)
Ferrocenyl iron (9)	$R_2>\mathbf{Fe}$	[−**5**]	(A179)
Tetrasubstituted lead (2)	$R_4-\mathbf{Pb}$	[−30.2]	(A106)
Trisubstituted antimony (1)	$R_3-\mathbf{Sb}$	[−12.7]	(A107)
Disubstituted selenium (2)	$R_2-\mathbf{Se}$	[6.0]	(A108)
Alkyl arsonic acid (3)	$R-\mathbf{(As=O)(OH)_2}$	[−**2.9**]	(A181)
Quaternary silicon	$R_4\mathbf{Si}$	−27.1	(A109)
Quaternary tin (7)	$R_4\mathbf{Sn}$	[−24.2]	(A110)
Disubstituted zinc (3)	$R_2\mathbf{Zn}$	[11.1]	(A111)
Disubstituted telluride (6)	$R_2\mathbf{Te}$	**[5.1]**	(A140)
Trisubstituted germanium (1)	$R_3\mathbf{GeH}$	[−27.8]	(A141)
Disubstituted arsinic acid (16)	$R_2\mathbf{(As=O)OH}$	[−24]	(A142)
Trisubstituted thallium (1)	$R_3\mathbf{Th}$	[1]	(A143)
Disubstituted cadmium (1)	$R_2\mathbf{Cd}$	[−2]	(A144)
Dialkyl ammonium carboxylate (4)	$R-\mathbf{CO_2{}^-\ {}^+NH_2}-R$	**[4.3]**	(A180)

[a] The alphanumerical terms, A1, A2, B2, . . . are a device used to identify each group value in the estimations provided in Table 5 and Table 1A (appendix); groups in bold in column 1 are new; atoms in bold in column 2 define the atoms included in the functional group; group values in bold in column 3 have been changed from earlier versions; refer to the text and Table 5 and Table 1A (appendix) for examples; R refers to any organic fragment that may contain other functional groups unless specified otherwise; X refers to any halogen; units: J mol^{-1} K^{-1}; values in brackets are tentative assignments and are based on the number of entries in parentheses reported in column 1.

[b] All group coefficients; C_k can be assumed to be 1.

An example illustrating the application of this protocol for hydrocarbons can be found in Table 5. Additional examples can be found in Table A1 in the supplementary material.

2.2. *Other cyclic and polycyclic hydrocarbons*

The total phase change entropy of non-benzenoid cyclic hydrocarbons or benzenoid molecules containing non-benzenoid rings is estimated by using Eq. (2). This contribution of the ring can be estimated using Eq. (3) which can be used to estimate $\Delta_0^{T_{\rm fus}}S_{\rm tpce}$ for any parent cycloalkane. The alphanumeric terms (A14) and (A15) are used to identify the intercept and slope associated with the estimation of cyclic hydrocarbons. Other group terms are defined in Table 2.

$$\Delta S_{\rm tpce} = \Delta_0^{T_{\rm fus}}S_{\rm tpce}({\rm ring}) + \Delta_0^{T_{\rm fus}}S_{\rm tpce}(aah) \qquad (2)$$

$$\Delta_0^{T_{\rm fus}}S_{\rm tpce}({\rm ring}) = ({\rm A14}) + ({\rm A15})[N-3], \qquad (3)$$

where N = number of ring atoms and A14 = 33.4, A15 = 3.7 J mol^{-1} K^{-1}.

If the cycloalkane contains carbon atoms other than cyclic secondary sp^3 carbon atoms (cyclic CH$_2$), then adjustments to this equation for the appropriate hybridization and substitution pattern for these groups is provided in Table 2. Polycyclic hydrocarbons are modeled using Eq. (4). Adjustments for the bridgehead carbons and other hybridizations and substitution patterns that may be present in the ring are obtained from Table 2. The contribution of any acyclic hydrocarbon components attached to the ring are modeled as described by Eq. (1) and added to the contribution of the cyclic components.

$$\Delta_0^{T_{\rm fus}}S_{\rm tpce}({\rm ring}) = [({\rm A14})]R + [({\rm A15})][N-3R], \qquad (4)$$

where N = total number of ring atoms; R = number of rings.

Examples can be found in Table 5. Molecules that contain both benzenoid and cyclic carbon atoms such as fluorene require some additional comments. In such cases the ring equation (Eq. (3)) is used to model the non-benzenoid cyclopentadiene ring. The four quaternary benzenoid carbon atoms that are common to the cyclopentadiene ring are treated as cyclic quaternary sp^2 carbon atoms and their contributions are obtained from Table 2. Thus the five-member ring in fluorene is modeled as a tetrasubstituted cyclopentadiene ring. The contributions of the remaining eight tertiary benzenoid carbon atoms making up the remainder of the aromatic ring are obtained from Table 1 and added as additional substituents. In cyclic molecules containing a long chain alkyl group, and modeled using Eq. (2), each heavy atom in the ring is counted as a functional group. Application of group coefficient B2 (Table 1) for consecutive methylene groups will depend on how many other groups are present. For example a group coefficient

Table 4
Adjustments of cyclic functional groups to the contributions of the cyclic hydrocarbon portions of the molecule.

Heteroatoms and functional groups comprising a portion of a ring[a]		Group value (G_k)[b]	
Cyclic ether	*R*–**O**–*R*	1.2	(A112)
Cyclic peroxide (4)	*R*–**OO**–*R*	[27.7]	(A113)
Cyclic ketone	*R*–**C(=O)**–*R*	−1.4	(A114)
Cyclic ester	*R*–**C(=O)O**–*R*	3.1	(A115)
Cyclic carbonate (6)	*R*–**OC(=O)O**–*R*	[1.3]	(A116)
Cyclic anhydride (17)	*R*–**C(=O)–O–C(=O)**–*R*	2.3	(A117)
Cyclic sp^2 nitrogen	*R*=**N**–*R*	0.5	(A118)
Cyclic tertiary amine	*R*$_2$ > **N**–R	−19.3	(A119)
Cyclic hydrazine (2)	*R*$_2$ > **NNH$_2$**	[**21.7**]	(A153)
Cyclic tertiary amine-N-nitro (16)	*R*$_2$ > **N**–(NO2)	[−**20.6**]	(A120)
Cyclic tertiary amine-N-nitroso	*R*$_2$ > **N**–(N=O)	[−**20.6**]	(A120)
Cyclic secondary amine	*R*–**NH**–*R*	2.2	(A121)
Cyclic tertiary amine-N-oxide (10)	*R*–**N(→O)**–*R*	[−22.2]	(A122)
Cyclic azoxy group (3)	*R*=**N(→O)**–*R*	[2.9]	(A123)
Cyclic sec amide	*R*–**C(=O)NH**–*R*	2.7	(A124)
Cyclic tertiary amide	*R*–**C(=O)N <** R,*R*	−21.7	(A125)
Cyclic tertiary amide (12)	R–**C(=O)N** < *R*$_2$	[−**16.7**]	(A146)
N subst cyclic carbamate (3)	*R*–**OC(=O)N**–R*R*	[−5.2]	(A126)
N,N subst cyclic carbamate (22)	R–**OC(=O)N <** *R*$_2$	−**22.2**	(A169)
Cyclic carbamate (2)	*R*–**OC(=O)N**–H*R*	[**15.3**]	(A154)
Cyclic N,N’-disubst urea (2)	R*R* > **NC(=O)N <** R*R*	[−**34.8**]	(A127)
Cyclic N,N-disubst urea (2)	*R*$_2$ > **NC(=O)NH$_2$**	[**0.3**]	(A170)
N-substituted cyclic imide (12)	*R*–**C(=O)N**(R)**C(=O)**–*R*	[−**13.6**]	(A128)
Cyclic imide (9)	*R*–**C(=O)N(H)C(=O)**–*R*	[**2.8**]	(A129)
Cyclic phosphorothioate (1)	*R*–**O–P(=S) < (O**R)(**O***R*)	[−15.6]	(A130)
Cyclic phosphazene (4)	N=**P(**X$_2$**)**–N	[−26.7]	(A155)
Cyclic sulfide	*R*–**S**–*R*	2.9	(A131)
Cyclic disulfide (4)	*R*–**SS**–*R*	[−6.4]	(A132)
Cyclic disulfide S-oxide (2)	*R*–**S(S=O)**–*R*	[**4.0**]	(A133)
Cyclic sulfoxide (1)	*R*–S(**=O)**–*R*	[−**2.2**]	(A134)
Cyclic sulfone (9)	*R*–S**(=O)$_2$**–*R*	[15.1]	(A164)
Cyclic thiocarbonate (1)	*R*–**OC(=O)S**–*R*	[14.3]	(A135)
Cyclic sulfite (1)	*R*–**OS(=O)O**–*R*	[−5.8]	(A150)
Cyclic thioester (1)	*R*–**(C=O)S**–*R*	[**17.0**]	(A167)
Cyclic dithioester (2)	*R*–**(C=S**)**S**–*R*	[11.0]	(A151)
Cyclic sulfate (1)	*R*–**OS(**→**O)$_2$O**–*R*	[0.9]	(A136)
Cyclic N-subst sulphonamide (1)	*R*–**S(**→**O)$_2$NH**–*R*	[−0.4]	(A137)
Cyclic tertiary sulfonamide (3)	*R*–**SO$_2$N**–*R*R	[−27.1]	(A152)
Cyclic carboxyl sulfimide (1)	*R*–**SO$_2$NH–(C=O)**–*R*	[**13.9**]	(A166)
Cyclic thiocarbamate (1)	*R*–**S–(C=O)NH**–*R*	[13.9]	(A138)
Cyclic isothiocarbamate (3)	*R*–**O–(C=S)NH**–*R*	[**2.6**]	A163)
Cyclic dithiocarbamate (1)	*R*–**S–(C=S)NH**–*R*	[**3.8**]	(A165)
Cyclic thiourea (1)	*R*–**NH(C=S)NH**–*R*	[**4.9**]	(A168)
Cyclic isothiourea (1)	*R*–**N=C–(NHR)–S**–*R*	[−**49.7**]	(A171)
Cyclic alkylboronate ester (5)	R–**B < (O***R*)$_2$	[−**54.2**]	(A172)
Cyclic quaternary silicon	R$_2$ > **Si <** *R*$_2$	−34.7	(A139)

[a] The alphanumerical terms, A1, A2, B2, . . . are a device used to identify each group value in the estimations provided in Table 5 and Table 1A (appendix); R refers to any alkyl or aryl group unless specified otherwise; X refers to any halogen; values in brackets are tentative assignments; functional groups in column 1 in bold are new groups; atoms in bold in column 2 define the atoms included in the functional group; group values in bold in column 3 are new values; all group values in this table are to be used with the ring equations (2) or (3); values in brackets are tentative assignments and are based on the number of entries in parentheses reported in column1; the R groups that comprise a portion of the ring structure are designated by italics; values in brackets are tentative assignments.

[b] All group coefficients; C_k can be assumed to be 1.

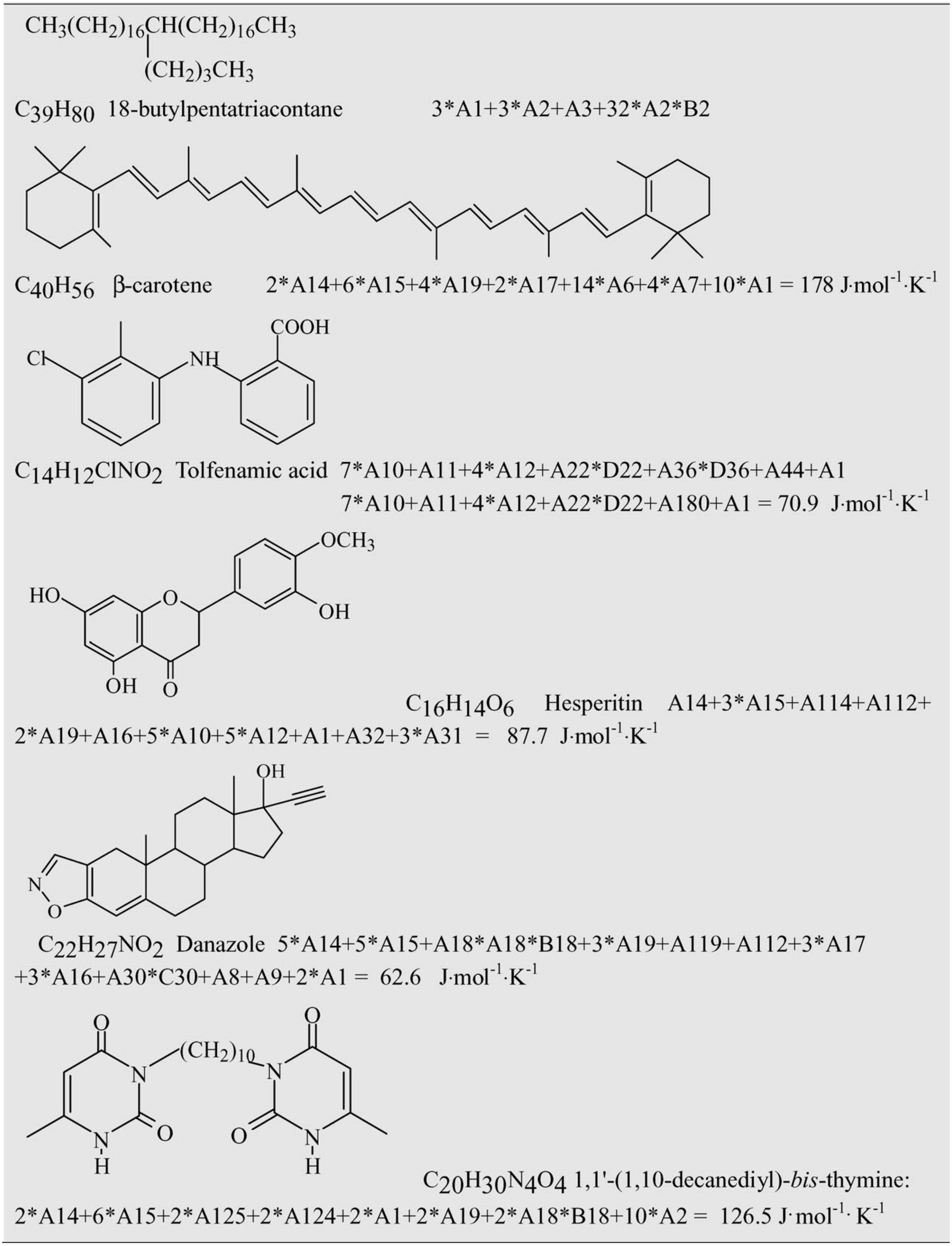
of 1 should be used for n-heptylcyclohexane which contains one CH_3 group, five cyclic CH_2 group$_s$ and one cyclic tertiary CH group, but a value of 1.31 should be used for the methylene groups in n-heptylcyclopentane.

2.3. *Aliphatic and benzenoid aromatic hydrocarbon derivatives*

Estimations involving derivatives of aliphatic and aromatic hydrocarbons, including benzenoid aromatic heterocycles consists of three parts: estimation of the contribution of the hydrocarbon component, the estimation of the contribution of the carbon(s) bearing the functional group(s), and the contribution of the functional group(s). The contribution of the hydrocarbon portion of the molecule is estimated as described above. Hydrocarbon group coefficients (C) are equal to 1.0 or as noted in Table 1. The contribution of the carbon bearing the functional group is also evaluated from Table 1. Acyclic functional groups are defined in Tables 3A and 3B and their contribution to the total phase change entropy is obtained from these tables. The contribution of functional groups listed in Table 3A depends on both the nature of the group, G_k, and the group coefficient, C_k, which depends on the total number of functional groups in the molecule. If there is only one functional group in the molecule, $C_{k(1)} = 1.0$. Otherwise a value C_{kn} is used unless indicated otherwise in Table 3A. Examples illustrating the application of this protocol can be found in Table 5 and in the supplementary material (Table A1).

Fluorine substitution is treated as an exception. The presence of fluorine in a molecule is counted as a single functional group regardless of the number of fluorine atoms present or on their location. Group coefficients for all other functional groups in Table 3A are evaluated on the basis of the total number of functional groups in the molecule as defined in Tables 1–4. For example, a molecule like 2,2,2-trichloroethanol would be considered to contain a total of four functional groups and the group coefficient listed in the last

Table 5
Estimation of $\Delta_0^{T_{\mathrm{fus}}}S_{\mathrm{tpce}}$ for some sample structures.



$CH_3(CH_2)_{16}CH(CH_2)_{16}CH_3$ with $(CH_2)_3CH_3$ on the CH

$C_{39}H_{80}$ 18-butylpentatriacontane 3*A1+3*A2+A3+32*A2*B2

$C_{40}H_{56}$ β-carotene 2*A14+6*A15+4*A19+2*A17+14*A6+4*A7+10*A1 = 178 J·mol^{-1}·K^{-1}

$C_{14}H_{12}ClNO_2$ Tolfenamic acid 7*A10+A11+4*A12+A22*D22+A36*D36+A44+A1
7*A10+A11+4*A12+A22*D22+A180+A1 = 70.9 J·mol^{-1}·K^{-1}

$C_{16}H_{14}O_6$ Hesperitin A14+3*A15+A114+A112+
2*A19+A16+5*A10+5*A12+A1+A32+3*A31 = 87.7 J·mol^{-1}·K^{-1}

$C_{22}H_{27}NO_2$ Danazole 5*A14+5*A15+A18*A18*B18+3*A19+A119+A112+3*A17
+3*A16+A30*C30+A8+A9+2*A1 = 62.6 J·mol^{-1}·K^{-1}

$C_{20}H_{30}N_4O_4$ 1,1'-(1,10-decanediyl)-*bis*-thymine:
2*A14+6*A15+2*A125+2*A124+2*A1+2*A19+2*A18*B18+10*A2 = 126.5 J·mol^{-1}· K^{-1}

column of the table would be used for each respective substituent. 2,2,2-Trifluoroethanol, in contrast, would be considered to contain only two functional groups, resulting in the use of group coefficients identified as B26 and B30 in Table 3A. Examples illustrating this protocol can be found in the supplementary material (Table A1).

The contributions of the functional groups listed in Table 3B are considerably easier to evaluate. These contributions are strictly additive and their contributions do not vary with the degree of substitution. These groups are counted as a single functional group in cases where a molecule contains any of the functional groups listed in Table 3A.

2.4. Cyclic functional groups

Estimations of molecules containing functional groups that form part of a non-benzenoid ring are computed in a manner similar to the estimations for cyclic hydrocarbons. The ring equation (Eqs. (3) or (4)) is first used to model a hydrocarbon ring or rings of similar size and structure. The functional groups that comprise a portion of the ring are added as adjustments to the calculation. Group values for cyclic functional groups can be found in Table 4. All the atoms in bold are included in the functional group but each heavy atom that comprises a part of the ring is counted individually for purposes of determining when to use the group coefficient for a CH_2 group. The group coefficient found in Table 2 for a cyclic tertiary sp^2 carbon is used to compute the contribution of this group whenever a cyclic functional group listed in Table 4 is directly attached to this type of carbon.

2.5. Total phase change entropy and enthalpy estimations

Table 5 provides some examples on the use of the group values listed in Tables 1–4 in estimating the total phase change entropy. Numerical details of each calculation can also be found in the supplementary material (Table A1).

3. Examples

3.1. Aliphatic hydrocarbons: 18-butylpentatriacontane

18-Butylpentatriacontane is estimated as illustrated in Table 5. The molecule contains four groups other than methylene groups. A coefficient of 1.31 is used for the two groups of consecutive methylene groups in the molecule, but a group coefficient of 1 is used for the three methylene groups in the butyl branch.

3.2. Cyclic hydrocarbons: β-carotene

The estimation of β-carotene illustrates the use of the ring equation (2). The two cyclohexyl rings are estimated first followed by adjustments for the four quaternary sp^2 carbons, the four cyclic quaternary sp^2 carbons and the two cyclic quaternary sp^3 carbon atoms. Estimation of the 14 tertiary sp^2 carbons, the four quaternary sp^2 carbons and the 10 methyl groups complete the estimation.

3.3. Aliphatic and aromatic hydrocarbon derivatives: tolfenamic acid

The estimation of tolfenamic acid is an example of an estimation when the contribution of two of the functional groups present depends on the total number of functional groups. The estimation consists of the addition of the contributions of the seven tertiary aromatic carbons, a quaternary aromatic carbon with an alkyl substituent, four quaternary aromatic carbons that can conjugate with the functional group attached, the contribution of the secondary amine, and the chlorine and carboxylic acid groups whose value does depend on the number of functional groups present.

In an alternative estimation, tolfenamic acid can also be viewed as a dipolar ion. A group value for a secondary ammonium carboxylate salt is available in the tables, A180. The use of this group in place of the secondary amine and carboxylic acid functional groups is also provided in Table 5. A numerical value of 50.3 is estimated for $\Delta_0^{T_{\text{fus}}} S_{\text{tpce}}$ treating tolfenamic acid as a dipolar ion and a value of 70.9 $\text{J mol}^{-1}\,\text{K}^{-1}$ is estimated treating this compound as an amino acid. These values can be compared to an experimental value for ΔS_{fus} calculated as 84.9 $\text{J mol}^{-1}\,\text{K}^{-1}$. The X-ray crystal structure is consistent with the amino acid structure [4].

3.4. Cyclic hydrocarbon derivatives: Danazole; 1,1′-(1,10-decanediyl)-bis-thymine

Danazole is an example of a steroidal compound containing a total of 5 rings and 20 ring atoms. The use of Eq. (4) provides the contribution a hydrocarbon with this number of rings and carbon atoms would contribute, once the cyclic tertiary sp^2 and sp^3 and quaternary sp^2 and sp^3 adjustments to the rings are included. Since the molecule however contains heteroatoms, a cyclic ether and cyclic sp^2 nitrogen, these adjustments are included by the appropriate cyclic function group contribution given in Table 4. The contribution of the acyclic components attached to the ring conclude the estimation.

1,1′-(1,10-Decanediyl)-*bis*-thymine is an example of an estimation where the heterocyclic ring is broken down into two independent groups, a cyclic tertiary (A125) and cyclic secondary amide (A124). Analysis of the ring as a cyclic N-substituted imide (A128) and cyclic secondary amine (A121) is an alternative but less desirable estimation since a cyclic secondary amine does not mimic the unsubstituted amide nitrogen of uracil very well. Following the use of the ring equation for the two rings, the estimation is adjusted for the four amide functions and the tertiary and quaternary sp^2 carbons. Since the tertiary sp^2 carbons are attached to functional groups, the group coefficient B18 is also used. The contribution of the 10 consecutive methylene groups conclude the estimation. Since each ring atom in a cyclic structure is counted as a group, the number of consecutive methylene groups does not exceed the sum of the remaining groups (12). Therefore the group coefficient for a methylene group is not used. In contrast, in an acyclic molecule, the entire amide functional group would be counted as a single functional group.

4. Results and discussion

4.1. Evaluation of new group values

New group values have been assigned by allowing the new group value to vary until the value of the following function:

$$\sum \left[\frac{\Delta_0^{T_{\text{fus}}} S_{\text{tpce}}(\text{exp}) - \Delta_0^{T_{\text{fus}}} S_{\text{tpce}}(\text{calc})}{\Delta_0^{T_{\text{fus}}} S_{\text{tpce}}(\text{exp}) + \Delta_0^{T_{\text{fus}}} S_{\text{tpce}}(\text{calc})} \right]^2 \qquad (4)$$

was minimized. New values are listed in bold in column 1 of Tables 3 and 4. All the compounds used in generating these new group values are included in the supplementary material. A few tentative group values reported earlier have also been changed due to additional data. These changes can be identified by noting that the group value is in bold in column 3 but the functional group in column 1 of Tables 1, 3 and 4 is not. The total phase change enthalpies used in modifying these values include values reported previously but are not included in this update.

4.2. Estimation of total phase change enthalpy

The total phase change entropy, $\Delta_0^{T_{\text{fus}}} S_{\text{tpce}}$, in most cases provides a good estimate of the entropy of fusion, $\Delta_{\text{fus}} S_{\text{m}}$ (T_{fus}). If there are no additional solid phase transitions then $\Delta_0^{T_{\text{fus}}} S_{\text{tpce}}$ becomes numerically equal to $\Delta_{\text{fus}} S_{\text{m}}$ (T_{fus}). From the experimental melting temperature and $\Delta_{\text{fus}} S_{\text{m}}$ (T_{fus}), it is possible to approximate the total phase change enthalpy, $\Delta_0^{T_{\text{fus}}} H_{\text{tpce}}$. Similarly, if there are no additional phase transitions, then the total phase change enthalpy,

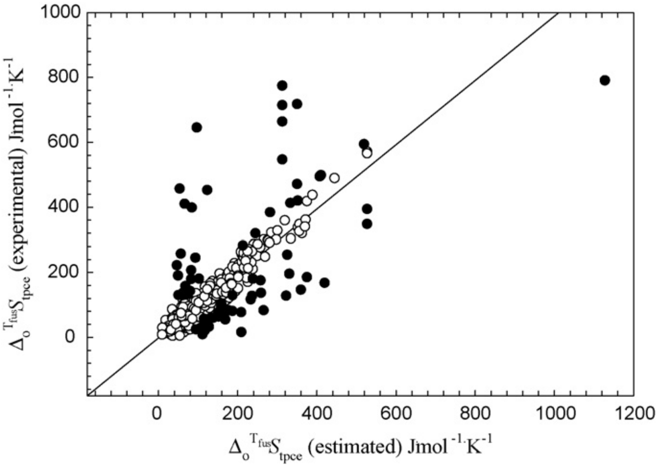


Fig. 1. A comparison of calculated and experimental total phase change entropies. The solid circles represent 73 data entries that exceeded 3 standard deviations and were not used in generating the statistics or the equation of the line through the data which consisted of 1016 entries. The equation of line obtained by a linear regression analysis is given by: $\Delta_0^{T_{\mathrm{fus}}} S_{\mathrm{tpce}}$ (experimental) = (0.991 ± 0.01) $\Delta_0^{T_{\mathrm{fus}}} S_{\mathrm{tpce}}$ (estimated) – (1.60 ± 18.7); r^2 = 0.9003.

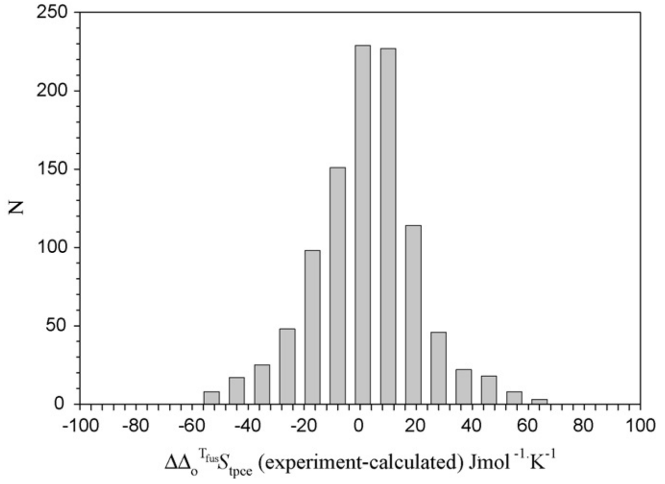


Fig. 2. A histogram illustrating the distribution of errors in $\Delta_0^{T_{\mathrm{fus}}} S_{\mathrm{tpce}}$ of 1016 entries.

$\Delta_0^{T_{\mathrm{fus}}} H_{\mathrm{tpce}}$, becomes numerically equivalent to the fusion enthalpy, $\Delta_{\mathrm{fus}} S_{\mathrm{m}}$ (T_{fus}). Compounds whose liquid phase is not isotropic at the melting point are not modeled properly by these estimations. Those compounds forming liquid crystal or cholesteric phases as well amphiphilic compounds are currently overestimated by these parameters. 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 anisotropic liquid behavior. Details regarding the entropies associated with the phase transitions of liquid crystals and amphiphilic compounds have previously been reported [2,3].

4.3. Statistics of the correlations

Fusion enthalpies and entropies of approximately 1000 compounds are reported in this compendium. Many measurements are on new compounds obtained from the pharmaceutical literature and as such have fairly complex structures. Some measurements are new measurement on compounds reported in earlier versions of this work. Since most of the group values reported in Tables 1–4 remain unchanged from previous versions, we have used the standard deviation previously reported for grounds of either including or excluding compounds in the statistics reported below. The standard deviation between experiment and calculation previously reported was ±18.6 J mol^{-1} K^{-1} for 547 compounds. Compounds with differences between experimental and calculated values greater than approximately 60 J mol^{-1} K^{-1} have not been included. This excluded 73 out of 1089 measurements. In a few additional measurements, sufficient information to calculate the total phase change entropy was not available. These entries and cases where decomposition was reported have also not been included in the statistics. The standard deviation associated with 1016 measurements included in the estimations, ±18.5 J mol^{-1} K^{-1}, is very similar to what was previously reported,

Fig. 1 illustrates the correlation obtained when experimental total phase change entropies are compared to those estimated using the protocol described above for compounds melting directly to an isotropic liquid. The solid circles represent values with errors greater than 3 standard deviations. These values were not included in the statistics reported. The equation of line obtained by a linear regression analysis is given by

$$\Delta_0^{T_{\mathrm{fus}}} S_{\mathrm{tpce}}\ (\text{experimental}) = (0.991 \pm 0.01)\Delta_0^{T_{\mathrm{fus}}} S_{\mathrm{tpce}}\ (\text{estimated}) - (1.60 \pm 18.7); \quad r^2 = 0.9003. \qquad (5)$$

Fig. 2 illustrates the distribution of errors in $\Delta_0^{T_{\mathrm{fus}}} S_{\mathrm{tpce}}$ of the 1016 compounds included. The estimations do not appear to be significantly biased in either direction.

Multiplication of the estimated total phase change entropy by the fusion temperature results in an estimation of the total phase change enthalpy, which for most compounds is equivalent to the fusion enthalpy. These results are shown in Fig. 3 which compares the experimental total phase change enthalpies to the value estimated. The equation of the line obtained by a linear regression analysis of the correlation is given by Eq. (6):

$$\Delta_0^{T_{\mathrm{fus}}} H_{\mathrm{tpce}}\ (\text{experimental}) = (0.972 \pm 0.01)\Delta_0^{T_{\mathrm{fus}}} H_{\mathrm{tpce}}\ (\text{estimated}) - (0.2 \pm 7.6); \quad r^2 = 0.8754 \qquad (6)$$

The distribution of errors in total phase change enthalpy is illustrated in Fig. 4. As might be expected from the results reported in

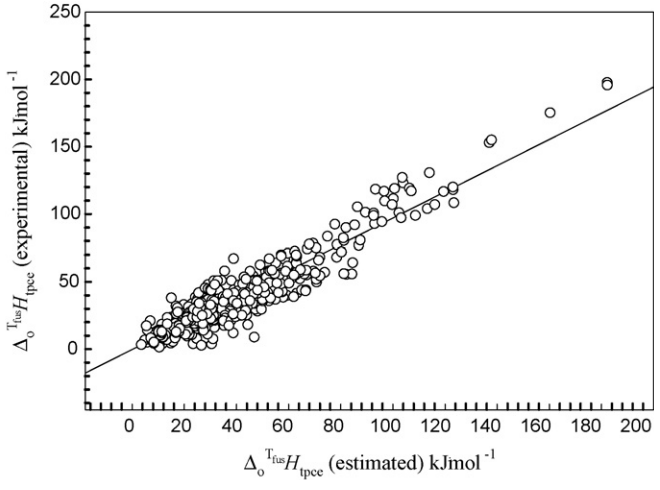


Fig. 3. A comparison of experimental and estimated total phase change enthalpies. The data consisted of 1016 entries. The equation of line obtained by a linear regression analysis is given by: $\Delta_0^{T_{\mathrm{fus}}} H_{\mathrm{tpce}}$ (experimental) = (0.973 ± 0.01) $\Delta_0^{T_{\mathrm{fus}}} H_{\mathrm{tpce}}$ (estimated) – (0.2 ± 7.6); r^2 = 0.8754.

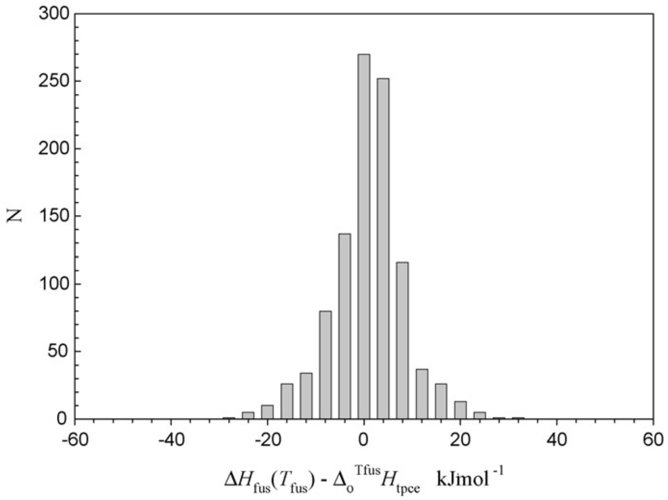


Fig. 4. A histogram illustrating the distribution of errors between experimental fusion enthalpy or total phase change enthalpy and estimated total phase change enthalpy of 1016 entries.

Fig. 2, the distribution of errors in the total phase change enthalpy also does not appear to be biased in either direction.

5. Conclusion

Literature fusion enthalpies for over a thousand compounds are reported along with a group estimation protocol used to estimate total phase change entropies. A total of 27 new group values to estimate total phase change entropies are assigned and 31 values previously assigned as tentative have been modified due to an influx of new data. The standard deviations associated with the new correlations are very similar to those obtained previously, $\pm 18.5\,\mathrm{J\,mol^{-1}\,K^{-1}}$ for total phase change entropy and $\pm 7.6\,\mathrm{kJ\,mol^{-1}}$ for total phase change enthalpy.

Appendix A. Supplementary data

Detailed evaluations of most compounds reported in this compendium can be found in Table A1. In addition to the reported enthalpies and entropies and literature references associated with each entry (Table A2), estimated values for both of these properties are included as well as the group method calculation used for the estimation. As noted in the tables, each group value has associated with it an alphanumeric term that can be used to identify the value used in each calculation. A few additional comments are also included for some individual entries. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tca.2009.05.008.

References

[1] J.S. Chickos, W.E. Acree Jr., J.F. Liebman, J. Phys. Chem. Ref. Data 28 (1999) 1535–1673.
[2] J.S. Chickos, W.E. Acree Jr., Thermochim. Acta 395 (2003) 59–113.
[3] W.E. Acree Jr., J.S. Chickos, J. Phys. Chem. Ref. Data 35 (2006) 1051–1330.
[4] K.V. Anderson, S. Larsen, B. Alhede, N. Getting, O. Buchardt, J. Chem. Soc., Perkin Trans. 2 (1989) 1443–1447.