Enthalpies of Combustion, Formation, Vaporization and Sublimation of Organics

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Earlier (Cardozo, 1986), a method was developed to estimate the enthalpy of combustion of a wide variety of organic compounds. The method, based on simple relationships for *n*-alkane combustion corrected for functional groups and branching, has been shown to apply to gaseous, liquid and solid compounds with errors less than 1%. In addition, the enthalpy thus obtained can be converted to a standard enthalpy of formation. This method compares favorably with the best estimation techniques available for the property.

In this note, a more refined set of group and branching corrections is given that makes it possible to estimate the standard enthalpies of combustion, formation, vaporization and sublimation with one simple method. Furthermore, an indicative method is given to convert the standard enthalpy of vaporization to the value at the normal boiling point.

The results, Table 1, are accurate enough for chemical engineering calculations to a large extent, except for the enthalpy of sublimation that are inherently inaccurate, as will be explained later. A detailed set of examples of estimations is given in Appendices 1 and 2.

Enthalpy of Combustion

The concept to estimate standard enthalpies of combustion is the same as described earlier (Cardozo, 1986), which is based on the determination of an equivalent *n*-alkane chain length N defined as:

$$N = \mathrm{C} + \sum_i \Delta N_i \qquad (1)$$

Here, C is the total number of carbon atoms in the molecule, while ΔN_i values are correction factors for functional groups and branching as given in Table 2 depending on whether the compound is in the gaseous (g), liquid (l) or solid (s) state.

With values of ΔN_i for the compound in question, N can

Table 1. Summary of Results

Property	Physical State	Range of C	Range of Property (kJ/mol)	Std. Dev. Calc. Exp. (kJ/mol)	Std. Dev. Calc. Exp. (%)	No. of Datum-Points Tested
Std. Enthalpy of Combustion (ΔH_c°)	Gaseous	$1 \rightarrow 32$	$-3{,}500 \rightarrow -1{,}000$	20	1.1	42
	Liquid	$1 \rightarrow 32$	$-19{,}000 \rightarrow -1{,}000$	15	0.5	772
	Solid	$2 \rightarrow 69$	$-41{,}000 \rightarrow -1{,}000$	19	0.3	389
Std. Enthalpy of Formation (ΔH_f°)	Gaseous	$1 \rightarrow 32$	$-4{,}600 \rightarrow +330$	4.8	0.5	1,206
	Liquid	$1 \rightarrow 32$	$-4{,}700 \rightarrow +290$	6.2	0.6	1,119
	Solid	$2 \rightarrow 69$	$-5{,}500 \rightarrow +520$	13	2.4	518
Std. Enthalpy of Vaporiz. of Nonpolar Liquids (ΔH_v°)*		$1 \rightarrow 32$	$15 \rightarrow 125$	1.6	4.3	556
Enthalpy of Vaporiz. at Normal Boiling Point of Nonpolar Liquids (ΔH_{vb})*		$1 \rightarrow 32$	$15 \rightarrow 120$	2.1	5.9	576
Std. Enthalpy of Sublimation (ΔH_s°)		$3 \rightarrow 32$	$70 \rightarrow 275$	15	11	115

*Usually debye 0 – 2.5

Table 2. Correction Factors for the Enthalpy of Combustion

A	Gas	$\Delta H_c^\circ = -198.435 - 614.924\, N_g$ kJ/mol	(1.7)
	Liquid	$\Delta H_c^\circ = -195.837 - 610.080\, N_l$ kJ/mol	(1.7)
	Solid	$\Delta H_c^\circ = -206.086 - 606.375\, N_s$ kJ/mol	(2.10)

		per	ΔN_i Gas	ΔN_i Liquid	ΔN_i Solid	Remark, 1
B1	Carbon-to-carbon bond, 2-methyl	bond	-0.012	-0.009	-0.009	(1.23)
B2	*Ibid.*, *i*-methyl ($i \neq 2$)	bond	-0.007	-0.004	-0.004	(1.39)
B3	*Ibid.*, 2-2-methyl	bond	-0.014	-0.011	-0.011	2,(1.27)
B4	*Ibid.*, *i*-*i*-methyl ($i \neq 2$)	bond	-0.010	-0.006	-0.006	2
B5	*Ibid.*, ethyl, as methyl but additional	bond	+0.005	+0.005	+0.005	
B6	*Ibid.*, others, as methyl but additional	bond	-0.006	-0.005	-0.005	
B7	Carbon-to-carbon double bond, 2-methylene	double bond	-0.214	-0.213	–	(1.17)
B8	*Ibid.*, 3-methylene	double bond	-0.208	-0.208	–	
B9	Single carbon-to-cyclic carbon bond, any length	bond	-0.018	-0.015	-0.010	3,(1.21)
B10	Additional correction for two branches per molecule	–	+0.001	+0.001	+0.001	(1.26)
B11	*Ibid.*, for three branches	–	+0.014	+0.012	+0.010	(1.31)
B12	*Ibid.*, for four branches	–	+0.034	+0.024	+0.020	4
C1	1-Alkenes	double bond	-0.189	-0.189	-0.189	(1.3)
C2	i-Alkenes ($i \neq 1$)	double bond	-0.206	-0.208	-0.218	(1.12)
C3	Additional correction for a vicinal pair of multiple C-C bonds	–	+0.083	+0.074	–	
C4	*Ibid.*, for conjugated multiple C-C bonds	–	-0.029	-0.026	-0.026	5,(1.13)
C5	*Ibid.*, for cisconfiguration	–	+0.004	+0.003	+0.003	6,(1.30)
C6	*Ibid.*, for transconfiguration	–	-0.003	-0.002	-0.002	6,(1.45)
D1	1-Alkynes	triple bond	-0.314	-0.318	-0.320	(1.13)
D2	*i*-Alkynes ($i \neq 1$)	triple bond	-0.341	-0.348	-0.350	(1.40)
E1	Cyclopropanes	–	-0.10	-0.10	–	7
E2	Cyclobutanes	–	-0.15	-0.15	–	7,(1.2)
E3	Cyclopentanes	–	-0.274	-0.277	-0.25	7,(1.30)
E4	Cyclohexanes	–	-0.315	-0.320	-0.29	7,(1.44)
E5	Cycloheptanes	–	-0.284	-0.289	–	7
E6	Cyclooctanes	–	-0.27	-0.27	–	7
E7	Spiroalkanes ($C^* \geqq 8$)	–	-0.635	-0.639	–	7,(1.42)
F1	Benzenes	–	-1.169	-1.182	-1.182	7,(1.18)
F2	Additional correction for orthoconfiguration	–	+0.003	-0.004	-0.004	6,(1.18)
F3	*Ibid.*, for metaconfiguration	–	-0.001	-0.007	-0.007	6
F4	*Ibid.*, for paraconfiguration	–	0	-0.006	-0.006	6,(1.18)
G1	α-naphthalenes	–	-2.103	-2.126	-2.126	7,(2.5)
G2	β-naphthalenes	–	-2.114	-2.129	-2.130	7
G3	Other linear polynuclear aromatic hydrocarbons	–	+0.216-0.2316C*	+0.200-0.2314C*	+0.238-0.2367C*	(2.8)
G4	Nonlinear polynuclear aromatic hydrocarbons	–	-0.003-0.2197C*	–	-0.069-0.2184C*	
G5	Perhydrolinear polynuclear aromatic hydrocarbons	–	+0.206-0.0872C*	+0.193-0.0855C*	+0.242-0.0870C*	
H1	Alcohols, primary	-OH	-0.245	-0.290	-0.303	(1.14)
H2	*Ibid.*, aliphatic/alicyclic, secondary	-OH	-0.274	-0.318	-0.320	(1.15)
H3	*Ibid.*, aliphatic, tertiary	-OH	-0.290	-0.334	-0.338	
H4	*Ibid.*, aromatic	-OH	-0.290	-0.331	-0.352	(1.18)
H5	*Ibid.*, aromatic, tertiary	-OH	-0.324	-0.363	–	
I	Aldehydes	=0	-0.522	-0.544	–	(1.3)
J1	Ketones, aliphatic/cyclic	=0	-0.576	-0.598	-0.60	(1.11)
J2	Quinones	(=0, =0)	–	–	$-0.290 - 0.2854\, C^* + 0.00162 (C^*)^2$	(1.41)
K1	Carboxylic acids, first	(=O, -OH)	-0.961	-1.022	-1.036	(1.4)
K2	*Ibid.*, second	(=O, -OH)	-0.95	-1.02	-1.027	
K3	*Ibid.*, third	(=O, -OH)	–	–	-0.96	
L1	Anhydrides, aliphatic	(=O, -O, =O)	-1.547	-1.593	-1.62	
L2	*Ibid.*, aromatic	(=O, -O, =O)	–	–	-1.62	

Table 2 (Continued)

		per	ΔN_i Gas	ΔN_i Liquid	ΔN_i Solid	Remark, 1
M1	Esters, first	$(=O, -O-)$	−0.924	−0.941	−	(1.8)
M2	*Ibid.*, second	$(=O, -O-)$	−0.877	−0.881	−	
M3	*Ibid.*, glyceryl, mono	$(=O, -O-)$	−	−	−0.916	8
M4	*Ibid.*, glyceryl, di/tri	$(=O, -O-)$	−	−	−0.877	8,(1.45)
M5	Additional correction for methyl esters	−	+0.026	+0.013	−	(1.17)
M6	*Ibid.*, for esters of formic acid	−	+0.057	+0.046	−	
M7	*Ibid.*, for esters of acetic acid	−	+0.004	−0.009	−	(1.8)
M8	*Ibid.*, for esters with conjugated C=C and C=0 bonds	−	+0.023	+0.020	−	
N	Lactones	−	−	−1.14	−1.23	7,(1.14)
01	Ethers	$-0-$	−0.204	−0.214	−0.256	(1.25)
02	Additional correction for methyl ethers	−	+0.022	+0.020	+0.015	(1.25)
03	*Ibid.*, for aromatic ethers	−	−0.041	−0.045	−	(1.25)
P1	Amines, aliphatic, mono, first	$-NH_2$	+0.253	+0.233	+0.22	(1.4)
P2	*Ibid.*, aliphatic, mono, second	$-NH_2$	+0.220	+0.201	−	
P3	*Ibid.*, aliphatic, di, first	$=NH$	+0.280	+0.268	−	
P4	*Ibid.*, aliphatic, tri, first	$\equiv N$	+0.30	+0.30	+0.316	(1.9)
P5	*Ibid.*, alicyclic, mono, first	$-NH_2$	+0.223	+0.206	+0.17	(1.28)
P6	*Ibid.*, aromatic, mono, first	$-NH_2$	+0.204	+0.177	+0.168	(1.39)
P7	*Ibid.*, aromatic, di, first	$=NH$	+0.223	+0.190	+0.19	
P8	*Ibid.*, aromatic, tri, first	$\equiv N$	+0.257	+0.247	−	
P9	Additional correction for methyl amines	−	+0.012	+0.008	−	
Q1	Amides, first	$(=0, -NH_2)$	−0.444	−0.524	−0.543	(2.4)
Q2	*Ibid.*, second	$(=0, -NH_2)$	−	−	−0.561	(1.6)
R	Anilides	$(=0, =NH)$	−	−	−0.49	(1.38)
S	Piperidines	−	−	−0.057	−	7
T1	Pyridines	−	−0.912	−0.942	−0.997	7,(1.22)
T2	Additional correction for α-pyridines	−	−0.007	−0.002	−0.002	
T3	*Ibid.*, for β- or γ-pyridines	−	−0.005	−0.004	−0.004	(1.22)
U	Quinolines	−	−1.847	−1.885	−	7
V	Tetrazoles	−	−	−	+0.097	7,(1.28)
W	Pyrroles	−	−0.60	−0.65	−0.69	7
X	Amino acids	−	−	−	Additional −0.043	9,(1.4)
Y	Dipeptides	−	−	−	Σ amino acids +0.44	9,(1.39)
Z	Diketopiperazines	−	−	−	Σ amino acids +0.59	9
AA	Lactams	−	−	−	−0.80	7
BB1	1-Nitro, aliphatic, first	$-NO_2$	−0.226	−0.272	−	
BB2	*i*-Nitro ($i \neq 1$), aliphatic, first	$-NO_2$	−0.256	−0.295	−0.304	(1.16)
BB3	Nitro, aromatic, first	$-NO_2$	−0.225	−0.251	−0.285	(1.18)
BB4	*Ibid.*, second	$-NO_2$	−	−	−0.215	(1.18)
BB5	*Ibid.*, third	$-NO_2$	−	−	−0.16	
CC1	Nitriles, aliphatic	$\equiv N$	−0.334	−0.362	−	(1.5)
CC2	*Ibid.*, aromatic	$\equiv N$	−0.317	−0.344	−	
DD	Nitrates	$-NO_3$	−0.31	−0.35	−	
EE1	Sulfides	$-S-$	+0.547	+0.533	−	(1.24)
EE2	Additional correction for methyl sulfides	−	+0.004	+0.003	−	(1.24)
FF1	Disulphides	$-S-S-$	+1.050	+1.022	−	(1.33)
FF2	Additional correction for methyl disulphides	−	+0.015	+0.009	−	
GG1	Thiols, primary, first	$-SH$	+0.544	+0.525	+0.516	
GG2	*Ibid.*, primary, second	$-SH$	+0.546	+0.520	−	
GG3	*Ibid.*, secondary, first	$-SH$	+0.531	+0.515	−	
GG4	*Ibid.*, tertiary, first	$-SH$	+0.522	+0.509	−	(1.23)
HH	Thiophenes	−	−0.305	−0.331	−	7,(1.21)
II	Thiaalicyclic compounds, additional correction to E values	$-S-$	+0.53	+0.50	−	7,(1.10)
JJ1	Sulfones, aliphatic	$-SO_2$	−0.020	−0.10	−0.10	(2.6)
JJ2	*Ibid.*, aromatic	$-SO_2$	−0.012	−0.05	−0.05	
KK	Sulfites, aliphatic	$-SO_3$	$-0.10-0.04C+3.34.10^{-3}(C)^2$	$-0.15-0.04C+3.25(C)^2$		

Table 2 (Continued)

		per	ΔN_i Gas	ΔN_i Liquid	ΔN_i Solid	Remark, 1
	Sulfates, aliphatic	$-SO_4$	$-0.42-0.04C+3.29.10^{-3}(C)^2$	$-0.48-0.04C+3.29.10^{-3}(C)^2$		
MM1	1-Fluoro, aliphatic, first	$-F$	-0.24	-0.26	-0.27	
MM2	*i*-Fluoro ($i \neq 1$), aliphatic, first	$-F$	-0.26	-0.28	-0.29	
MM3	Fluoro, aromatic, first	$-F$	-0.264	-0.265	–	
MM4	Perfluoro, aliphatic	$\Sigma(-F)$	$-0.1884-0.26162F^*$	$-0.2063-0.26242F^*$	–	10
MM5	*Ibid.*, alicyclic	$\Sigma(-F)$	$-0.0027-0.26882F^*$	$-0.0090-0.27145F^*$	–	10,(1.2)
MM6	*Ibid.*, aromatic	$\Sigma(-F)$	$-0.3176-0.17900F^*$	$-0.3172-0.18025F^*$	–	10
NN1	1-Chloro, aliphatic	$-Cl$	-0.287	-0.307	-0.305	(1.1)
NN2	*i*-Chloro ($i \neq 1$), aliphatic	$-Cl$	-0.309	-0.328	–	
NN3	Additional correction for two chloro-atoms per molecule, aliphatic	–	$+0.014$	$+0.018$	–	
NN4	Chloro, aromatic, first	$-Cl$	-0.294	-0.308	-0.306	(2.2)
NN5	*Ibid.*, second	$-Cl$	-0.282	-0.291	-0.295	
NN6	Additional correction for $>C=C-Cl$ configuration, aliphatic	–	$+0.021$	$+0.028$	–	(1.1)
001	1-Bromo, aliphatic	$-Br$	-0.303	-0.329	–	
002	*i*-Bromo ($i \neq 1$), aliphatic	$-Br$	-0.323	-0.346	–	
003	Additional correction for two bromo-atoms per molecule, aliphatic	–	$+0.009$	$+0.010$	–	
004	Bromo, aromatic, first	$-Br$	-0.29	-0.31	–	(1.19)
005	*Ibid.*, second	$-Br$	-0.28	-0.28	–	
PP1	1-Iodo, aliphatic, first	$-I$	-0.312	-0.345	–	
PP2	*i*-Iodo ($i \neq 1$), aliphatic, first	$-I$	-0.339	-0.369	–	
PP3	Iodo, alicyclic, first	$-I$	-0.339	-0.369	–	
PP4	Iodo, aromatic, first	$-I$	-0.305	-0.323	-0.323	
QQ1	Monosaccharides	Furanose	–	–	-0.558	F,11
QQ2	*Ibid.*	Pyranose	–	–	-0.551	F,11
RR1	Di- and oligosaccharides	Furanose	–	–	-0.54	11,(1.37)
RR2	*Ibid.*	Pyranose	–	–	-0.514	11,(1.37)

NOTE:

- The basis for calculation of N always is formed by counting the total number of carbon atoms C of the molecule in question, starting with the longest chain of single-bonded ones; 2-Methyl-1,3-butadiene [compound 20, Appendix 1, indicated as (1.20)] is calculated as 2-methylene-3-butene.
- For compounds with one or more rings, the ring-forming carbon atoms count in the determination of C plus a specific correction for the structure, such as (1.21).
- In several cases, the number of ring-forming carbon atoms C^* determine the value of ΔN_i such as (2.8) with $C^*=14$. For a compound such as *i*-ethylanthracene, $C^*=14$ and $C=16$.
- The limits of applicability for calculation of N are given at each correction factor. Without such indication, the factor may be taken as many times as necessary and/or for aliphatic, aromatic. . . compounds; the factors Q1 and Q2 indicate that all molecules with maximal two amide groups are included in this work.
- In most cases ΔN_i is given with three decimal points or as an equation corresponding to three such points, indicating an accuracy of prediction of 2 kJ/mol. When only two decimal points are given, this indicates either a lack of sufficient data (four or less) or an inconsistency of the data available.
- In general, the number of corrections should not exceed C.

Specific Remarks:

1. The numbers between brackets refer to examples in Appendices 1 and 2.
2. The factor should be applied per bond.
3. The factor counts double for two rings directly bound together.
4. For more than four carbon-to-carbon branches per molecule, an indicative value for the correction factor can be calculated as $\Delta N_i(g) = -0.033+0.017n$, $\Delta N_i(l) = -0.022+0.012n$ and $\Delta N_i(s) = -0.020+0.010n$, where n = number of branches.
5. The factor also can be used for conjugated $C=C$ and $C=O$ bonds, with exception of esters, see M8.
6. The factor is of general nature and can be used for all compounds with the indicated structure.
7. The factor applies to the ring structure with ring-forming carbon atoms counting for determination of C. Functional groups, connected to a ring-forming carbon atom, are taken as secondary groups.
8. Corrections M3 and M4 determine N once (M3) for monoglyceryl esters, and 2 × M4 for diglyceryl esters and 3 × M4 for triglyceryl esters.
9. The correction for amino acids is calculated by the normal procedure plus an additional constant equal to -0.043. For amino acid derivatives, corrections consist of the correction factors of the basic amino acids plus additional structural corrections as indicated.
10. For perfluoro compounds, the total number of fluoro atoms F^* is taken to calculate ΔN_i.
11. The oxygen bridge is considered as an ether bond.

be found from Eq. 1 and the standard enthalpy of combustion ΔH_c° from Eqs. 2 to 4. Here, ΔH_c° is defined as the difference between the enthalpy of a compound and that of its products of combustion in the gaseous state, all at the standard state of 298.15 K and 1.01×10^5 Pa. The products of combustion are $H_2O(g)$, CO_2, SO_2, N_2, and HX (g) with X = halogen

$$\Delta H_c^\circ(g) = -198.435 - 614.924\ N_g\ (\mathrm{kJ/mol}) \quad (2)$$

$$\Delta H_c^\circ(\mathrm{l}) = -195.837 - 610.080\ N_l\ (\mathrm{kJ/mol}) \quad (3)$$

$$\Delta H_c^\circ(s) = -206.086 - 606.375\ N_s\ (\mathrm{kJ/mol}) \quad (4)$$

Although the enthalpy of melting, at the normal melting point, is not an additive property, the error made by neglecting this fact is small and is within the limits of the method proposed here to estimate values for the solid state.

Enthalpy of Formation

The method described before can also be used to estimate the enthalpy of formation ΔH_f° (kJ/mol) of a compound in the gaseous, liquid or solid standard state, 298.15 K and 1.01×10^5 Pa. The property is calculated from Eq. 5, in which the letters $C, H, F, \ldots$ stand for the numbers of atoms per molecule and X = any halogen atom. The numerical values given in Eq. 5—the standard enthalpies of formation of the combustion products—are mean values from the major databanks used

$$\begin{aligned}\Delta H_f^\circ = &-393.65\ \mathrm{C} - 241.90\ (H - X)/2 \\ &-272.32\ F - 92.34\ \mathrm{Cl} - 36.33\mathrm{Br} \\ &+ 26.36\ \mathrm{I} - 296.95\ \mathrm{S} - \Delta H_c^\circ\ (\mathrm{kJ/mol}) \quad (5)\end{aligned}$$

Enthalpy of Vaporization

The third property of organic compounds which can be estimated with Eqs. 2 and 3 and the group corrections of Table 2, is the standard enthalpy of vaporization ΔH_v°, 298.15 K and 1.01×10^5 Pa. This property is the difference between the standard enthalpies of combustion (l) and (g)

$$\Delta H_v^\circ = 2.598 + 614.924 N_g - 610.080 N_l\ (\mathrm{kJ/mol}) \quad (6)$$

For practical chemical engineering purposes, it is often necessary to estimate the enthalpy of vaporization ΔH_{vb}, at the normal boiling point, T_b (K) and 1.01×10^5 Pa. Many methods are known that relate to the enthalpy of vaporization and temperature. With a good fit, Majer and Svoboda (1985) apply a two-parameter relation proposed by Tékăc et al. (1981)

$$\Delta H_v = (1 - T_r)^\beta \times e^{-\beta T_r}\ (\mathrm{kJ/mol}) \quad (7)$$

in which T_r is the reduced temperature. For some compounds, mostly polar, a three-parameter version of Eq. 7 is applied

$$\Delta H_v = (1 - T_r)^\beta \times e^{-\alpha T_r}\ (\mathrm{kJ/mol}) \quad (8)$$

In this note, Eq. 7 will be used together with ΔH_v° from Eq. 6 and be corrected for the difference between the standard enthalpy of vaporization ΔH_v° and the enthalpy of vaporization at 298.15 K and the corresponding boiling pressure, $\Delta H_{v,298}$. Usually this difference is small and becomes negligible at normal boiling points above 400 K. On a purely empirical basis it is found that the difference is

$$\Delta H_v^\circ - \Delta H_{v,298} = 0.35 e^{-0.02(T_b - 298.15)}\ (\mathrm{kJ/mol}) \quad (9)$$

Combination of Eqs. 6, 7 and 9 now gives the final relation used in this note to estimate the enthalpy of vaporization ΔH_{vb}

$$\begin{aligned}\Delta H_{vb} = &[2.60 + 614.924 N_g - 610.080 N_l \\ &- 0.35 e^{-0.02(T_b - 298.15)}] \\ &\times \left[\frac{T_c - T_b}{T_c - 298.15}\right]^\beta \times e^{\beta(298.15 - T_b)/T_c}\ (\mathrm{kJ/mol}) \quad (10)\end{aligned}$$

A reasonable approximation of the value of β is found from the n-alkane series as

$$\beta = 0.263 \times e^{0.014\ N_l} \quad (11)$$

This value of β is used for all compounds scrutinized in this work.

Enthalpy of Sublimation

Another property that can be estimated is the standard enthalpy of sublimation ΔH_s°, by substraction of the standard enthalpies of combustion (s) and (g)

$$\Delta H_s^\circ = -7.651 + 614.924 N_g - 606.375 N_s \quad (12)$$

However, due to such factors as the enthalpy of melting not being an additive property and transitions in the solid phase at sublimation, it cannot be expected that such a simple approach as presented by Eq. 12 yields accurate estimated values.

A survey of over 100 compounds shows that the values of ΔH_s° thus calculated have a standard deviation of 15 kJ/mol (or about 11%) compared to the literature values with a mean deviation of ±14 kJ/mol. Therefore, estimation of the standard enthalpy of sublimation with the method described here should be considered as approximate only. Some examples are given in Appendix 2. It is clear that the estimated values of ΔH_f° (s) are the major source of error of the estimation of ΔH_s°.

Notation

C = number of carbon atoms per molecule
C* = *ibid.* forming one or more rings
ΔH_c° = enthalpy of combustion (lower or net value) at 298.15 K and 1.01×10^5 Pa, kJ/mol
ΔH_f° = enthalpy of formation at 298.15 K and 1.01×10^5 Pa, kJ/mol
ΔH_s° = enthalpy of sublimation at 298.15 K and 1.01×10^5 Pa, kJ/mol
ΔH_v = enthalpy of vaporization at any temperature and 1.01×10^5 Pa, kJ/mol
ΔH_{vb} = *ibid.* at boiling temperature and 1.01×10^5 Pa, kJ/mol
ΔH_v° = *ibid.* at 298.15 K and 1.01×10^5 Pa, kJ/mol
$\Delta H_{v,298}$ = *ibid.* at 298.15 K and corresponding boiling pressure, kJ/mol
N = equivalent alkane chain length

ΔN_i = group correction factor
T_b = boiling temperature, K
T_c = critical temperature, K
T_r = reduced temperature

Greek letters

α, β = constants Eqs. 7, 8, 10 and 11
δ = calculated literature value
δ^* = ($\delta/\Delta H_s^\circ$ literature) × 100, %

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**Indicates major source of data*

Appendix 1. Examples of Estimation of the Enthalpies of Combustion, Formation and Vaporization

No.	Compound	Physical State	Calculation of N		Normal Boiling Point, K	Crit. Temp., K
1.1	Vinyl chloride	g	2 + Cl + NN1 + NN6	= 1.545	260	425
	C_2H_3Cl	l		= 1.532		
1.2	Octafluorocyclobutane	g	4 + E2 + MM5	= 1.697	267	389
	C_4F_8	l		= 1.659		
1.3	Acrolein	g	3 + Cl + C4 + I	= 2.260	326	510
	C_3H_4O	l		= 2.241		
1.4	Asparagine	s	4 + Kl + Pl + Ql + X	= 2.598	–	–
	$C_4H_8O_3N_2$					
1.5	Propionitrile	g	3 + CCl	= 2.666	371	564
	C_3H_5N	l		= 2.638		
1.6	Succinamide	s	4 + Ql + Q2	= 2.896	–	–
	$C_4H_8O_2N_2$					
1.7	Propane	g	3	= 3.000	231	370
	C_3H_8	l		= 3.000		
1.8	Ethyl acetate	g	4 + Ml + M7	= 3.080	350	523
	$C_4H_8O_2$	l		= 3.050		
1.9	Trimethyl amine	g	3 + P4 + 3 × P9	= 3.336	276	433
	C_3H_9N	l		= 3.324		
1.10	Thiacyclobutane	g	3 + E2 + II	= 3.38	368	600E
	C_3H_6S	l		= 3.34		
1.11	Methyl ethyl ketone	g	4 + Jl	= 3.424	353	537
	C_4H_8O	l		= 3.402		
1.12	Crotononitrile	g	4 + C2 + C6 + CCl	= 3.457	395	590
	C_4H_5N	l		= 3.428		
1.13	Vinylacetylene	g	4 + Cl + C4 + Dl	= 3.468	278	455
	C_4H_4	l		= 3.467		
1.14	l-Gulonic acid γ-lactone	s	6 + Hl + 3 × H2 + N	= 3.507	–	–
	$C_6H_{10}O_6$					
1.15	2-Butanol	g	4 + H2	= 3.762	373	536
	$C_4H_{10}O$	l		= 3.682		
1.16	2-Nitrobutane	g	4 + BB2	= 3.744	413	611E
	$C_4H_9NO_2$	l		= 3.705		
1.17	Methyl methacrylate	g	5 + B7 + Ml + M5 + M8	= 3.911	373	563
	$C_5H_8O_2$	l		= 3.879		
1.18	2,4-Dinitrophenol	s	6 + Fl + F2 + F4 + H4 + BB3 + BB4	= 3.956	–	–
	$C_6H_4N_2O_5$					
1.19	Bromobenzene	g	6 + Fl + 004	= 4.541	429	670
	C_6H_5Br	l		= 4.508		
1.20	2-Methyl-1,3-butadiene	g	5 + B7 + Cl + C4	= 4.568	307	484
	C_5H_8	l		= 4.572		
1.21	3-Methylthiophene	g	5 + B9 + HH	= 4.677	389	611
	C_5H_6S	l		= 4.654		
1.22	3-Picoline	g	6 + B9 + Tl + T3	= 5.065	417	645
	C_6H_7N	l		= 5.039		

Appendix 1 (Continued)

No.	Compound	Physical State	Calculation of N		Normal Boiling Point, K	Crit. Temp., K
1.23	2-Methyl-2-butanethiol	g	5 + Bl + GG4	= 5.510	372	570
	$C_5H_{12}S$	l		= 5.500		
1.24	Butyl methyl sulfide	g	5 + EE1 + EE2	= 5.551	397	594E
	$C_5H_{12}S$	l		= 5.536		
1.25	Anisole	g	7 + Fl + 01 + 02 + 03	= 5.608	427	646
	C_7H_8O	l		= 5.579		
1.26	Isopropyl ether	g	6 + 2 × Bl + B10 + 01	= 5.773	342	500
	$C_6H_{14}O$	l		= 5.769		
1.27	3,3-Dimethyl-l-butene	g	6 + 2 × B3 + B10 + C1	= 5.784	314	480
	C_6H_{12}	l		= 5.790		
1.28	5-Phenylaminotetrazole	s	7 + Fl + P7 + V	= 6.105	–	–
	$C_7H_7N_5$					
1.29	2,4-Dimethyl-3-pentanone	g	7 + 2 × Bl + B10 + Jl	= 6.401	398	582
	$C_7H_{14}O$	l		= 6.385		
1.30	cis 1,3-Dimethylcyclopentane	g	7 + 2 × B9 + B10 + C5 + E3	= 6.695	364	552
	C_7H_{14}	l		= 6.697		
1.31	2,2,3-Trimethylbutane	g	7 + Bl + 2 × B3 + B11	= 6.974	354	531
	C_7H_{16}	l		= 6.981		
1.32	*n*-Heptane	g	7	= 7.000	372	540
	C_7H_{16}	l		= 7.000		
1.33	Propyl disulfide	g	6 + FF1	= 7.050	469	679E
	$C_6H_{14}S_2$	l		= 7.022		
1.34	1,2,4-Trimethylbenzene	g	9 + 3 × B9 + B11 + F1 + F2 + F4	= 7.794	443	649
	C_9H_{12}	l		= 7.775		
1.35	p-Ethyltoluene	g	9 + 2 × B9 + B10 + F1 + F4	= 7.796	435	638
	C_9H_{12}	l		= 7.783		
1.36	Eugenol	l	10 + B9 + Cl + Fl + F2 + F4			
	$C_{10}H_{12}O_2$		+ H4 + 01 + 02 + 03	= 8.034	–	–
1.37	Sucrose	s	12 + 3 × B9 + B11 + 3 × Hl + 5 × H2 +			
	$C_{12}H_{22}O_{11}$		+ 01 + RR1 + RR2	= 8.161	–	–
1.38	Benzanilide	s	13 + B9 + 2 × Fl + R	= 10.136	–	–
	$C_{13}H_{11}NO$					
1.39	Valylphenylanaline	s	5 + B2 + Kl + Pl + X = 4.137		–	–
	$C_{14}H_{20}N_2O_2$		9 + B9 + Fl + Kl + P6 + X = 6.897			
			Y = 0.44			
			——— +	= 11.474		
1.40	Diphenylbutadiyne	s	16 + 2 × B9 + B10 + C4 + 2 × D2 + 2 × Fl	= 12.891	–	–
	$C_{16}H_{10}$					
1.41	Pentacene-6,13-quinone	s	22 + J2	= 16.215	–	–
	$C_{22}H_{12}O_2$					
1.42	7-Hexadecylspiro (4,5) decane	l	26 + B9 + E7	= 25.346	–	–
	$C_{26}H_{50}$					
1.43	13-Phenylpentacosane	s	31 + B9 + Fl	= 29.808	–	–
	$C_{31}H_{56}$					
1.44	13-Cyclohexylpentacosane	l	31 + B9 + E4	= 30.665	–	–
	$C_{31}H_{62}$					
1.45	Glyceroltribrassidate	s	69 + 3 × C2 + 3 × C6 + 3 × M4	= 65.709	–	–
	$C_{69}H_{128}O_6$					

No.	ΔH_c° kJ/mol Lit.	δ kJ/mol	ΔH_f° kJ/mol Lit.	δ kJ/mol	ΔH_v° kJ/mol Lit.	δ kJ/mol	ΔH_{vb} kJ/mol Lit.	δ kJ/mol
1.1	−1,151.3	2.8	28.4	−1.5	19.3	−1.3	20.4	−1.4
	–	–	9.2	−0.3				
1.2	–	–	−1,542.6	−1.2	22.6	5.3	24.4	5.7
	–	–	−1,565.2	−6.3				
1.3	–	–	−74.5	−2.1	–	–	30.4	−6.8
	−1.560.1	−2.9	−106.5	4.8				
1.4	−1,751.9	−29.6	−789.4	28.7	–	–	–	–
1.5	–	–	51.5	−0.6	36.2	−3.6	32.3	−3.5
	−1,800.6	−4.6	15.5	4.0				
1.6	−1.961.8	−0.4	−581.5	1.5	–	–	–	–

Appendix 1 (Continued)

No.	ΔH_c° kJ/mol Lit.	δ kJ/mol	ΔH_f° kJ/mol Lit.	δ kJ/mol	ΔH_v° kJ/mol Lit.	δ kJ/mol	ΔH_{vb} kJ/mol Lit.	δ kJ/mol
1.7	−2,043.4	0.2	−104.7	−0.6	16.3	0.9	19.0	0.8
	–	–	−120.1	−2.3				
1.8	–	–	−450.5	0.7	35.2	0.6	32.0	0.4
	−2,062.7	6.1	−485.9	0.3				
1.9	–	–	−23.5	3.8	22.2	3.9	22.9	4.1
	−2,223.3	−0.4	−45.7	−0.1				
1.10	–	–	60.6	12.7	36.0	7.4	32.3	6.7
	−2,228.3	−5.2	24.7	5.2				
1.11	–	–	−238.7	0.4	34.9	−2.3	31.3	−1.9
	−2,268.4	−2.9	−273.3	2.4				
1.12	–	–	140.7	4.2	40.3	−3.2	34.1	−2.5
	−2,279.5	−7.7	107.8	7.1				
1.13	–	–	304.8	−32.2	–	–	34.5	−14.1
	–	–	–	–				
1.14	−2,352.7	20.1	−1,220.5	−18.3	–	–	–	–
1.15	–	–	−292.9	−1.6	49.8	−2.3	40.8	−0.3
	−2,440.9	−1.2	−342.5	0.6				
1.16	–	–	−163.6	1.2	43.8	0.7	34.3	2.9
	−2,455.1	−1.1	−207.5	0.5				
1.17	–	–	−332.0	−0.4	–	–	34.3	1.7
	–	–	−371.4	−2.1				
1.18	−2,612.1	7.2	−232.8	−8.0	–	–	–	–
1.19	–	–	105.4	3.4	44.5	0.2	36.9	0.4
	–	–	60.9	3.1				
1.20	−3,010.8	3.4	75.3	−3.8	26.8	−4.5	25.8	−4.9
	−2,982.4	−2.7	48.0	1.3				
1.21	–	–	82.6	0.9	39.5	−0.2	34.2	0.0
	−3,036.8	1.6	43.1	1.1				
1.22	–	–	106.4	−1.9	44.4	−1.4	37.5	−1.3
	−3,269.6	−0.4	61.9	−0.4				
1.23	–	–	−127.1	−2.8	35.7	−0.3	31.4	−0.3
	−3,553.7	2.4	−162.8	−2.5				
1.24	–	–	−102.2	−2.5	40.6	−2.0	34.5	−1.7
	–	–	−142.8	−0.6				
1.25	–	–	−68.0	−8.3	46.8	0.7	39.0	0.3
	−3,604.6	5.1	−114.8	−8.9				
1.26	–	–	−319.1	12.3	32.3	0.7	29.1	0.8
	−3,702.8	−12.6	−351.5	11.7				
1.27	–	–	−60.5	2.4	26.7	0.3	25.6	0.2
	−3,724.2	−4.0	−87.6	2.5				
1.28	−3,909.1	1.1	305.2	0.6	–	–	–	–
1.29	–	–	−311.3	−3.0	41.6	1.8	34.6	1.7
	−4,095.6	4.4	−356.1	−1.5				
1.30	–	–	−135.9	2.4	34.3	−0.5	30.4	−0.5
	−4,277.6	−3.9	−170.1	2.8				
1.31	–	–	−204.5	0.7	32.1	0.0	28.9	0.2
	−4,452.5	−2.3	−236.5	0.6				
1.32	–	–	−187.7	−0.1	36.7	−0.2	31.5	0.0
	−4,465.1	−1.3	−224.2	−0.2				
1.33	–	–	−117.3	1.9	53.6	0.2	41.9	0.2
	−4,478.2	−1.6	−171.5	2.2				
1.34	–	–	−13.8	10.7	47.9	4.0	39.5	2.1
	−4,931.2	−8.0	−61.8	6.8				
1.35	–	–	−3.2	1.3	46.6	1.7	37.7	1.2
	−4,943.2	−0.9	−49.6	−0.6				
1.36	−5,123.3	26.1	−263.3	−27.4	–	–	–	–
1.37	−5,156.7	2.0	−2,227.0	−3.0	–	–	–	–
1.38	−6353.8	1.5	−94.6	−1.0	–	–	–	–
1.39	−7,162.3	−1.3	−765.8	−0.7	–	–	–	–
1.40	−8,023.7	0.8	518.4	−3.4	–	–	–	–
1.41	−10,035.7	−2.9	−72.8	−0.3	–	–	–	–
1.42	−15,688.0	29.1	−590.4	−33.1	–	–	–	–
1.43	−18,284.7	3.8	−687.0	−8.4	–	–	–	–
1.44	−18,904.8	0.9	−792.7	−5.4	–	–	–	–
1.45	−40,048.1	−2.3	−2,616.7	23.6	–	–	–	–

NOTE:
E = estimate according to Reid et al. (1987), p. 12; δ = calculated − literature value

Appendix 2. Examples of Estimation of the Enthalpy of Sublimation

No.	Compound	Physical State	Calc. of N		ΔH_f° kJ/mol Lit.	δ kJ/mol	ΔH_s° kJ/mol Lit.	δ kJ/mol	δ^*
2.1	Pentaerythritol	g	$5+2\times B3+B10+4\times H1$	$=3.993$	-776.7	10.9	143.9	19.6	13.6
	$C_5H_{12}O_4$	s		$=3.767$	-920.6	-8.7			
2.2	2-Chlorobenzoic acid	g	$7+B9+F1+F2+K1+NN4$	$=4.561$	-325.0	-3.6	79.5	11.9	14.9
	C_7H_5O	s		$=4.462$	-404.5	-15.5			
2.3	p-Cresol	g	$7+B9+F1+F4+H4$	$=5.523$	-125.4	-3.1	73.9	13.0	17.5
	C_7H_8O	s		$=5.450$	-199.3	-16.1			
2.4	Hexanamide	g	$6+Q1$	$=5.556$	-324.2	4.9	98.7	1.2	1.2
	$C_6H_{13}ON$	s		$=5.457$	-423.0	3.8			
2.5	1-Naphthol	g	$10+G1+H4$	$=7.607$	-29.9	2.0	91.2	17.7	19.4
	$C_{10}H_8O$	s		$=7.522$	-121.0	-15.9			
2.6	Dibutyl sulfone	g	$8+JJ1$	$=7.98$	-509.8	-7.9	100.4	8.7	8.7
	$C_8H_{18}SO_2$	s		$=7.90$	-610.2	-16.6			
2.7	Benzophenone	g	$13+2\times B9+B10+2\times F1+$	$=10.051$	54.3	-2.2	88.9	10.0	11.2
	$C_{13}H_{10}O$	s	$+J1$	$=10.017$	-34.5	-12.3			
2.8	Anthracene	g	$14+G3$	$=10.974$	230.9	-4.9	101.7	14.8	14.5
	$C_{14}H_{10}$	s		$=10.924$	129.2	-19.7			
2.9	1,2-Diphenylethane	g	$14+2\times B9+B10+2\times F1$	$=11.627$	142.9	0.9	91.4	6.4	7.0
	$C_{14}H_{14}$	s		$=11.617$	51.5	-5.6			
2.10	Dotriacontane	g	32	$=32.000$	-697.2	-6.3	271.1	-5.2	-1.9
	$C_{32}H_{66}$	s		$=32.000$	-967.6	-1.8			

NOTE: $\delta^* = (\delta/\Delta H_s^\circ \text{ literature})\times 100$

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