R & D NOTES

Prediction of the Enthalpy of Combustion of Organic Compounds

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In many instances, particularly when preparing plant designs, the enthalpy of combustion of compounds must be estimated. We present in this note a simple and accurate method to obtain such enthalpies at 298.15 K. Basically, we develop correction factors for a wide variety of functional groups and branching modes to correct simple relationships for alkane combustion. The method has been shown to apply to gaseous, liquid, and solid compounds with errors less than 1%. In addition, the enthalpy of combustion can be converted to a standard enthalpy of formation; as such, the method compares favorably to the best estimation techniques now available for the property.

Enthalpy of Combustion

It is well known that for most homologous series, there is a first-order correspondence between the total number of carbon atoms and the enthalpy of combustion (Handrick, 1956). We have utilized this concept to estimate enthalpies of combustion by developing correction factors to determine an equivalent alkane chain length, N, such that, with this parameter, one can then utilize simple relations developed for n-alkanes. Thus we define N as

$$N = C + \sum_i \Delta N_i \tag{1}$$

Here C is the total number of carbon atoms in the molecule, while ΔN_i values are correction factors for functional groups and chain branching. Values of ΔN_i vary depending upon whether the compound is a gas (g), liquid (l), or solid (s). In Table 1 we show values of ΔN_i applicable to many compound types. In cases where there may be an ambiguity, clarifying remarks are given with the table. It can be seen that a wide variety of organic compounds may be treated, including aliphatic, naphthenic, and aromatic materials.

With values of ΔN_i for the compound of interest, N can be found from Eq. 1 and the enthalpy of combustion ΔH_c° from Eqs. 2 through 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 10^5 Pa (1 bar). The products of combustion are $H_2O(g)$, CO_2, SO_2, N_2, and HX(g) with X = halogen.

$$\Delta H_c^\circ(g) = -198.42 - 615.14\,N \quad \text{(kJ/mol)} \tag{2}$$

$$\Delta H_c^\circ(l) = -196.98 - 610.13\,N \quad \text{(kJ/mol)} \tag{3}$$

$$\Delta H_c^\circ(s) = -206.21 - 606.56\,N \quad \text{(kJ/mol)} \tag{4}$$

In Appendix I we illustrate the applicability of the method to a number of compound types, both simple and quite complex. (A more detailed statistical comparison between calculated and literature values of ΔH_c° is available upon request from the author.)

The method was applied to a large number of compounds for which the equivalent alkane chain length N ranged from 1 to 66. Further limitations were an upper limit equal to one for the ratio between the number of corrections and the number of carbon atoms and, for halides, an upper limit equal to one for the ratio between halogen and hydrogen atoms. These limitations were fixed because it was noted that beyond the indicated limits the application of the method yielded low estimates. This is illustrated by the following results for chlorinated gaseous ethanes, using calculated and literature values as indicated.

	N calc.	$\frac{\Delta H_c^\circ \text{ calc.}}{\Delta H_c^\circ \text{ lit.}}$
Hexachloroethane	0.32	0.833
Pentachloroethane	0.60	0.910
1,1,2,2-tetrachloroethane	0.88	0.971
1,1,2-trichloroethane	1.16	0.985
1,1- and 1,2-dichloroethane	1.44	1.000
Monochloroethane	1.72	1.003
Ethane	2.00	1.000

In the development of the method, a reliable value of the enthalpy of combustion was located for 1,168 compounds. Of these, 908 were used in the correlation program to develop ΔN_i

Table 1. Group Correction Factors for Calculation of the Enthalpy of Combustion, ΔH_c^o (kJ/mol)

A	*n*-Alkanes	Gas	$\Delta H_c^o =$	$-198.42-615.14\,N$			
		Liquid	$\Delta H_c^o =$	$-196.98-610.13\,N$			
		Solid	$\Delta H_c^o =$	$-206.21-606.56\,N$			

		Per	ΔN_i Gas	ΔN_i Liquid	ΔN_i Solid	Remarks
B_1	Carbon to carbon branch, Alkanes	branch		for *g*, 1, and *s*: $-0.031 + 0.012 \ln C$		1
B_2	Carbon to carbon branch, all other compounds	branch	−0.02	−0.02	−0.02	—
C	Cyclo-paraffines	—	−0.30	−0.29	−0.26	2
D_1	1-Alkenes	double bond	−0.189	−0.189	−0.189	3
D_2	*i*-Alkenes ($i \neq 1$)	double bond	−0.205	−0.208	−0.218	3
D_3	cis	—	+0.004	+0.003	+0.003	3
D_4	trans	—	−0.003	−0.002	−0.002	3
E_1	1-Alkynes	triple bond	−0.314	−0.342	—	3
E_2	*i*-Alkynes ($i \neq 1$)	triple bond	−0.34	−0.347	—	3
F_1	Alcohols, primary	—OH	−0.246	−0.297	−0.30	—
F_2	Alcohols, secondary	—OH	−0.27	−0.32	−0.33	—
F_3	Alcohols, tertiary	—OH	−0.30	−0.36	−0.33	—
G	Aldehydes	=O	−0.525	−0.551	−0.52	—
H	Ketones	=O	−0.576	−0.609	−0.57	—
I	Carboxylic acids	—OOH	−0.94	−1.033	−1.038	—
J	Esters	—OO—	−0.857	−0.93	−0.90	—
K	Lactones	—	−1.08	−1.13	−1.19	2
L	Ethers	—O—	−0.197	−0.212	−0.25	—
M_1	Amines, primary	$-NH_2$	+0.24	+0.21	+0.18	—
M_2	Amines, secondary	=NH	+0.30	+0.27	+0.16	—
M_3	Amines, tertiary	≡N	+0.32	+0.33	+0.14	—
N	Amides	$-ONH_2$	—	−0.542	−0.542	
O	Lactams	—	—	—	−0.80	2
P	Amino Acids	—	—	—	additional −0.043	4
Q	Dipeptides	—	—	—	Σ amino acids +0.44	4
R	Diketopiperazines	—	—	—	Σ amino acids +0.59	4
S_1	1-Nitro-	$-NO_2$	−0.22	−0.27	—	—
S_2	2-Nitro-	$-NO_2$	−0.26	−0.27	−0.28	—
S_3	Dinitro-	$=(NO_2)_2$	—	−0.50	−0.50	—
S_4	Trinitro-	$=(NO_2)_3$	—	—	−0.64	—
T	Nitriles	≡N	−0.322	−0.36	—	—
U	Sulphides	—S—	+0.553	+0.535	—	—
V	Disulphides	—S—S—	+1.049	—	—	—
W	Thiols, primary	—SH	+0.546	+0.524	—	—
X_1	Fluoro-	—F	−0.26	−0.26	—	—
X_2	Chloro-	—Cl	−0.28	−0.30	−0.30	—
X_3	Bromo-	—Br	−0.30	−0.33	—	—
X_4	Iodo-	—I	−0.31	−0.34	−0.34	—
Y_1	Benzenes	—	−1.167	−1.173	−1.173	2
Y_2	ortho	—	−0.006	−0.006	−0.006	—
Y_3	meta	—	−0.002	−0.002	−0.002	—
Y_4	para	—	−0.001	−0.001	−0.001	—
Z	lin.-Polynuclear hydrocarbons	—	—	—	$0.248-0.236\,C$	5
AA	Quinones	—	—	—	−0.86	—
BB	Pyridines	—	−0.914	−0.95	—	2
CC	Anilides	—	—	—	−0.50	6
DD	Tetrazoles	—	—	—	+0.12	2
EE	Pyrroles	—	−0.60	−0.65	−0.69	2
FF	Thiophenes	—	−0.303	−0.327	—	2
GG_1	Monosaccharides	Furanose rig	—	—	−0.52	2
GG_2	Monosaccharides	Pyranose ring	—	—	−0.50	2
HH_1	Di- and oligosaccharides	Furanose ring	—	—	−0.50	2,7
HH_2	Di- and oligosaccharides	Pyranose ring	—	—	−0.47	2,7

Table 2. Comparison of Values of Enthalpy of Formation of a Gas (kJ/mol) at Standard Conditions

Compound	Gas Phase ΔH_f° Lit.	N This Work	ΔH_f° Calc. Benson	ΔH_f° Lit. This Work
Propane	−103.9	3.0	1.2	−1.5
n-Heptane	−187.9	7.0	0.1	−0.1
2,2,3-Trimethylbutane	−204.9	6.977	−1.5	2.8
trans-2-Butene	−11.2	3.792	1.3	−0.8
3,3-Dimethyl-1-butene	−43.2	5.771	14.2	−23.0
2-Methyl-1,3-butadiene	75.8	4.586	0.0	6.8
2-Pentyne	129.0	4.66	−2.5	−0.8
p-Ethyltoluene	−3.3	7.792	0.1	−1.1
2-Methylnaphthalene	116.2	(8.868)	2.9	(−4.2)
cis-1,3-Dimethylcyclopentane	−135.9	6.664	0.2	−16.7
2-Butanol	−292.5	3.73	1.5	0.3
p-Cresol	−125.5	5.542	0.8	8.6
Isopropylether	−319.0	5.763	2.1	5.9
p-Dioxane	315.3	m.n.a.	−8.0	—
Methyl ethyl ketone	−238.5	3.424	−0.8	0.1
Ethyl acetate	−443.2	3.143	−9.5	31.9
Methyl methacrylate	−332.0	3.934	9.3	13.5
Trimethylamine	−23.9	3.32	0.6	−5.8
Propionitrile	50.7	2.678	1.3	8.8
2-Nitrobutane	−163.7	3.74	7.5	−1.3
3-Picoline	106.2	5.066	m.n.a.	−1.1
1,1-Difluoroethane	−494.0	1.48	4.2	29.7
Octafluorocyclobutane	−1,529.0	m.n.a.	−14.2	—
Bromobenzene	105.1	4.533	8.8	−1.2
Trichloroethylene	−5.9	m.n.a.	−4.6	—
Butyl methyl sulphide	−102.2	5.553	−0.9	−1.6
2-Methyl-2-butanethiol	−127.1	(5.526)	3.2	(6.7)
Propyl disulphide	−117.3	7.049	−3.1	0.7
3-Methylthiophene	82.9	4.677	0.4	0.4

Values in brackets are nearest approximations. m.n.a., method not applicable.

values shown in Table 1. ΔH_c° values for the other 260 compounds were then used to check the accuracy of the method. Defining $\eta = \Delta H_c^\circ$ calc./ΔH_c° lit., it was shown that $0.995 < \eta < 1.005$ in 79%, and $0.99 < \eta < 1.01$ in 92% of the tests. No errors exceeded 5%. The largest errors occurred when values of N ranged between 1 and 2.

Enthalpy of Formation

Because of the direct relation between the enthalpy of formation and the enthalpy of combustion, the method described above can also be used for estimation of the enthalpy of formation ΔH_f°(kJ/mol) in the gaseous as well as in the liquid or solid standard state, 298.15 K and 1 bar (10^5 Pa).

The enthalpy of formation is calculated from Eq. 5

$$\Delta H_f^\circ = -393.78C - 241.99\,(H - X)/2 - 271.81F - 92.37Cl - 36.26Br + 24.81I - 297.26S - \Delta H_c^\circ\,(\text{kJ/mol}) \qquad (5)$$

In Eq. 5 the letters C, H, F, . . . stand for the number of atoms per molecule and X = any halogen atom.

A comparison with the method for calculation of the enthalpy of formation for ideal gases developed by Benson et al. (1969) is given in Table 2. The compounds are those given by Reid et al. (1977) in their critical review of various methods to estimate the enthalpy of formation. For the same compounds, and where the method described in this study permits, the estimation is

Table 3. Comparison of Values of Enthalpy of Formation of a Liquid (kJ/mol) at Standard Conditions

Compound	Liquid Phase ΔH_f° Lit.	N This Work	ΔH_f° Calc.–Lit. This Work
n-Heptane	−224.5	7.0	0.1
2,2,3-Trimethylbutane	−237.1	6.977	−1.4
3,3-Dimethyl-1-butene	−88.3	5.771	−8.2
2-Methyl-1,3-butadiene	49.4	4.583	6.9
p-Ethyltoluene	−49.9	7.786	1.4
2-Methylnaphthalene	56.7	(8.868)	(9.4)
cis-1,3-Dimethylcyclopentane	−170.3	6.673	−11.7
2-Butanol	−342.9	3.68	0.1
Isopropylether	−351.5	5.748	−1.1
Methyl ethyl ketone	−273.4	3.391	−3.7
Ethyl acetate	−479.3	3.07	6.3
Methyl methacrylate	−371.4	3.861	−12.8
Trimethylamine	−45.8	3.33	4.2
Propionitrile	14.7	2.64	6.7
2-Nitrobutane	−207.7	3.73	16.4
3-Picoline	61.8	5.03	−5.5
Bromobenzene	60.7	4.497	−2.9
Butyl methyl sulphide	−143.0	5.535	−1.1
2-Methyl-2-butanethiol	−162.9	(5.504)	(−0.1)
Propyl disulphide	−171.5	(7.049)	(18.1)
3-Methylthiophene	43.3	4.653	0.5

Values in brackets are nearest approximations.

Remarks (Table 1)

1. The correction factor for branched alkanes has an upper limit of −0.03.
2. The carbon atoms forming the ring in cyclic compounds count in determination of *C*. Functional groups, connected to a carbon atom that is part of a ring which itself is connected to two other carbon atoms, are considered as secondary groups. Furthermore, for a carbon atom branched to a carbon atom that is part of a ring, a branch correction should be applied.
3. The correction factors are of general nature and can be used for all compounds with multiple bonds. The cis/trans corrections are valid for all compounds having such structural isomers.
4. The correction for amino acids is calculated by the normal procedure of addition of the group corrections for amine and carboxylic acid plus an additional constant equal to −0.043. For the amino acid derivatives, the correction consists of the correction factors of the basic acid plus an additional structural correction.
5. The correction for linear polynuclear hydrocarbons is calculated for the number of carbon atoms that form the basic structure. It is observed that nonlinear polynuclear hydrocarbons like phenanthrene or chrysene fit well, but for condensed polynuclear hydrocarbons like pyrene of fluoranthrene, the calculated enthalpy of combustion is up to 2% too high.
6. For anilides, the correction factor given is valid for the structural components (NH— and =O). For the rest of the molecule, the normal rules apply.
7. The oxygen bridge is considered as an ether bond.

Table 4. Comparison of Values of Enthalpy of Formation of a Solid (kJ/mol) at Standard Conditions

Compound	Solid Phase		
	ΔH_f° Lit.	N This Work	ΔH_f° Calc.–Lit. This Work
2-Methylnaphthalene	44.9	5.868	−1.2
p-Cresol	−199.3	5.476	2.6
α-Naphthol	−112.2	7.558	−3.0
Ethyl 4-ethyl-3,5-dimethyl-pyrrole-2-carboxylate	−523.4	9.33	0.3
Benzanilide	−90.0	10.134	−7.0
Diphenylacetylene	319.9	11.267	−2.4
Dotriacontane	−970.5	32	0.0
Glyceroltribrassidate	−2,613.4	65.640	−17.9

extended to liquids in Table 3 and to solids in Table 4. In the latter case, a few additional compounds are added since the list of Reid et al. contains only two compounds for which the estimation could be done.

From the comparison it is concluded that the method described in this work can be used to estimate the enthalpy of formation of organic compounds accurately and simply. Although less accurate than the method of Benson, it has the advantage of being much easier to use and, in addition, it is applicable to the gaseous, liquid, and solid states.

Notation

C = number of carbon atoms
ΔH_f° = enthalpy of formation at 298.15 K and one bar (10^5 Pa), kJ/mol
ΔH_c° = enthalpy of combustion (lower or net value) at 298.15 K and one bar (10^5 Pa), kJ/mol
N = equivalent alkane chain length
ΔN_i = group correction factor, Table 1
$\eta = \Delta H_c^\circ$ calc./ΔH_c° lit.

Literature Cited

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Manuscript received Apr. 10, 1985.

Appendix I. Examples of Calculation of Enthalpy of Combustion

Compound	Structure	Physical State	Calculation of N*		ΔH_c^o, kJ/mol Lit.	ΔH_c^o, kJ/mol Calc.	η
Vinyl chloride	CH_2=$CHCl$	gas	$2 + D_1 + X_2$	= 1.531	− 1,157	− 1,140	0.985
Ethane	CH_3CH_3	gas	2	= 2.0	− 1,429	− 1,429	1.000
Acrolein	CH_2=$CHCHO$	liquid	$3 + D_1 + G$	= 2.260	− 1,560	− 1,576	1.010
Asparagine	$H_2NCOCH_2CH(NH_2)COOH$	solid	$4 + I + M_1 + N + P$	= 2.557	− 1,754	− 1,757	1.002
Succinamide	H_2NCOCH_2—CH_2CONH_2	solid	$4 + 2 \times N$	= 2.916	− 1,962	− 1,975	1.007
Crotononitrile	CH_3CH=$CHCN$	liquid	$4 + D_2 + D_4 + T$	= 3.430	− 2,286	− 2,290	1.002
Vinylacetylene	CH_2=CH—C≡CH	gas	$4 + D_1 + E_1$	= 3.497	− 2,364	− 2,350	0.994
L-Gulonic acid-γ-lactone	CH_2OH—$CHOH$—CH—$CHOH$—$CHOH$—CO (O)	solid	$6 + F_1 + 3 \times F_2 + K$	= 3.52	− 2,352	− 2,341	0.995
2,4-Dinitrophenol	$C_6H_3(OH)(NO_2)_2$	solid	$6 + F_2 + S_3 + Y_1 + Y_2 + Y_4$	= 3.990	− 2,614	− 2,626	1.005
Methyl propyl sulphide	CH_3—S—C_3H_7	gas	$4 + U$	= 4.553	− 3,000	− 2,999	1.000
Phthalic acid	$C_6H_4(COOH)_2$	solid	$8 + 2 \times B_2 + 2 \times I + Y_1 + Y_2$	= 4.705	− 3,093	− 3,060	0.989
Isopentylamine	$CH_3CH(CH_3)CH_2CH_2NH_2$	liquid	$5 + B_2 + M_1$	= 5.19	− 3,346	− 3,364	1.005
Anisole	C_6H_5—O—CH_3	liquid	$7 + L + Y_1$	= 5.615	− 3,613	− 3,623	1.003
5-Phenylaminotetrazole	(CN_4H)—NH—C_6H_5	solid	$7 + M_2 + Y_1 + DD$	= 6.107	− 3,909	− 3,910	1.000
2,4-Dimethyl-3-Pentanone	$CH_3CH(CH_3)COCH(CH_3)CH_3$	liquid	$7 + 2 \times B_2 + H$	= 6.351	− 4,070	− 4,072	1.001
2,2,3-Trimethylbutane	$CH_3C(CH_3)_2CH(CH_3)CH_3$	liquid	$7 + 3 \times B_1$	= 6.977	− 4,455	− 4,454	1.000
α-Naphthol	$C_{10}H_7OH$	solid	$10 + F_2 + Z$	= 7.558	− 4,787	− 4,791	1.001
1,2,4-Trimethylbenzene	$C_6H_3(CH_3)_3$	gas	$9 + 3 \times B_2 + Y_1 + Y_2 + Y_4$	= 7.766	− 4,982	− 4,976	0.999
Eugenol	$C_6H_3(OH)(OCH_3)(CH_2$—CH=$CH_2)$	liquid	$10 + B_2 + D_1 + F_2 + L + Y_1 + Y_2 + Y_4$	= 8.079	− 5,123	− 5,126	1.001
Sucrose	(O) $(CH(CH_2OH)$—$CHOH$—$CHOH$—$CHOH$—$CH)$ O $((CH_2OH)CH$—$CHOH$—$CHOH$—$C(CH_2OH))$ (O)	solid	$12 + 3 \times B_2 + 3 \times F_1 + 5 \times F_2 + L + HH_1 + HH_2$	= 8.17	− 5,160	− 5,162	1.000
2-2′-Difluorobiphenyl	FC_6H_4—C_6H_4F	gas	$12 + 2 \times B_2 + 2 \times X_1 + 2 \times Y_1$	= 9.106	− 5,794	− 5,800	1.001
Ethyl 4-ethyl-3,5-dimethyl-pyrrole-2-carboxylate	$(C_4HN)(C_2H_5)(CH_3)_2(CO_2C_2H_5)$	solid	$11 + 4 \times B_2 + J + EE$	= 9.33	− 5,865	− 5,865	1.000
Benzanilide	C_6H_5—NH—CO—C_6H_5	solid	$13 + B_2 + 2 \times Y_1 + CC$	= 10.134	− 6,357	− 6,353	0.999
Diphenylacetylene	C_6H_5≡CC_6H_5	solid	$14 + 2 \times B_2 + E_2 + 2 \times Y_1$	= 11.267	− 7,043	− 7,040	1.000
Valylphenylalanine	$(C_6H_5)CH_2CH(NH)COH$ | $CH_3CH(CH_3)CH(NH_2)CO$	solid	valine: $5 + B_2 + I + M_1 + P$ phen.al.: $9 + B_2 + I + M_1 + P + Y_1$ dipept.: Q	= 4.079 = 6.906 = 0.44 + 11.425	− 7,164	− 7,136	0.996
Dicyclohexylmethane	$(C_6H_{11})_2CH_2$	liquid	$13 + 2 \times B_2 + 2 \times C$	= 12.38	− 7,724	− 7,750	1.003
Pentacene-6,13-quinone	$C_{22}H_{12}O_2$	solid	$22 + Z + AA$	= 16.202	−10,041	−10,034	0.999
5-Butyldocosane	$CH_3(CH_2)_3$—$CH(C_4H_9)$—$(CH_2)_{16}CH_3$	liquid	$26 + B_1$	= 25.997	−16,056	−16,059	1.000
Dotriacontane	$CH_3(CH_2)_{30}CH_3$	solid	32	= 32.0	−19,616	−19,616	1.000
Glyceroltribrassidate	$CH_2(OCOR)CH(OCOR)CH_2(OCOR)$ with R≡$CH_3(CH_2)_7CH$=$CH(CH_2)_{10}CH_2$—(trans)	solid	$69 + 3 \times D_2 + 3 \times D_4 + 3 \times J$	= 65.640	−40,041	−40,021	0.999

*See Table 1 for letter group identifications.