Supplementary Material

to

Group contribution revisited: the enthalpy of formation of organic compounds with "chemical accuracy"

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Table S1. Experimental (CAPEC data base and NIST data base) and increments (difference between experimental value for the species and that of the species with 1 CH_2 group less, so the previous entry in the table).

Alcohols	CAPEC incr.	NIST	NIST incr.
Ethanol		-234	
1-Propanol	-20.25	-256	-22.00
1-Butanol	-19.40	-277	-21.00
2-Butanol		-293	
1-Pentanol	-22.30	-298	-21.00
2-Pentanol		-314	
3-Pentanol			
1-Hexanol	-19.60	-316	-18.00
1-Heptanol	-19.90	-334.5	-18.50
2-Heptanol			
1-Octanol	-20.20	-356	-21.50
1-Nonanol	-24.60	-377.9	-21.90
1-Decanol	-20.10	-395	-17.10
1-Undecanol	-20.70		
1-Dodecanol	-17.50	-436.5	-20.75
1-Tetradecanol	-20.75	-474.8	-19.15
1-Eicosanol	-20.70		

Table S2. Experimental and model values for alkanes. All values in kJ/mol. When available, Rossini et al. data [21] were used when comparing with the present model (model – exp), otherwise CAPEC data (not shown) were used. The last rows with values in red are the average increment for the Rossini data set (-20.63 kJ/mol), whereas the value in the last row (0.53) is the averaged absolute difference between the model Eq. (2) and the experimental values.

n-alkanes	Rossini	Rossini incr.	NIST	model ΔHf	model-exp	ABS (model-exp)
ethane	-84.73		-84	-84.72	0.01	0.01
propane	-103.92	-19.19	-104.7	-105.35	-1.43	1.43
butane	-124.82	-20.90	-126	-125.98	-1.16	1.16
pentane	-146.55	-21.73	-147	-146.61	-0.06	0.06
hexane	-167.31	-20.76	-167	-167.24	0.07	0.07
heptane	-187.95	-20.64	-188	-187.87	0.08	0.08
octane	-208.6	-20.65	-208.5	-208.5	0.10	0.1
nonane	-229.2	-20.60	-228.3	-229.13	0.07	0.07
decane	-249.84	-20.64	-249.7	-249.76	0.08	0.08
undecane	-270.48	-20.64	-270.3	-270.39	0.09	0.09
dodecane	-291.1	-20.62	-290	-291.02	0.08	0.08
tridecane	-311.72	-20.62	-311.5	-311.65	0.07	0.07
tetradecane	-332.36	-20.64	-332.1	-332.28	0.08	0.08
pentadecane	-353.01	-20.65	-354.8	-352.91	0.10	0.1
hexadecane	-373.6	-20.59	-374.8	-373.54	0.06	0.06
heptadecane	-394.21	-20.61	-393.9	-394.17	0.04	0.04
octadecane	-414.85	-20.64	-414.6	-414.8	0.05	0.05
nonadecane	-435.45	-20.60	-435.1	-435.43	0.02	0.02
eicosane	-456.1	-20.65	-455.8	-456.06	0.04	0.04
heneicosane				-476.69	1.21	1.21
docosane				-497.32	1.18	1.18
dotriacontane				-517.95	1.25	1.25
tetracosane				-538.58	1.42	1.42
pentacosane				-559.21	1.49	1.49
hexacosane				-579.84	1.56	1.56
octacosane				-621.1	-1.10	1.1
triacontane				-662.36	-1.36	1.36
dotriacontane				-703.62	-1.62	1.62
hexatriacontane				-786.14	-1.14	1.14
averaged increment		-20.63				
averaged absolute difference						0.53

Table S3. Experimental and model values for mono-methylalkanes. All values in kJ/mol. When available, Rossini et al. data [21] were used when comparing with the present model (model – exp), otherwise NIST data, and when both were not available CAPEC data (not shown). The red value 1.91 kJ/mol in the last row is the averaged absolute difference between the model Eq. (3) and the experimental values.

Monomethyl alkanes	Rossini	NIST	NIST incr.	model ΔHf	model-exp	ABS (model-exp)
2-methylpropane	-131.7	-134.9		-131.08	0.62	0.62
2-methylbutane	-154.6	-154.1	-19.20	-151.71	2.89	2.89
2-methylpentane	-174.43	-174.3	-20.20	-172.34	2.09	2.09
3-methylpentane	-171.8	-171.6		-172.34	-0.54	0.54
3-methylhexane	-192.4	-192.5		-192.97	-0.57	0.57
2-methylhexane	-195.1	-195.5	-21.20	-192.97	2.13	2.13
3-methylheptane	-212.78	-212.6		-213.6	-0.82	0.82
4-methylheptane	-212.24	-212.1		-213.6	-1.36	1.36
2-methylheptane	-215.63	-215.5	-20.00	-213.6	2.03	2.03
2-methyloctane				-234.23	1.67	1.67
4-methyloctane				-234.23	0.97	0.97
2-methylnonane		-260.2	-22.35	-254.86	5.34	5.34
5-methylnonane		-258.6		-254.86	3.74	3.74
averaged absolute difference						1.91

Table S4. Experimental and model values for the n-alcohols. All values in kJ/mol. The model was compared (model-exp) using the NIST data when available and otherwise from the CAPEC data base data. The value in the last column (1.54 kJ/mol) is the averaged absolute difference between the model Eq. (4a+4b) and experimental data.

n-Alcohols	NIST	model ΔHf	model-exp	ABS (model-exp)
ethanol	-234	-233.99	0.96	0.96
1-propanol	-256	-254.62	0.58	0.58
1-butanol	-277	-275.25	-0.65	0.65
2-butanol	-293	-296.98	-4.08	4.08
1-pentanol	-298	-295.88	1.02	1.02
2-pentanol	-314	-317.61	-3.81	3.81
3-pentanol		-317.61	-0.88	0.88
1-hexanol	-316	-316.51	-0.01	0.01
1-heptanol	-334.5	-337.14	-0.74	0.74
2-heptanol		-358.87	-3.47	3.47
1-octanol	-356	-357.77	-1.17	1.17
1-nonanol	-377.9	-378.4	2.80	2.8
1-decanol	-395	-399.03	2.27	2.27
1-undecanol		-419.66	2.34	2.34
1-dodecanol	-436.5	-440.29	-0.79	0.79
1-tetradecanol	-474.8	-481.55	-0.55	0.55
1-eicosanol		-605.33	-0.13	0.13
averaged absolute difference				1.54

Table S5. Experimental and model values for the aldehydes. All values in kJ/mol. Experimental data were taken from the CAPEC data base (please note, see Ref. 15, that explicit values were never published in the open literature). Note the very small differences between model and experimental values for this series.

Aldehydes	model ΔHf	model-exp	ABS (model-exp)
acetaldehyde	-166.36	-0.16	0.16
butanal	-207.62	-0.62	0.62
pentanal	-228.25	-0.45	0.45
hexanal	-248.88	-0.28	0.28
heptanal	-269.51	-0.11	0.11
octanal	-290.14	0.06	0.06
nonanal	-310.77	0.13	0.13
decanal	-331.4	0.30	0.3
dodecanal	-372.66	0.64	0.64
averaged absolute difference			0.31

Table S6. Experimental and model values for the ketones. All values in kJ/mol. The averaged absolute difference between the experimental NIST data base values and the present model is 1.10 kJ/mol.

Ketones (2-alkanones)	NIST	model ΔHf	model-exp	ABS (model-exp)
2-propanone	-218.00	-217.72	0.28	0.28
2-butanone	-238.50	-238.35	0.15	0.15
2-pentanone	-259.10	-258.98	0.12	0.12
2-hexanone	-279.98	-279.61	0.37	0.37
2-nonanone	-340.80	-341.50	-0.70	0.70
3-pentanone	-257.00	-258.98	-1.98	1.98
3-hexanone	-278.25	-279.61	-1.36	1.36
4-heptanone	-298.3	-300.24	-1.94	1.94
2-nonanone	-340.8	-341.50	-0.70	0.70
5-nonanone	-344.9	-341.50	3.40	3.40
averaged absolute difference				1.10

Table S7. Experimental and model values for mono- and dicarboxylic acids. All values in kJ/mol. Experimental values were taken from NIST for comparison with model values, and if not available CAPEC data base values were used.

Carboxylic acids	NIST	NIST incr.	model ΔHf	model-exp	ABS (model-exp)
acetic acid	-433		-433.36	-0.36	0.36
propanoic acid	-455.8	-22.8	-453.99	1.81	1.81
butanoic acid	-475.9	-20.1	-474.62	1.28	1.28
pentanoic acid	-491	-15.1	-495.25	1.25	1.25
hexanoic acid	-512	-21	-515.88	-0.78	0.78
heptanoic acid	-538.6	-26.6	-536.51	2.09	2.09
octanoic acid	-555	-16.4	-557.14	-2.14	2.14
nonanoic acid	-578	-23	-577.77	0.23	0.23
decanoic acid			-598.4	-4.10	4.1
undecanoic acid			-619.03	-0.03	0.03
dodecanoic acid			-639.66	0.34	0.34
tetradecanoic acid			-680.92	0.08	0.08
nonadecanoic acid			-784.07	-0.07	0.07
averaged absolute difference					1.12
propanedioic acid			-802.63	-1.43	1.43
butanedioic acid			-823.26	-0.36	0.36
pentanedioic acid			-843.89	-1.29	1.29
hexanedioic acid			-864.52	0.48	0.48
averaged absolute difference					0.89

Table S8. Experimental and model values for methyl (upper part) and other di-alkyl ethers (lower part). All values in kJ/mol. For the comparison between model and experiment NIST data were used but if not available CAPEC data base values.

Methyl-alkyl-Ethers	NIST	model ΔHf	model-exp	ABS (model-exp)
dimethylether	-184.1	-175	9.10	9.10
ethyl methyl ether	-216.4	-217.36	-0.96	0.96
methyl propyl ether		-237.99	0.21	0.21
methyl n-butyl ether		-258.62	-0.52	0.52
decyl methyl ether	-381.1	-382.4	-1.30	1.30
averaged absolute difference				2.42

Di-alkyl ethers	NIST	NIST incr.	model ΔHf	model-exp	ABS (model-exp)
diethylether	-252		-252.72	-0.72	0.72
di-n-propylether	-296	-44	-293.98	2.02	2.02
di-n-butylether	-334	-38	-335.24	-1.24	1.24
di-n-pentylether	-390	-56	-376.5	13.50	13.50
di-n-hexylether			-417.76	-2.26	2.26
ethyl propyl ether			-273.35	-1.15	1.15
averaged absolute difference					3.48

Table S9. Experimental and model values for alkenes. All values in kJ/mol. The absolute average deviation between model and experimental data is only 0.17 kJ/mol when we adopt the data from Rossini et al. [22, 23].

1-Alkenes	Rossini	Rossini incr.	NIST	model ΔHf	model-exp	ABS (model-exp)
ethylene	52.32		52.4	62.5		
1-propene	20.43	-31.89	20.4	20.14	-0.29	0.29
1-butene	1.17	-19.26	-0.63	-0.49	-1.66	1.66
1-pentene	-20.94	-22.11	-22	-21.12	-0.19	0.19
1-hexene	-41.70	-20.77	-42	-41.75	-0.05	0.05
1-heptene	-62.34	-20.64	-63	-62.38	-0.04	0.04
1-octene	-82.99	-20.64	-82.9	-83.01	-0.02	0.02
1-nonene	-103.59			-103.64	-0.05	0.05
1-decene	-124.23	-20.64	-124.5	-124.27	-0.04	0.04
1-undecene	-144.87			-144.9	-0.03	0.03
1-dodecene	-165.47	-20.60	-165.3	-165.53	-0.06	0.06
1-tridecene	-186.11			-186.16	-0.05	0.05
1-tetradecene	-206.75			-206.79	-0.04	0.04
1-pentadecene	-227.40			-227.42	-0.02	0.02
1-hexadecene	-248.00	-20.60	-248.4	-248.05	-0.05	0.05
1-octadecene	-289.24			-289.31	-0.07	0.07
1-eicosene	-330.48			-330.57	-0.09	0.09
averaged absolute difference						0.17

Table S10. Experimental and model values for the 2-enes and 3-enes. All values in kJ/mol. The averaged absolute difference between the experimental and model values was calculated as 0.55 kJ/mol, adopting the Rossini et al. values and if not available NIST data and for trans-2-octene from the CAPEC data base.

2-, 3-alkenes	Rossini	NIST	model ΔHf	model-exp	ABS (model-exp)
trans-2-butene	-10.07	-10.80	-11.22	-1.15	1.15
trans-2-pentene	-31.78	-32.00	-31.85	-0.07	0.07
trans-2-hexene	-52.59	-48.00	-52.48	0.11	0.11
trans-3-Hexene	-52.59	-48.00	-52.48	0.11	0.11
trans-2-heptene		-73.00	-73.11	-0.11	0.11
trans-3-heptene		-73.00	-73.11	-0.11	0.11
trans-2-octene			-93.74	1.56	1.56
cis-2-butene	-5.70		-6.72	-1.02	1.02
cis-2-pentene	-27.26		-27.35	-0.09	0.09
cis-2-hexene	-48.40		-47.98	0.42	0.42
cis-3-hexene	-48.40		-47.98	0.42	0.42
cis-2-heptene		-70.00	-68.61	1.39	1.39
averaged absolute difference					0.55

Table S11. Experimental and model values for the 1-alkenes with an alkyl substituent *not directly attached* to the double bond carbon atom. The model was compared (model-exp) using the data available from Rossini et al. [22] and if not available from the CAPEC data base. The averaged absolute difference between the model values according to Eq. (6) and the experimental values was found to be 2.54 kJ/mol.

1-Alkenes + substituent NOT at double bond	Rossini	model ΔHf	model-exp	ABS (model-exp)
3-methyl-1-butene	-28.97	-26.22	2.75	2.75
3-methyl-1-pentene	-46.14	-46.85	-0.71	0.71
3-ethyl-1-pentene		-67.48	-3.38	3.38
4-methyl-1-pentene	-48.82	-46.85	1.97	1.97
3-methyl-1-hexene		-63.48	3.21	3.21
4-methyl-1-hexene,		-63.48	3.22	3.22
averaged absolute difference				2.54

Table S12. Experimental and model values for the 2-alkenes with an alkyl substituent *directly attached* to the double bond. The last row provides the averaged absolute difference between the experimental Rossini data [22] and our model, being 1.00 kJ/mol.

=2-Alkenes + subsituent at double bond	Rossini	NIST	model ΔHf	model-exp	ABS (model-exp)
2-methyl-2-butene	-42.6	-41	-42.85	-0.25	0.25
2,3-dimethyl-2-butene	-67.6	-70	-68.58	-0.98	0.98
2-methyl-2-pentene	-62.63		-63.48	-0.85	0.85
trans-3-methyl-2-pentene	-65.4	-63.5	-63.48	1.92	1.92
averaged absolute difference					1.00

Table S13. Experimental and model values for the 1-alkenes with an alkyl substituent directly attached to the double bond carbon atom. The last row provides the averaged absolute difference between the experimental Rossini data [22] and, if not available CAPEC data base values. The averaged absolute difference between model and experimental values was found to be 1.21 kJ/mol.

2-(M)ethyl-1-alkenes	Rossini	NIST	model ΔHf	model-exp	ABS (model-exp)
2-methyl-1-propene	-14.00		-14.72	-0.72	0.72
2-methyl-1-butene	-36.34	-35.00	-35.35	0.99	0.99
2-ethyl-1-butene	-54.10		-55.98	-1.88	1.88
2-methyl-1-pentene	-56.78		-55.98	0.80	0.80
2-ethyl-1-pentene			-76.61	-1.97	1.97
2-methyl-1-hexene			-76.61	0.62	0.62
2-ethyl-1-butene	-54.1		-55.98	-1.88	1.88
2,3-dimethyl-1-butene	-61.88	-64	-61.08	0.80	0.8
averaged absolute difference					1.21

Table S14. Experimental and model values for alkynes. All values in kJ/mol. [i] For explanation see text. The Rossini data originate from Ref. [25]. Model values are compared to Rossini's data and if not available with NIST data.

1-alkynes	Rossini	NIST	model ΔHf	model-exp	ABS (model-exp)
ethyne	226.9		229	2.1	2.1
1-propyne	185.6	185.4	186.64	1.04	1.04
1-butyne	166.2	166	166.01	-0.19	0.19
1-pentyne	144.45	144.3	145.38	0.93	0.93
1-hexyne		122.3	124.75	2.45	2.45
1-heptyne		103	104.12	1.12	1.12
1-octyne		80.7	83.49	2.79	2.79
1-nonyne		62.3	62.86	0.56	0.56
1-decyne		41.9	42.23	0.33	0.33
3-methyl-1-butyne	136.5		140.28	3.78	3.78
averaged absolute difference					1.53
2-, 3-, 4- and 5-alkynes	Rossini [i]	NIST [i]	model ΔHf	model-exp	ABS (model-exp)
2-butyne	145	145-148	144.28	-0.72	0.72
2-pentyne	128.95	128.9	123.65	-5.25	5.25
3-hexyne		105.4	103.02	-2.38	2.38
3-heptyne		82.8	82.39	-0.41	0.41
3-octyne		62.5	61.76	-0.74	0.74
2-octyne		63.8	61.76	-2.04	2.04
4-octyne		60.1	61.76	1.66	1.66
3-nonyne		42	41.13	-0.87	0.87
4-decyne		19.9	20.5	0.6	0.6
2-decyne		23.6	20.5	-3.1	3.1
5-decyne		18.7	20.5	1.8	1.8
averaged absolute difference					1.78

Table S15. Experimental and model values for the primary amines. All values in kJ/mol. The differences between model and experimental data are based on the Rossini value for ethylamine [24, page 623], NIST values when available, and otherwise CAPEC data base values. The averaged absolute difference is 1.20 kJ/mol without taking into account methylamine, for explanation see text.

n-alkylamines	Rossini	NIST	model ΔHf	model-exp	ABS (model-exp)
methylamine		***-23.50***	***-29.36***	***-5.86***	***5.86***
ethylamine	-48.57		-49.99	-1.42	1.42
propylamine		-70.00	-70.62	-0.62	0.62
butylamine		-95.00	-91.25	3.75	3.75
pentylamine			-111.88	1.12	1.12
hexylamine			-132.51	0.79	0.79
heptylamine			-153.14	0.86	0.86
octylamine		-173.50	-173.77	-0.27	0.27
nonamine			-194.40	0.80	0.80
averaged absolute difference					1.20

Table S16. Experimental and model values for substituted benzenes. Experimental data from Rossini et al. [28, 29]. (a) Benzene and mono-alkylbenzenes. Evaluation of (model-exp) using experimental data from Rossini et al., if not available NIST (only benzene, (1-methylethyl)). (b) Di-alkylbenzenes. Experimental data from Rossini et al., if not available NIST (only ethyltoluene), and otherwise the CAPEC data base. (c). Tri-alkylbenzenes. Experimental data from Rossini et al., if not available from the CAPEC data base. (d) Tetra-alkylbenzenes. Experimental data from Rossini et al.

(a)

Mono-alkyl substituted benzenes	Rossini	Rossini incr.	NIST	model ΔHf	model-exp	ABS (model-exp)
benzene	82.99		82.9	84.5	1.51	1.51
methylbenzene (toluene)	50.08	-32.91	50	48.14	-1.94	1.94
benzene, (1-methylethyl)-			3.9	1.78	-2.12	2.12
benzene, (1-methylpropyl)- (=sec-Butylbenzene)	-17.5		-17.4	-14.85	2.65	2.65
benzene, ethyl-	29.8	-20.28		27.51	-2.29	2.29
benzene, propyl	7.83	-21.97	7.8	6.88	-0.95	0.95
benzene, butyl-	-13.82	-21.65	-13	-13.75	0.07	0.07
benzene, pentyl-	-34.46	-20.64		-34.38	0.08	0.08
benzene, hexyl-	-55.05	-20.59		-55.01	0.04	0.04
benzene, heptyl-	-75.70	-20.65		-75.64	0.06	0.06
benzene, octyl-	-96.30	-20.60		-96.27	0.03	0.03
benzene, nonyl-	-116.94	-20.64		-116.9	0.04	0.04
benzene, decyl	-137.58	-20.64		-137.53	0.05	0.05
benzene, n-undecyl	-158.18	-20.60		-158.16	0.02	0.02
benzene, dodecyl	-178.83	-20.64		-178.79	0.04	0.04
tridecylbenzene	-199.43	-20.60		-199.42	0.01	0.01
benzene, tetradecyl-	-220.1	-20.67		-220.05	0.05	0.05
n-hexadecylbenzene	-261.31	-20.61		-261.31	0.00	0.00
isobutylbenzene	-21.6			-18.85	2.75	2.75
tert-butylbenzene	-22.7			-18.85	3.85	3.85
averaged absolute difference						0.88

(b)

Di-substituted alkylbenzenes	Rossini	NIST	model ΔHf	model-exp	ABS (model-exp)
benzene, 1,2-dimethyl	19	19	18.28	-0.72	0.72
benzene, 1,3-dimethyl	17.3	17.2	18.28	0.98	0.98
benzene, 1,4-dimethyl	18	17.9	18.28	0.28	0.28
benzene, 1,2-diethyl-	-19		-22.98	-3.98	3.98
benzene, 1,3-diethyl-	-21.9		-22.98	-1.08	1.08
benzene, 1,4-diethyl-	-22.3		-22.98	-0.68	0.68
benzene, 1-methyl-3-propyl-			-22.98	1.16	1.16
benzene, 1,3-bis(1-methylethyl)-			-74.44	3.16	3.16
benzene, 1-methyl-4-(1-methylethyl)-			-28.08	0.92	0.92
benzene, 1-methyl-2-propyl-	-21.6		-22.98	-1.38	1.38
benzene, 1-methyl-4-propyl-	-25		-22.98	2.02	2.02
benzene, 1-methyl-3-ethyl-	-1.9		-2.35	-0.45	0.45
benzene, 1-methyl-2-ethyl-	1.2		-2.35	-3.55	3.55
benzene, 1-methyl-4-ethyl-	-3.3		-2.35	0.95	0.95
benzene, 1-Methyl·2-Isopropyl	-25.5		-28.08	-2.58	2.58
m-ethyltoluene		-1.9	-2.35	-0.45	0.45
averaged absolute difference					1.52

(c)

Tri-substituted alkylbenzenes	Rossini	model ΔHf	model-exp	ABS (model-exp)
benzene, 2-ethyl-1,3-dimethyl-	-29.8	-33.21	-3.41	3.41
benzene, 1-ethyl-2,4-dimethyl-		-33.21	-2.41	2.41
benzene, 1-ethyl-3,5-dimethyl-	-35.6	-33.21	2.39	2.39
benzene, 1,2,4-trimethyl-	-13.9	-12.58	1.32	1.32
benzene, 1,2,3-trimethyl-	-9.6	-12.58	-2.98	2.98
benzene, 1,3,5-trimethyl-		-12.58	3.32	3.32
1,1'-biphenyl, 4,4'-dimethyl-		114.28	2.98	2.98
benzene, 2-ethyl-1,4-dimethyl-		-33.21	-1.03	1.03
benzene, 4-ethyl-1,2-dimethyl-		-33.21	-1.12	1.12
averaged absolute difference				2.33

(d)

Tetra-substituted alkylbenzenes	Rossini	model ΔHf	model-exp	ABS (model-exp)
benzene, 1,2,3,5-tetramethyl-	-44.85	-44.94	-0.09	0.09
benzene, 1,2,3,4-tetramethyl-	-41.95	-44.94	-2.99	2.99
benzene, 1,2,4,5-tetramethyl-	-45.3	-44.94	0.36	0.36
averaged absolute difference				1.15

Table S17. Experimental and model values for substituted naphthalenes. All values in kJ/mol. Experimental data from Rossini et al. [29], if not available from the CAPEC data base. The model value for naphthalene equals the Rossini experimental value as naphthalene is taken as a Group itself.

Naphthalenes	Rossini c.s.	NIST	model ΔHf	model-exp	ABS (model-exp)
naphthalene	151.78	150,6			
naphthalene, 1-methyl-	116.94	116.1	115.44	-1.46	1.46
naphthalene, 2-methyl-	116.19		115.44	-0.66	0.66
naphthhalene, 2,7-dimethyl			85.58	1.78	1.78
1-ethylnaphthalene			94.81	-2.09	2.09
2,6-dimethylnaphthalene			85.58	1.61	1.61
averaged absolute difference					1.52