Bond Additivity Corrections for G3B3 and G3MP2B3 Quantum Chemistry Methods

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Supporting Information (8 pages in total)

Heats of formation for the reference set of molecules used for obtaining the BAC parameters are listed in Table S1. The experimental heats of formation used are those recommended by IUPAC-subcommittee.[1] Unless otherwise noted, most of the recommended experimental values have been taken from evaluations or reviews. For comparison, the experimental values used in the previous BAC-G2[2] test set are provided.

TABLE S1: Experimental Heats of Formation for the Reference Set of Molecules

molecules	heat of formation (kcal/mol)	
	current work[1]	previous work[2]
C	171.29	171.29
CCl_4	-22.90 ± 0.14	-22.90
CF_4	-223.21	-223.00
CH_2 $^1A_1$	102.46 ± 0.95	102.80
CH_2 $^3B_1$	93.40 ± 0.95	93.80
CH_2Cl_2	-22.80 ± 0.19	-22.80
CH_2F_2	-108.30 ± 1.90	-108.30
H_2CNH	21.58	21.58
CH_2NH_2	35.70	35.70
CH_2O	-25.96	-25.96
CH_2OH	-4.26 ± 0.31	-2.10
$CH_2(OH)_2$	-93.50	-93.50
CH_3	35.02 ± 0.10	34.89
CH_3Cl	-19.60 ± 0.16	-19.60
CH_3F	-55.60	-55.60
CH_3NH	42.40	42.40
CH_3NH_2	-5.50	-5.50
CH_3NHNH_2	22.60	22.60
CH_3NO_2	-17.86	-17.86
CH_3O	4.20 ± 0.90	4.20
CH_3ONO	-15.60	-15.60
CH_3ONO_2	-28.60	-28.60
CH_3OO ^2A”	2.50	2.50
CH_3OOH	-31.31	-31.31
CH_3SH	-5.50 ± 0.14	-5.50
CH_3SiH_3	-6.93	-6.93

CH_4	-17.88	-17.88
$CHCl_3$	-24.70 ± 0.31	-24.70
CHF_3	-166.89	-166.70
CO	-26.41 ± 0.04	-26.41
CO_2	-94.05 ± 0.03	-94.05
CS	66.63 ± 0.90	65.00
CS_2	28.01	28.01
HCN	32.27 ± 1.90	32.27
HCO	10.31	10.00
HCOOH	-90.54 ± 0.12	-90.54
HNCS	30.00	30.00
OCS	-33.99	-33.94
CH $^4\Sigma$ -	157.41	157.41
CH_3PH_2	-4.36	-4.36
CCl_2F_2	-117.90	-117.90
C ^{5}S	267.70	267.70
CH_3OH	-48.18 ± 0.05	-48.18
$-CH_2CH_2O-$	-12.58	-12.58
$-CH_2CH_2S-$	19.69	19.69
C_2H $^2\Sigma$ +	135.00 ± 0.69	135.00
HCCH	54.50 ± 0.24	54.50
HC(O)CHO	-50.66	-50.66
H_2CCH_2	12.53	12.53
C_2H_5	28.92 ± 0.38	29.00
CH_2CO	-11.40 ± 0.38	-11.40
$CH_3CH_2NH_2$	-11.35	-11.35
CH_3CH_2OH	-56.10	-56.10
CH_3CH_2ONO	-24.80	-24.80
CH_3CH_2SH	-11.00	-11.00
CH_3CHO	-39.63 ± 0.10	-39.63
CH_3CO	-2.44 ± 0.29	-2.44
CH_3NHCH_3	-4.43	-4.43
CH_3OCH_3	-43.99	-43.99
CH_3OOCH_3	-30.00 ± 0.31	-30.00
CH_3SCH_3	-8.89	-8.89
$OS(CH_3)_2$	-36.09	-36.09
$SiH_2(CH_3)_2$	-22.70	-22.70
CH_3COOH	-103.26	-103.26
CH_3CH_3	-20.10	-20.10
$-CH_2CH_2CH_2-$	12.73	12.73
$-CH_2OCH_2OCH_2O-$	-113.20	-113.20
CH_2CCH_2	45.63	45.63
CH_2CHCH_2	40.84	39.10
CH_3CCH	44.39	44.39
$CH_3CH_2CH_3$	-24.98 ± 0.07	-24.98
CH_3CH_2CHO	-44.79	-44.79

CH_3CHCH_2	4.83	4.83
CH_3COCH_3	-51.91 ± 0.10	-51.91
$CH_3CH_2CH_2CH_3$	-30.07	-30.36
$CH_2CHCHCH_2$	26.11	26.11
CH_3CCCH_3	34.71	
$CH_3CH(CH_3)_2$	-32.41	-32.41
C_6H_{12}	-29.50	
C_6H_6	19.81	19.81
OH	8.90 ± 0.09	9.39
H	52.10	52.10
HCl	-22.06 ± 0.02	-22.06
HF	-65.32 ± 0.17	-65.32
HN_3	70.30	70.30
HNO	27.02 ± 0.06	23.80
HO_2 ^{2}A”	3.50	3.50
$HONO_2$	-32.28	-32.28
HONO CIS	-18.34	-18.34
HONO TRANS	-18.84	-18.84
NH $^3\Sigma$ -	84.10 ± 2.38	84.10
HOCl	-18.67	-18.64
HNO ^{3}A”	45.50 ± 0.06	45.50
H_2	0.01	0.01
H_2NF	-5.00	-5.00
H_2O	-57.80 ± 0.01	-57.80
HOOH	-32.54	-32.54
NH_2	45.14 ± 0.31	44.30
NH_3	-10.98 ± 0.08	-10.98
H_2NNH_2	22.75	22.75
ClO	24.30 ± 0.02	24.30
FOF	5.90	5.90
ClNO	12.36	12.36
NO $^2\Pi$	21.57	21.57
N_2O	19.61	19.61
O	59.55 ± 0.02	59.55
OClO	22.80 ± 0.31	22.80
$ClNO_2$	3.00	3.00
NO_2	7.93	7.93
O_2 $^3\Sigma$ -	0.01	0.01
$FONO_2$	2.39	2.39
NO_3 $^2B_2$	17.60 ± 0.33	17.60
$ONNO_2$	19.80	19.80
O_3 $^1A_1$	34.10	34.10
O_2NNO_2	2.17 ± 0.40	2.17
NF_2	8.50	8.50
N	112.97 ± 0.10	112.97
FNNF Cis	17.90	17.90

N_2	0.01	0.01
F	18.97 ± 0.07	18.97
F_2	0.01	0.01
Cl	28.99	28.99
Cl_2	0.01	0.01
Si	107.55	107.55
$SiCl_4$	-158.20	-158.20
SiH_2 $^3B_1$	84.60	84.60
SiH_3	46.40	46.40
SiO	-24.60	-24.60
SiO_2	-66.60	-66.60
SiS	27.60	27.60
PH_2	32.80	32.80
P	75.61	75.61
PH $^3\Sigma$ -	56.80	56.80
P_2	34.20	34.20
PN	42.80	42.80
H_2S	-4.92 ± 0.12	-4.92
S	66.24 ± 0.04	66.24
SH	34.20 ± 0.68	34.20
SO $^3\Sigma$ -	1.20 ± 0.31	1.20
SO_2	-70.94 ± 0.05	-70.94
SO_3	-94.57	-94.57
SiF_4	-386.00[a]	
P_4	14.10[a]	
PH_3	1.70	1.70
$SiCl_2$	-40.30[a]	
SF_6	-291.70[a]	
ClSSCl	-4.00[a]	
$(CH_3)_2SO_2$	-89.20[a]	
$(CH_3)_3CSH$	-26.20[a]	
C_4H_8S	-8.20[a]	
-CHCHSC(CH_3)CH-	20.00[a]	
$C_5H_{10}S$	-15.20[a]	
$-CH_2SCH_2-$	19.60[a]	
Cl_2SO_2	-84.80[a]	
$C_{10}H_8$	36.08	

[a] - Heats of formation same as the ones used in Curtiss et al.[3,4]

Since the experimental heats of formation recommended by IUPAC-subcommittee are the most recent, we use these heats of formation for comparisons in our current work. Heats of formation for the molecules in the extended test set are given in Table S2. Unless otherwise indicated in Table S2, the heats of formation of molecules are those used in Curtiss et al.[3,4] Heats of formation of Al and B compounds, along with their uncertainties, are taken from different literature sources.

TABLE S2: Compounds Added into Test set of Molecules

molecules	$H_{f,298K}$ (kcal/mol)
C_2Cl_6	-32.1
C_2Cl_4	-3.0
C_2F_4	-157.9
$-CH_2CH_2NH-$	28.3
NCCN	73.8
$-CH=CHCH_2-$	66.2
-CH2CHCHCH2-	34.7
$-CH_2C(=CH_2)CH_2-$	47.9
$CH_3CH_2NO_2$	-24.4
CH_3CN	17.7
CN	105.6
CO $^3\Pi$	114.3
FNO	-15.7
HNCO	-24.9
HNNH Trans	50.9
HOF	-23.5
$HOSO_2$	-92.0
$O=C(NH_2)_2$	-58.7
O_3 Cyclic	70.0
$OHCH_2CH_2OH$	-93.9
SiH_3SiH_3	19.1
SiH_2 $^1A_1$	64.8
SiH_4	8.2
ClOO	23.3
C_2H_3	71.8
CH_2S	24.3
CH $^2\Pi$	142.5
CH_2CHCCH	70.40[5]
HCCCCH	111.00[6]
CH_3S ($^2A'$)	29.8
SCl_2	-4.2
S_2	30.7
C_2H_5Cl	-26.8
PF_3	-229.1
PCl_3	-69.0
PCl_5	-86.1
PF_5	-381.1
PO	-9.0[7]
PO_2 ($^2A_1$)	-69.6[7]
HOPO Cis	-112.4[8]
$HOPO_2$	-171.4[8]
$(HO)_2P$	-90.1[7]
$(HO)_2PO$	-158.8[7]

$(HO)_3P$	-188.8[7]
$CClF_3$	-169.2[9]
C_2F_6	-321.3[3]
$POCl_3$	-134.0[3]
CF_3CN	-118.4[4]
ClF_3	-38.0[4]
AlH_3	30.8 ± 4.8[10]
AlF_3	-139.7 ± 1.2[10]
$AlCl_3$	-289.0 ± 0.7[10]
BH_3	21 ± 2.4[10]
BF_3	-271.5 ± 0.2[11]
BCl_3	-96.68 ± 0.31[10]
AlH	59.6 ± 0.8[10]
AlF	-63.1 ± 0.7[10]
AlCl	-12.2 ± 0.7[10]
BH	106.6 ± 1.7[10]
BF	-27.701[12]
BCl	41.2 ± 6.0[10]

Table S3 lists the compounds for which the BAC-G2 had deviations higher than 1 kcal/mol. The table includes compounds not only from original reference set used for BAC-G2, but also from those in the extended test set.

TABLE S3: Errors in BAC Predicted Heats of Formation at 298 K for Compounds with Highest Errors for BAC-G2 or BAC-G3B3

Molecule	error in heat of formation at 298 K (kcal/mol)					
	BAC-G3B3	raw-G3B3	BAC-G3MP2B3	raw-G3MP2B3	BAC-G2	raw-G2
organic compounds						
CH_2Cl_2	0.8	1.0	0.6	0.0	1.1	-0.7
CS_2	-1.0	-3.0	-1.1	-5.3	-1.1	-2.2
C	-0.2	-0.1	0.2	-0.1	-1.2	-0.1
H_2CNH	-0.3	-0.6	-0.4	-0.8	-1.2	-1.0
$CHCl_3$	0.8	1.1	0.6	-0.4	1.3	-1.1
CS	0.4	-0.7	-0.6	-3.0	1.4	-0.7
$C\ ^5S$	-0.3	0.1	0.2	0.3	-1.5	0.4
CH_2OH	0.2	0.1	0.4	0.3	-1.6	0.4
HCN	-1.3	-1.7	-1.0	-1.8	-1.6	-1.2
CH_2CHCH_2	-0.6	-0.9	-0.1	-1.0	1.4	0.9
$CH_2\ ^1A_1$	-0.4	-0.8	-0.4	-1.0	-1.7	-1.2
CH_3O	0.3	0.1	0.3	0.3	1.8	0.5
$CH\ ^4\Sigma^-$	-0.1	0.1	-0.5	-0.7	2.3	3.9
$C_2H\ ^2\Sigma^+$	-0.2	-0.4	-0.2	-1.1	2.7	3.6
$-CH_2CH_2NH-$	2.1	2.5	2.1	2.6	1.4	2.0

-CH=CHCH$_2$-	2.2	1.9	2.1	1.2	1.3	2.7
C_2Cl_4	-2.2	-2.2	-2.3	-4.8	-1.8	-4.6
$OHCH_2CH_2OH$	2.7	2.5	3.0	3.0	2.3	1.2
$O=C(NH_2)_2$	3.1	3.0	3.9	4.3	2.8	1.8
C_2F_4	-3.4	-3.9	-3.1	-4.1	-1.3	-7.8
HNCO	-3.7	-4.3	-3.1	-3.9	-3.9	-4.7
CO ($^3\Pi$)	-3.7	-3.9	-4.3	-4.8	-2.0	-2.3
CH_2S	4.1	3.1	4.1	2.0	4.0	3.4
-$CH_2CHCHCH_2$-	4.6	4.3	4.5	3.5	3.6	5.3
C_2Cl_6	-7.3	-6.8	-6.4	-8.8	-7.7	-11.4
inorganic compounds						
H_2NNH_2	1.0	1.3	0.6	1.7	1.1	0.8
HN_3	-0.1	-0.3	0.4	0.1	-1.2	-0.5
$ONNO_2$	0.6	-0.3	-0.1	0.5	1.2	-1.4
H_2	-0.3	-0.5	-0.9	-1.1	-1.4	-1.4
HNO	-1.1	-1.6	-1.6	-1.7	1.5	-2.5
N	-0.3	0.0	-0.1	0.0	-1.5	0.0
O_2 $^3\Sigma$ -	-1.0	-0.1	-1.1	0.4	1.6	2.4
O_3 $^1A_1$	-0.8	0.2	-1.0	1.3	-1.6	-1.1
F	-0.1	-0.1	0.0	-0.1	1.9	-0.1
SiO	0.5	0.2	0.5	-1.0	2	1.7
$SiH_2(CH_3)_2$	0.4	1.4	0.3	1.5	2.2	0.9
NO_3 $^2B_2$	0.8	0.0	1.8	2.3	3.9	1.5
PF_3	2.1	5.8	2.3	5.5	-4.4	5.3
HNNH trans	-2.4	-2.6	-2.7	-2.8	-3.5	-3.1
HOF	2.5	3.0	2.6	3.4	2.3	2.1
Si_2H_6	-3.4	-1.7	-3.3	-1.6	-1.1	-3
$HOSO_2$	3.9	7.3	3.8	7.8	1.6	8.1
O_3 cyclic	-4.2	-3.6	-5.6	-3.3	-4.3	-4.5
ClOO	4.2	5.2	4.5	5.7	5.2	6.4
FNO	-5.0	-5.5	-5.3	-5.3	-5.2	-7.7
PCl_5	-7.2	1.1	-7.8	-2.2	-7.7	0.4

From the table, we observe that the BAC-G3B3 procedure has addressed many of the errors for those species for which BAC-G2 is not accurate within 2 kcal/mol. In particular, highly oxidative species or species involving dative bonds (e.g. NO_3, HN_3 etc.) have improved significantly. Other molecules in the table show consistent predicted values across the row, independent of the quantum chemistry method or whether BAC corrections are applied. This suggests that perhaps the experimental values may be in error. Further investigation of both the experimental and theoretical values to ascertain their accuracy is recommended. The recent changes in the recommended values of experimental heats of formation (see Table S4) are, for the most part, supported by the findings of the BAC-G3B3 method.

Specifically, the NIST Computational Chemistry Comparison and Benchmark Database has suggested alternative experimental heats of formation for some molecules whose heats of formation vary significantly from the experimental values used in this

work. For example, the following compounds have significant changes in experimental heats of formation (Table S4). Using the alternative heats of formation for those compounds would reduce the errors in the BAC-G3B3 predicted heats of formation. Those compounds would no longer be outliers (errors < 2 kcal/mol).

TABLE S4: Heats of Formation (kcal/mol) at 298 K Suggested by NIST Computational Chemistry Comparison and Benchmark Database

compound	alternative $\Delta H_f^0{}_{298}$	this work $\Delta H_f^0{}_{298}$
$-CH_2CH_2NH-$	30.1	28.3
$OHCH_2CH_2OH$	-92.6	-93.9
$O=C(NH_2)_2$	-56.6	-58.7
CH_2S	27.4	24.3
$-CH_2CHCHCH_2-$	37.5	34.7

Table S5 shows the differences in experimental heats of formation of molecules reported in various literature sources.

TABLE S5: Different Experimental Heats of Formation Reported in Literature

molecules	previous work[2]	Chase et al. and Binkley et al. [13,14]	IUPAC-subcommittee	
	$H_{f,298K}$	$H_{f,298K}$	$H_{f,298K}$	reference
OH	9.30	9.40	8.90	[15]
NH_2	44.30	45.10	45.14	[16]
HNO	23.80		27.02	[17]
CH_2 ($^3B_1$)	93.80	93.70	93.40	[16]
CH_2 ($^1A_1$)	102.80	102.80	102.46	[16]
CH_3	34.85	35.00	35.02	[16]
CN	103.97	104.90	105.60	[16]
HCO	10.00	10.0	10.31	[18,19]
CH_2OH	-2.10		-4.26	[20]
C_2H_3	72.40	71.6	71.77	[16]
C_2H_5	29.00	28.9	28.92	[16]
CH_3CN	15.37	18.0	17.70	[21]
$CH_2CH=CH_2$	39.10		40.84	[16]
n-C_4H_{10}	-30.36	-30.0	-30.07	[22]
HOF	-23.42		-23.52	[12]
CHF_3	-166.70	-166.6	-166.89	[16]
CF_4	-223.00	-223.0	-223.21	[23]
CS	65.00		66.63	[16]
OCS	-33.94		-33.99	[24]
HOCl	-18.64	-17.8	-18.67	[24,25]

Experimental heats of formation from Chase et al. and Binkley et al. have been used for comparison against G3 and G3X predicted heats of formation presented in Curtiss et al.[26]

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