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Citation: *The Journal of Chemical Physics* **113**, 9377 (2000); doi: 10.1063/1.1321306

View online: <http://dx.doi.org/10.1063/1.1321306>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/jcp/113/21?ver=pdfcov>

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## ARTICLES

## A set of standard enthalpies of formation for benchmarking, calibration, and parametrization of electronic structure methods

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(Received 22 March 2000; accepted 8 September 2000)

A comprehensive set of 600 experimental standard enthalpies of formation ( $\Delta H_f^0$ ) is presented. With its diverse species, many possessing less usual geometries and bonding situations, this compilation is capable of uncovering deficiencies in approaches of quantum chemistry that are not detectable with smaller sets of  $\Delta H_f^0$  values. Its usefulness in benchmarking, calibration, and parametrization of new electronic structure methods is illustrated with the development of the B3LYP/6-311++G\*\* bond density functional scheme. This scheme, which is sufficiently inexpensive in terms of computer time and memory to allow predictions even for molecules as large as the C<sub>60</sub> fullerene, requires only single point calculations at optimized geometries. It yields values of  $\Delta H_f^0$  with the average absolute error of 3.3 kcal/mol, rivaling more expensive methods in accuracy (especially for larger systems). A list of species that are poorly handled by a typical hybrid density functional used in conjunction with a moderate-size basis set is given. This list is intended for rigorous testing of new density functionals. © 2000 American Institute of Physics.  
[S0021-9606(00)30345-2]

### I. INTRODUCTION

The last decade of the twentieth century has witnessed extraordinary progress in electronic structure theory and its applications. Energies of small molecules, ions, and radicals are now routinely predicted within 1 kcal/mol, while quantum-chemical calculations on medium-size organic species that were once the domain of semiempirical methods are now dominated by *ab initio* approaches, which are also making inroads into modeling of small peptides and other biologically important systems. These impressive strides have been made possible by a confluence of substantial gains in hardware performance, efforts directed toward improvements in the computational economy of software, and the development of new formalisms.

The new formalisms of electronic structure theory, such as extrapolative approaches that aim at predicting thermochemical data with chemical accuracy,<sup>1-3</sup> density functionals of increasing sophistication,<sup>4,5</sup> and semiempirical methods,<sup>6,7</sup> are emerging at a rapid pace. Benchmarking, calibration, and parametrization of those formalisms call for extensive calculations, in which the computed properties are compared with their experimental counterparts for a large number of chemical systems. Test sets of standard enthalpies of formation ( $\Delta H_f^0$ ) that enable quantitative assessments of the accuracy of thermodynamic predictions are of particular interest. Several such sets have been published in the chemical literature. For instance, large compilations of experimentally deter-

mined values of  $\Delta H_f^0$  were employed in parametrizations of semiempirical methods such as PM3.<sup>8,9</sup> Those compilations were later augmented with new data pertaining to compounds of a few additional elements.<sup>10-12</sup> On the other hand, the old values of  $\Delta H_f^0$  have never been updated for compounds of elements such as boron.<sup>13,14</sup>

In 1991, a test set consisting of 55 dissociation energies, 38 ionization potentials (IPs), 25 electron affinities (EAs), and 7 proton affinities (PAs) was published.<sup>15</sup> This “G2-1 set”<sup>1</sup> was subsequently revised and appended with more data. The resulting “extended G2 neutral molecule test set” of 148  $\Delta H_f^0$  values<sup>16</sup> has been employed in parametrizations of new density functionals<sup>4,5</sup> as well as (with a corrected standard enthalpy of formation of COF<sub>2</sub>) in assessments of the B3LYP/6-311++G(3df,2p) level of theory and various extrapolative methods of the G2 and CBS families.<sup>17</sup> A further augmentation with 88 IPs, 58 EAs, and 8 PAs produced the G2/97 test set of 302 energies,<sup>18</sup> which found an immediate use in parametrizations of the G3,<sup>1</sup> G3(MP2), G3//B3LYP, and G3(MP2)//B3LYP<sup>2</sup> approaches.<sup>19</sup> Other, less extensive test sets are also available. Predictions of the G2, G2(MP2), CBS-4, and CBS-Q methods were compared with the values of  $\Delta H_f^0$  determined experimentally for 166 molecules, radicals, anions, and cations.<sup>20</sup> A compilation of analogous data for a large number of diverse hydrocarbons was also published.<sup>21</sup>

Needless to say, successful development and implementation of new electronic structure methods hinges upon the availability of test sets comprising reliable experimental values of  $\Delta H_f^0$  of chemical species with diverse bonding situations. Unfortunately, none of the aforementioned compilations is suitable for serving as such a test set. On one hand,-

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although the tables assembled in the process of parametrization of semiempirical methods contain diverse compounds, the quality of the quoted data is often substandard. On the other hand, the data included in the G2/97 test set is highly reliable but too narrow in scope to be useful for evaluating the performance of quantum-chemical methods in calculations on “less usual” and/or larger-size species. The implications of this lack of diversity are well illustrated by the recent studies that have uncovered large errors in the standard enthalpies of formation of hypervalent species such as  $\text{PCl}_5$ ,  $\text{SF}_6$ , and  $\text{H}_2\text{SO}_4$  predicted by density functional theory (DFT) methods, which otherwise perform reasonably well even for the “difficult” molecules such as  $\text{O}_3$ .<sup>6,22,23</sup> As parametrization of density functionals and extrapolative methods will almost certainly remain a viable option for the reduction of residual errors in the treatment of electron correlation,<sup>24</sup> the need for a single source of reliable data pertaining to a large number of chemical species is quite urgent.

A compilation addressing this need is presented here.

## II. DATA ACQUISITION AND ORGANIZATION

The process of gathering the data compiled in Table I involved several stages. First, in light of the scarcity of reliable experimental values of  $\Delta H_f^0$  for compounds of heavier elements,<sup>25</sup> it was decided at the commencement of this project that only the species containing the first- and second-row elements should be included in the test set. A massive literature search was then undertaken, in which the previously published compilations<sup>8–14,16,20,21</sup> were employed as the initial source of entries. Almost immediately, the search revealed a disturbingly high incidence of incorrect data in many of the older publications.<sup>8–14</sup> Rather surprisingly, in most cases this problem was found not to stem from an inadequate accuracy of experimental values but from trivial mistakes and omissions such as typographic errors, incorrect literature citations, wrong conversion factors, unreasonable assumptions and circular arguments employed in the treatment of experimental data, the unjustified use of bond additivity schemes, occasional confusion about the reference states for elements, and a common failure to make the distinction between two thermodynamic conventions for the electron. Many of these mistakes were uncovered even in such widely used references as the JANAF tables,<sup>26</sup> where they propagate undisturbed from one edition to another.

Second, in the process of data acquisition and verification, over 100 literature sources were consulted.<sup>26–131</sup> In all instances, the original experimental data were carefully evaluated for reliability. Third, where necessary, the values of  $\Delta H_f^0$  were corrected to ensure the adherence to “the ion convention” (“the stationary electron convention”), according to which the standard enthalpy of the electron is set to zero. Similarly, some older data were adjusted to conform to the commonly used reference states of the elements,<sup>27</sup> i.e., white phosphorus for P and orthorhombic crystalline sulfur for S. Values of  $\Delta H_f^0$  derived from standard enthalpies of protonation/deprotonation, ionization potentials, electron affinities, and standard enthalpies of other processes were recalculated to ensure their consistency with the data for the

auxiliary species included in the test set.

The resulting compilation of the standard enthalpies of formation of 600 species is presented in Table I. The test set comprises 514 neutrals (452 singlets, 51 doublets, and 11 triplets), 55 anions (51 singlets, 3 doublets, and 1 triplet), and 31 cations (27 singlets and 4 doublets). The entries in Table I are ordered according to ascending numbers of nuclei and electrons. Where needed, the electronic states of the species are indicated. The uncertainties of the quoted values of  $\Delta H_f^0$  vary widely for several reasons. First of all, like the enthalpies themselves, the errors are size extensive quantities that increase with the molecular size. Second, species with somewhat less accurate values of  $\Delta H_f^0$ , such as carbenes (entries 78, 79, 93, 113, 115, 131, 139, and 152), benzynes (entries 391–396), polycondensed benzenoid hydrocarbons (entries 538, 554, 562, 569, 570, 584, 585, 591–594, and 596), molecules with dative bonds (entries 436, 441, 525, and 565), and others, have been included in the present set in order to ensure diversity of electronic structures and bonding situations. For the same reason, several data for hypervalent molecules, ions, and radicals of sulfur, phosphorus, and chlorine have been admitted into this compilation. The scarcity of accurate values of  $\Delta H_f^0$  is particularly acute for compounds of lithium (8 entries), beryllium (8 entries), boron (20 entries), sodium (18 entries), magnesium (6 entries), and aluminum (16 entries). For these compounds and for those of phosphorus and silicon, the experimental errors are often quite large despite the deliberate selection of only the most reliable values from among the available data. In a few cases, the errors are simply not available and as such are marked “n/a” in Table I.

## III. EXAMPLE OF APPLICATION: PARAMETRIZATION AND ASSESSMENT OF B3LYP/6-311++G\*\* BOND DENSITY FUNCTIONAL SCHEMES

In the bond density function (BDF) approach, the standard enthalpy of formation  $\Delta H_f^0(X)$  of a species  $X$  is approximated by

$$\Delta H_f^0(X) = E(X) + e_Q Q(X) + e_S N_S(X) + \sum_I e_1(Z_I) + \sum_{I-J} e_2(\rho_{IJ}, R_{IJ}, Z_{IJ}, \alpha_{IJ}, \beta_{IJ}), \quad (1)$$

where  $E(X)$ ,  $Q(X)$ , and  $N_S(X)$  are, respectively, the total energy, the charge, and the number of unpaired electrons in  $X$ .<sup>6</sup> In Eq. (1), the first sum runs over all the nuclei present in  $X$  and the second one over all the attractor interaction lines  $I-J$  that connect them. The quantities  $e_Q$  and  $e_S$ , as well as the atomic equivalents  $e_1(Z)$  that depend on the nuclear charge  $Z$ , are obtained by fitting the predicted values of  $\Delta H_f^0$  to their experimental counterparts for members of a pre-defined training set. The BDF  $e_2(\rho_{IJ}, R_{IJ}, Z_{IJ}, \alpha_{IJ}, \beta_{IJ})$  is a function of five variables: the electron density  $\rho_{IJ}$  at the bond critical point on the line  $I-J$ , its arclength  $R_{IJ}$ , the product  $Z_{IJ}$  of the nuclear charges  $Z_I$  and  $Z_J$  of the attractors  $I$  and  $J$ ,<sup>132</sup> the geometric mean  $\alpha_{IJ}$  of the two negative eigenvalues of the density Hessian at the bond critical point, and the corresponding positive eigenvalue  $\beta_{IJ}$ . Since the actual form

TABLE I. The set of 600 experimental values of  $\Delta H_f^0$ .

Entry	Species (el state or mult)	Number of		$\Delta H_f^0$ (kcal/mol)		Source	Entry	Species (el state or mult)	Number of		$\Delta H_f^0$ (kcal/mol)		Source
		Nuclei	Elec	Value	Error				Nuclei	Elec	Value	Error	
1	H <sup>+</sup>	1	0	365.7	0.0	26	66	SF <sup>-</sup>	2	26	-49.9	2.5	41
2	H·	1	1	52.1	0.0	27	67	ClO <sup>-</sup>	2	26	-28.3	0.5	36
3	Li <sup>+</sup>	1	2	162.4	0.0	26	68	Si <sub>2</sub> ( <sup>3</sup> Σ <sub>g</sub> <sup>-</sup> )	2	28	139.9	n/a	30
4	H <sup>-</sup>	1	2	34.7	0.0	26	69	NaCl	2	28	-43.6	n/a	30
5	Li·	1	3	38.1	0.2	27	70	AlS·( <sup>2</sup> Σ <sup>+</sup> )	2	29	57.0	2.0	26
6	Be <sup>+</sup>	1	3	289.9	1.2	26	71	P <sub>2</sub>	2	30	34.3	n/a	30
7	Be	1	4	77.4	1.2	27	72	AlCl	2	30	-12.3	1.5	26
8	B <sup>+</sup>	1	4	325.2	3.0	26	73	AlS <sup>-</sup>	2	30	-3.0	2.1	42
9	Li <sup>-</sup>	1	4	23.8	0.02	26	74	SiS (singlet)	2	30	25.3	3.0	26
10	F <sup>-</sup>	1	10	-59.3	0.3	28	75	SiCl·( <sup>2</sup> Π <sub>1/2</sub> )	2	31	47.4	1.6	26
11	Na <sup>+</sup>	1	10	144.2	0.2	26	76	S <sub>2</sub>	2	32	30.7	0.1	27
12	Mg <sup>+</sup>	1	11	211.5	0.3	26	77	Cl <sub>2</sub>	2	34	0.0	n/a	29
13	Na·	1	11	25.7	0.2	27	78	CH <sub>2</sub> ( <sup>3</sup> B <sub>1</sub> )	3	8	92.8	0.5	43
14	Mg	1	12	35.2	0.2	27	79	CH <sub>2</sub> ( <sup>1</sup> A <sub>1</sub> )	3	8	101.8	0.5	44
15	Al <sup>+</sup>	1	12	216.7	1.0	26	80	NH <sub>2</sub> ·( <sup>2</sup> B <sub>1</sub> )	3	9	45.1	0.3	32
16	Na <sup>-</sup>	1	12	13.0	0.02	26	81	OH <sub>2</sub>	3	10	-57.8	0.01	26
17	Cl <sup>-</sup>	1	18	-54.4	0.06	28	82	NH <sub>2</sub> <sup>-</sup>	3	10	27.3	0.4	28
18	H <sub>2</sub> <sup>+</sup> ·( <sup>2</sup> Σ <sub>g</sub> <sup>+</sup> )	2	1	355.8	0.0	26	83	FH <sub>2</sub> <sup>+</sup>	3	10	184.9	1.9	45
19	H <sub>2</sub>	2	2	0.0	n/a	29	84	LiOH	3	12	-54.7	1.2	46
20	LiH	2	4	33.3	n/a	30	85	HO≡C·( <sup>2</sup> Σ <sup>+</sup> )	3	13	135.1	0.7	32
21	BeH·( <sup>2</sup> Σ <sup>+</sup> )	2	5	81.7	n/a	30	86	HCN	3	14	31.5	1.0	47
22	Li <sub>2</sub>	2	6	51.6	0.7	26	87	HCC <sup>-</sup>	3	14	66.3	0.6	48
23	CH·( <sup>2</sup> Π <sub>r</sub> )	2	7	142.5	n/a	30	88	HCO <sup>+</sup>	3	14	197.6	2.0	26
24	NH( <sup>3</sup> Σ <sup>-</sup> )	2	8	85.2	0.4	31	89	HCO·( <sup>2</sup> A <sup>'</sup> )	3	15	10.0	0.2	32
25	OH·( <sup>2</sup> Π <sub>i</sub> )	2	9	9.4	0.1	32	90	SiH <sub>2</sub> ( <sup>1</sup> A <sub>1</sub> )	3	16	65.2	0.7	49
26	FH	2	10	-65.1	0.2	26	91	SiH <sub>2</sub> ( <sup>3</sup> B <sub>1</sub> )	3	16	86.2	1.0	49
27	HO <sup>-</sup>	2	10	-32.8	0.05	28	92	HCO <sup>-</sup>	3	16	2.7	0.2	28
28	LiF	2	12	-80.1	n/a	30	93	CHF (singlet)	3	16	34.2	3.0	50
29	BeO	2	12	32.6	3.0	26	94	PH <sub>2</sub> ·( <sup>2</sup> B <sub>1</sub> )	3	17	33.1	0.6	32
30	NaH	2	12	29.7	4.6	26	95	SH <sub>2</sub>	3	18	-4.9	0.2	26
31	CH·( <sup>2</sup> Σ <sup>+</sup> )	2	13	104.9	0.5	33	96	HOF	3	18	-19.6	0.3	51
32	BeF·( <sup>2</sup> Σ <sup>+</sup> )	2	13	-40.6	2.0	26	97	PH <sub>2</sub> <sup>-</sup>	3	18	6.4	2.0	28
33	BO·( <sup>2</sup> Σ <sup>+</sup> )	2	13	0.0	2.0	26	98	ClH <sub>2</sub> <sup>+</sup>	3	18	210.5	1.9	45
34	CO	2	14	-26.4	0.04	26	99	NaOH	3	20	-45.7	1.9	46
35	N <sub>2</sub>	2	14	0.0	n/a	29	100	MgOH <sup>+</sup>	3	20	146.0	5.0	39
36	CN <sup>-</sup>	2	14	17.2	1.1	28	101	FHF <sup>-</sup>	3	20	-170.2	1.6	52
37	BF (singlet)	2	14	-27.7	3.3	26	102	BO <sub>2</sub> ·( <sup>2</sup> Π <sub>g</sub> )	3	21	-68.0	2.0	26
38	LiNa	2	14	43.4	0.3	34	103	CO <sub>2</sub>	3	22	-94.1	0.01	26
39	NO·( <sup>2</sup> Π)	2	15	21.6	0.04	26	104	N <sub>2</sub> O	3	22	19.6	0.1	26
40	SiH·( <sup>2</sup> Π <sub>r</sub> )	2	15	90.0	2.0	26	105	FCN	3	22	8.6	4.0	26
41	O <sub>2</sub> ( <sup>3</sup> Σ <sub>g</sub> <sup>-</sup> )	2	16	0.0	n/a	29	106	BeF <sub>2</sub>	3	22	-190.3	1.0	26
42	NO <sup>-</sup> ·( <sup>2</sup> Σ <sup>-</sup> )	2	16	21.0	0.1	35	107	FBO	3	22	-144.0	3.1	26
43	HS·( <sup>2</sup> Π <sub>i</sub> )	2	17	34.2	0.7	32	108	NCO <sup>-</sup>	3	22	-52.8	1.0	53
44	ClH	2	18	-22.1	0.05	26	109	HOSi <sup>+</sup>	3	22	155.2	1.9	45
45	F <sub>2</sub>	2	18	0.0	n/a	29	110	NO <sub>2</sub> ·( <sup>2</sup> A <sub>1</sub> )	3	23	7.9	0.2	26
46	HS <sup>-</sup>	2	18	-19.5	2.0	28	111	O <sub>3</sub>	3	24	34.1	0.4	26
47	FO <sup>-</sup>	2	18	-26.3	3.5	36	112	FNO	3	24	-15.7	0.4	26
48	NaO·( <sup>2</sup> Π)	2	19	20.8	1.0	37	113	CClH (singlet)	3	24	78.0	2.0	50
49	F <sub>2</sub> <sup>-</sup> ·( <sup>2</sup> Σ <sub>u</sub> <sup>+</sup> )	2	19	-69.3	1.6	38	114	NaCN	3	24	22.5	0.5	26
50	NaF	2	20	-69.4	0.5	26	115	CF <sub>2</sub> (singlet)	3	24	-44.0	2.0	50
51	MgO	2	20	36.0	5.0	39	116	NO <sub>2</sub> <sup>-</sup>	3	24	-44.5	0.2	54
52	MgF·( <sup>2</sup> Σ <sup>+</sup> )	2	21	-56.6	2.0	26	117	NF <sub>2</sub> ·( <sup>2</sup> B <sub>1</sub> )	3	25	10.1	2.0	26
53	AlO·( <sup>2</sup> Σ <sup>+</sup> )	2	21	16.0	1.9	26	118	HOCl	3	26	-17.8	0.5	26
54	Na <sub>2</sub> <sup>+</sup> ·( <sup>2</sup> Σ <sup>+</sup> )	2	21	146.7	0.3	40	119	F <sub>2</sub> O	3	26	5.9	0.4	26
55	BeCl·( <sup>2</sup> Σ <sup>+</sup> )	2	21	14.5	3.0	26	120	HOS <sup>-</sup>	3	26	-37.8	2.0	55
56	Na <sub>2</sub>	2	22	34.0	0.3	26	121	COS	3	30	-33.1	0.3	26
57	SiO	2	22	-24.6	n/a	30	122	ClCN	3	30	32.9	1.0	56
58	CS	2	22	66.9	n/a	30	123	MgF <sub>2</sub>	3	30	-173.7	4.0	26
59	AlF	2	22	-63.5	0.8	26	124	Na <sub>2</sub> O	3	30	-8.6	1.9	37
60	PO·( <sup>2</sup> Π <sub>1/2</sub> )	2	23	-5.6	1.0	26	125	FAIO	3	30	-139.0	4.0	26
61	SiF·( <sup>2</sup> Π <sub>1/2</sub> )	2	23	-4.8	3.0	26	126	SCN <sup>-</sup>	3	30	-5.2	1.0	53
62	SO( <sup>3</sup> Σ <sup>-</sup> )	2	24	1.2	0.3	26	127	SO <sub>2</sub>	3	32	-70.9	0.05	26
63	PF( <sup>3</sup> Σ <sup>-</sup> )	2	24	-12.5	5.0	26	128	CINO	3	32	12.4	0.1	26
64	ClO·( <sup>2</sup> Π <sub>3/2</sub> )	2	25	24.2	0.5	26	129	FPO	3	32	-96.7	0.7	57
65	FCl	2	26	-13.2	n/a	30	130	SiF <sub>2</sub> (singlet)	3	32	-140.5	3.0	26

TABLE I. (Continued.)

Entry	Species (el state or mult)	Number of		$\Delta H_f^0$ (kcal/mol)		Source	Entry	Species (el state or mult)	Number of		$\Delta H_f^0$ (kcal/mol)		Source
		Nuclei	Elec	Value	Error				Nuclei	Elec	Value	Error	
131	CCIF (singlet)	3	32	7.4	3.2	50	196	P <sub>4</sub>	4	60	14.1	0.5	26
132	ClO <sub>2</sub> ·( <sup>2</sup> B <sub>1</sub> )	3	33	25.0	1.5	26	197	AlCl <sub>3</sub>	4	64	-139.7	0.7	26
133	SF <sub>2</sub>	3	34	-70.9	4.0	58	198	SiCl <sub>3</sub> ·( <sup>2</sup> A <sub>1</sub> )	4	65	-93.3	2.0	26
134	Al <sub>2</sub> O	3	34	-34.7	4.0	26	199	S <sub>2</sub> Cl <sub>2</sub>	4	66	-4.0	1.0	26
135	ClO <sub>2</sub> <sup>-</sup>	3	34	-24.4	1.5	36	200	PCl <sub>3</sub>	4	66	-69.0	1.3	26
136	HSS <sup>-</sup>	3	34	-16.0	3.5	55	201	CH <sub>4</sub>	5	10	-17.9	0.1	26
137	CS <sub>2</sub>	3	38	28.0	0.2	26	202	NH <sub>4</sub> <sup>+</sup>	5	10	150.7	1.9	45
138	BeCl <sub>2</sub>	3	38	-86.1	2.5	26	203	BH <sub>4</sub> <sup>-</sup>	5	10	-14.8	4.5	71
139	CCl <sub>2</sub> (singlet)	3	40	55.0	2.0	50	204	C <sub>2</sub> H <sub>3</sub> <sup>+</sup>	5	14	266.6	1.9	45
140	CIPO	3	40	-51.4	1.2	57	205	C <sub>2</sub> H <sub>3</sub> ·( <sup>2</sup> A')	5	15	71.6	0.8	32
141	Cl <sub>2</sub> O	3	42	21.0	1.6	26	206	C <sub>2</sub> H <sub>5</sub> <sup>-</sup>	5	16	56.2	0.6	48
142	MgCl <sub>2</sub>	3	46	-93.8	0.5	26	207	HOCH <sub>2</sub> ·( <sup>2</sup> A)	5	17	-4.1	0.8	32
143	AlCl <sub>2</sub> ·( <sup>2</sup> A <sub>1</sub> )	3	47	-67.0	5.0	26	208	CH <sub>3</sub> O·( <sup>2</sup> A')	5	17	4.1	0.9	32
144	SiCl <sub>2</sub> (singlet)	3	48	-40.3	0.8	26	209	SiH <sub>4</sub>	5	18	8.2	0.5	26
145	SCl <sub>2</sub>	3	50	-4.2	0.8	26	210	CH <sub>3</sub> O <sup>-</sup>	5	18	-32.3	0.7	28
146	BH <sub>3</sub>	4	8	25.5	2.4	26	211	PH <sub>4</sub> <sup>+</sup>	5	18	179.4	1.9	45
147	CH <sub>3</sub> ·( <sup>2</sup> A <sub>2</sub> )	4	9	35.0	0.1	32	212	Na(NH <sub>3</sub> ) <sup>+</sup>	5	20	104.1	0.5	72
148	NH <sub>3</sub>	4	10	-11.0	0.1	26	213	CH <sub>2</sub> CN·( <sup>2</sup> B <sub>1</sub> )	5	21	59.8	2.0	73
149	CH <sub>3</sub> <sup>-</sup>	4	10	33.1	0.7	28	214	H <sub>2</sub> C=C=O	5	22	-11.4	0.4	56
150	H <sub>3</sub> O <sup>+</sup>	4	10	142.7	1.9	45	215	CH <sub>2</sub> CN <sup>-</sup>	5	22	24.2	2.0	67
151	HCCH	4	14	54.2	0.2	26	216	HCOOH	5	24	-90.5	0.1	56
152	H <sub>2</sub> C=C (singlet)	4	14	101.6	4.0	48	217	CH <sub>3</sub> S·( <sup>2</sup> A')	5	25	29.8	0.4	32
153	H <sub>2</sub> CO	4	16	-26.0	0.1	56	218	HSCH <sub>2</sub> ·( <sup>2</sup> A)	5	25	36.3	2.0	32
154	SiH <sub>3</sub> ·( <sup>2</sup> A <sub>1</sub> )	4	17	47.9	0.6	32	219	CH <sub>3</sub> Cl	5	26	-20.0	0.5	26
155	PH <sub>3</sub>	4	18	1.3	0.4	57	220	CH <sub>2</sub> F <sub>2</sub>	5	26	-107.7	0.4	26
156	H <sub>2</sub> O <sub>2</sub>	4	18	-32.5	0.04	59	221	CH <sub>3</sub> S <sup>-</sup>	5	26	-14.3	2.2	28
157	SiH <sub>3</sub> <sup>-</sup>	4	18	14.7	2.1	28	222	CH <sub>2</sub> SH <sup>-</sup>	5	26	22.8	3.0	28
158	H <sub>3</sub> S <sup>+</sup>	4	18	192.3	1.9	45	223	HNO <sub>3</sub>	5	32	-32.1	0.1	26
159	HOHF <sup>-</sup>	4	20	-143.8	0.9	60	224	HOCO <sub>2</sub> <sup>-</sup>	5	32	-177.8	2.5	74
160	H <sub>2</sub> F <sub>2</sub>	4	20	-136.9	0.8	26	225	CHF <sub>3</sub>	5	34	-166.6	0.8	26
161	Na(H <sub>2</sub> O) <sup>+</sup>	4	20	62.4	n/a	61	226	O=C=C=C=O	5	34	-22.4	0.4	75
162	HN <sub>3</sub>	4	22	70.3	n/a	62	227	O(BeF) <sub>2</sub>	5	34	-287.9	5.0	26
163	HNCO	4	22	-24.3	2.0	26	228	B <sub>2</sub> O <sub>3</sub>	5	34	-199.8	1.0	26
164	(E)-HONO	4	24	-18.8	0.3	26	229	N <sub>2</sub> O <sub>3</sub>	5	38	19.8	0.2	26
165	HCOO <sup>-</sup>	4	24	-110.9	2.0	63	230	CF <sub>4</sub>	5	42	-223.0	0.3	26
166	(CN) <sub>2</sub>	4	26	73.3	0.2	56	231	CH <sub>2</sub> Cl <sub>2</sub>	5	42	-22.8	0.3	26
167	OBBO	4	26	-109.0	2.0	26	232	CHF <sub>2</sub> Cl	5	42	-115.3	0.8	56
168	HOHCl <sup>-</sup>	4	28	-127.1	0.2	64	233	F <sub>3</sub> NO	5	42	-39.0	5.0	26
169	BF <sub>3</sub>	4	32	-271.4	0.4	26	234	BF <sub>4</sub> <sup>-</sup>	5	42	-409.8	2.0	76
170	COF <sub>2</sub>	4	32	-149.1	1.4	65	235	HOSO <sub>2</sub> <sup>-</sup>	5	42	-165.6	2.5	74
171	(Z)-N <sub>2</sub> F <sub>2</sub>	4	32	16.4	1.2	26	236	SiF <sub>4</sub>	5	50	-356.0	0.2	26
172	(E)-N <sub>2</sub> F <sub>2</sub>	4	32	19.4	1.2	26	237	SO <sub>2</sub> F <sub>2</sub>	5	50	-181.3	2.0	26
173	FNO <sub>2</sub>	4	32	-26.0	5.0	26	238	CF <sub>3</sub> Cl	5	50	-169.2	0.8	26
174	NF <sub>3</sub>	4	34	-31.6	0.3	26	239	FCIO <sub>3</sub>	5	50	-5.1	0.7	26
175	H <sub>2</sub> S <sub>2</sub>	4	34	3.7	n/a	62	240	H <sub>2</sub> S <sub>3</sub>	5	50	7.3	n/a	62
176	FOOF	4	34	4.6	0.2	66	241	SiH <sub>2</sub> Cl <sub>2</sub>	5	50	-75.3	2.0	77
177	CF <sub>3</sub> <sup>-</sup>	4	34	-156.7	2.2	67	242	AlF <sub>4</sub> <sup>-</sup>	5	50	-467.6	2.4	78
178	AlF <sub>3</sub>	4	40	-289.0	0.6	26	243	SF <sub>4</sub>	5	52	-182.4	5.0	26
179	SO <sub>3</sub>	4	40	-94.6	0.2	26	244	CHCl <sub>3</sub>	5	58	-24.7	0.3	26
180	CINO <sub>2</sub>	4	40	2.9	0.4	26	245	CF <sub>2</sub> Cl <sub>2</sub>	5	58	-117.5	1.9	26
181	Na <sub>2</sub> F <sub>2</sub>	4	40	-202.3	3.0	26	246	SO <sub>2</sub> Cl <sub>2</sub>	5	66	-84.8	0.5	26
182	(LiCl) <sub>2</sub>	4	40	-143.1	3.0	26	247	CFCl <sub>3</sub>	5	66	-69.0	1.5	26
183	PF <sub>3</sub>	4	42	-229.1	0.9	26	248	SiHCl <sub>3</sub>	5	66	-119.3	1.6	77
184	ClF <sub>3</sub>	4	44	-38.0	0.7	26	249	CCl <sub>4</sub>	5	74	-22.9	0.5	26
185	COCl <sub>2</sub>	4	48	-52.6	0.8	26	250	Cl <sub>3</sub> PO	5	74	-133.8	0.4	26
186	AlF <sub>2</sub> Cl	4	48	-238.8	1.5	26	251	SiCl <sub>4</sub>	5	82	-158.4	0.3	26
187	FSSF	4	50	-68.4	2.4	58	252	C <sub>2</sub> H <sub>4</sub>	6	16	12.5	0.1	26
188	S=SF <sub>2</sub>	4	50	-71.0	2.4	58	253	CH <sub>3</sub> OH	6	18	-48.2	0.1	56
189	BCl <sub>3</sub>	4	56	-96.3	0.5	26	254	N <sub>2</sub> H <sub>4</sub>	6	18	22.8	0.2	26
190	Na <sub>2</sub> Cl <sub>2</sub>	4	56	-135.3	2.0	26	255	CH <sub>3</sub> CN	6	22	17.7	0.1	79
191	AlFCl <sub>2</sub>	4	56	-189.0	1.5	26	256	CH <sub>3</sub> NC	6	22	39.1	1.7	56
192	CCl <sub>3</sub> ·( <sup>2</sup> A <sub>1</sub> )	4	57	17.5	2.5	68	257	CH <sub>3</sub> CO·( <sup>2</sup> A')	6	23	-2.4	0.3	32
193	BCl <sub>3</sub> <sup>-</sup> ·( <sup>2</sup> A <sub>1</sub> )	4	57	-103.9	4.6	69	258	H <sub>2</sub> C=CHO·( <sup>2</sup> A'')	6	23	2.5	2.2	32
194	SOCl <sub>2</sub>	4	58	-50.8	n/a	62	259	CH <sub>2</sub> =CHF	6	24	-33.2	0.4	56
195	CCl <sub>3</sub> <sup>-</sup>	4	58	-32.8	2.0	70	260	CH <sub>2</sub> CHO <sup>-</sup>	6	24	-39.6	2.2	28

TABLE I. (Continued.)

Entry	Species (el state or mult)	Number of		$\Delta H_f^0$ (kcal/mol)		Source	Entry	Species (el state or mult)	Number of		$\Delta H_f^0$ (kcal/mol)		Source
		Nuclei	Elec	Value	Error				Nuclei	Elec	Value	Error	
261	H <sub>2</sub> NCHO	6	24	-44.5	n/a	80	326	Oxirane-H <sup>+</sup>	8	24	168.1	1.9	45
262	(LiOH) <sub>2</sub>	6	24	-176.1	2.4	46	327	CH <sub>3</sub> CH <sub>2</sub> O· ( <sup>2</sup> A'')	8	25	-3.7	0.8	32
263	CH <sub>3</sub> SH	6	26	-5.5	0.2	56	328	CH <sub>3</sub> SiH <sub>3</sub>	8	26	-7.0	1.0	88
264	(CHO) <sub>2</sub>	6	30	-50.7	0.2	56	329	CH <sub>2</sub> =CHC≡CH	8	28	70.8	0.5	90
265	CH <sub>2</sub> =CHCl	6	32	5.5	0.5	81	330	HCOOCH <sub>3</sub>	8	32	-85.0	0.2	56
266	CH <sub>2</sub> =CF <sub>2</sub>	6	32	-80.5	1.0	75	331	CH <sub>3</sub> COOH	8	32	-103.4	0.4	56
267	SiH <sub>2</sub> =SiH <sub>2</sub>	6	32	65.7	0.9	82	332	Si <sub>2</sub> H <sub>6</sub>	8	34	19.1	0.4	88
268	NCC=CCN	6	38	126.5	0.4	75	333	C <sub>2</sub> H <sub>5</sub> Cl	8	34	-26.8	0.3	56
269	(NaOH) <sub>2</sub>	6	40	-149.1	2.4	46	334	CH <sub>3</sub> COSH	8	40	-41.8	2.0	56
270	CF <sub>3</sub> CN	6	46	-118.4	0.7	26	335	(E)-NCCH=CHCN	8	40	81.3	0.6	91
271	N <sub>2</sub> O <sub>4</sub>	6	46	2.2	0.4	26	336	CH <sub>3</sub> CF <sub>3</sub>	8	42	-178.9	0.8	81
272	B <sub>2</sub> F <sub>4</sub>	6	46	-342.2	1.0	26	337	Si(CH <sub>3</sub> ) <sub>2</sub> H <sub>2</sub> Cl	8	42	-50.2	1.7	88
273	C <sub>2</sub> F <sub>4</sub>	6	48	-157.4	0.7	26	338	(COOH) <sub>2</sub>	8	46	-175.0	0.6	75
274	CH <sub>2</sub> =CCl <sub>2</sub>	6	48	0.6	0.3	56	339	ClCH <sub>2</sub> COOH	8	48	-104.0	2.2	56
275	(E)-CHCl=CHCl	6	48	1.2	2.0	56	340	CH <sub>3</sub> CHCl <sub>2</sub>	8	50	-30.5	0.3	56
276	(Z)-CHCl=CHCl	6	48	1.1	2.0	56	341	ClCH <sub>2</sub> CH <sub>2</sub> Cl	8	50	-32.1	0.3	81
277	HOSO <sub>2</sub> F	6	50	-180.0	2.0	26	342	CF <sub>3</sub> COOH	8	56	-246.5	0.4	56
278	N <sub>2</sub> F <sub>4</sub>	6	50	-2.0	2.5	26	343	1,3-dithiol-2-one	8	60	-3.6	1.2	56
279	HSO <sub>4</sub> <sup>-</sup>	6	50	-231.9	3.1	83	344	CH <sub>3</sub> CCl <sub>3</sub>	8	66	-34.6	0.4	56
280	CFCl=CF <sub>2</sub>	6	56	-123.1	5.0	81	345	CHCl <sub>2</sub> CH <sub>2</sub> Cl	8	66	-34.6	0.5	81
281	NCSSCN	6	58	83.6	1.5	56	346	1,3-dithiole-2-thione	8	68	60.5	1.6	56
282	PF <sub>5</sub>	6	60	-381.1	0.7	26	347	Al <sub>2</sub> F <sub>6</sub>	8	80	-629.5	4.0	26
283	(LiCl) <sub>3</sub>	6	60	-240.1	5.0	26	348	CHCl <sub>2</sub> CCl <sub>3</sub>	8	98	-33.9	2.2	56
284	SF <sub>5</sub> ·( <sup>2</sup> A <sub>1</sub> )	6	61	-218.1	3.2	58	349	C <sub>2</sub> Cl <sub>6</sub>	8	114	-32.9	1.1	81
285	PF <sub>5</sub> <sup>-</sup> ·( <sup>2</sup> A <sub>1</sub> )	6	61	-398.4	3.6	84	350	S <sub>8</sub>	8	128	24.0	0.2	26
286	(COCl) <sub>2</sub>	6	62	-80.3	1.5	56	351	Al <sub>2</sub> Cl <sub>6</sub>	8	128	-309.7	0.8	26
287	CHCl=CCl <sub>2</sub>	6	64	-1.9	2.1	56	352	CH <sub>3</sub> CH=CH <sub>2</sub>	9	24	4.8	0.2	56
288	H <sub>2</sub> S <sub>4</sub>	6	66	10.6	n/a	62	353	Cyclopropane	9	24	12.7	0.1	56
289	B <sub>2</sub> Cl <sub>4</sub>	6	78	-116.9	1.2	26	354	CH <sub>3</sub> CH <sub>2</sub> OH	9	26	-56.2	0.1	56
290	C <sub>2</sub> Cl <sub>4</sub>	6	80	-3.0	0.7	26	355	(CH <sub>3</sub> ) <sub>2</sub> O	9	26	-44.0	0.1	56
291	PCl <sub>5</sub>	6	100	-89.9	1.4	85	356	CH <sub>3</sub> CONH <sub>2</sub>	9	32	-57.0	0.2	56
292	C <sub>2</sub> H <sub>5</sub> ·( <sup>2</sup> A')	7	17	28.9	0.4	32	357	CH <sub>3</sub> CH <sub>2</sub> SH	9	34	-11.1	0.1	56
293	CH <sub>3</sub> NH <sub>2</sub>	7	18	-5.5	0.1	56	358	CH <sub>3</sub> SCH <sub>3</sub>	9	34	-9.0	0.1	56
294	C <sub>2</sub> H <sub>5</sub> <sup>-</sup>	7	18	34.4	1.0	86	359	Furan	9	36	-8.3	0.2	56
295	N <sub>2</sub> H <sub>5</sub> <sup>+</sup>	7	18	184.6	1.9	45	360	β-propiolactone	9	38	-67.6	0.2	75
296	CH <sub>3</sub> OH <sub>2</sub> <sup>+</sup>	7	18	137.2	1.9	45	361	CH <sub>2</sub> =CClCH <sub>3</sub>	9	40	-5.0	2.2	56
297	CH <sub>3</sub> C≡CH	7	22	44.2	0.2	56	362	CH <sub>3</sub> SOCH <sub>2</sub> <sup>-</sup>	9	42	-29.2	2.0	67
298	CH <sub>2</sub> =C=CH <sub>2</sub>	7	22	45.5	0.3	56	363	1,3,5-triazine	9	42	54.0	0.2	92
299	Cyclopropene	7	22	66.2	0.6	56	364	Thiophene	9	44	27.5	0.2	56
300	Oxirane	7	24	-12.6	0.1	56	365	C(CN) <sub>4</sub>	9	58	160.8	2.2	93
301	CH <sub>3</sub> CHO	7	24	-39.7	0.1	56	366	B <sub>3</sub> O <sub>3</sub> F <sub>3</sub>	9	66	-565.3	1.0	26
302	CH <sub>2</sub> =CHOH	7	24	-29.8	2.0	87	367	FN=C(NF <sub>2</sub> ) <sub>2</sub>	9	72	22.7	0.8	75
303	CH <sub>2</sub> =CHCN	7	28	43.2	0.4	56	368	F <sub>2</sub> C(NF <sub>2</sub> ) <sub>2</sub>	9	74	-109.0	0.9	75
304	Na(H <sub>2</sub> O) <sub>2</sub> <sup>+</sup>	7	30	-15.2	n/a	61	369	Cl <sub>2</sub> O <sub>7</sub>	9	90	65.0	n/a	62
305	CH <sub>3</sub> NO <sub>2</sub>	7	32	-17.8	0.1	56	370	B <sub>3</sub> O <sub>3</sub> Cl <sub>3</sub>	9	90	-390.0	2.0	26
306	CH <sub>3</sub> ONO	7	32	-15.9	0.2	56	371	(CH <sub>3</sub> ) <sub>3</sub> CH·( <sup>2</sup> A')	10	25	21.5	0.4	32
307	Thiirane	7	32	19.6	0.3	56	372	(CH <sub>3</sub> ) <sub>2</sub> NH	10	26	-4.4	0.2	56
308	CH <sub>3</sub> COF	7	32	-105.7	0.8	56	373	CH <sub>3</sub> CH <sub>2</sub> NH <sub>2</sub>	10	26	-11.3	0.2	56
309	B(OH) <sub>3</sub>	7	32	-237.2	0.6	26	374	(CH <sub>3</sub> ) <sub>2</sub> CH <sup>-</sup>	10	26	28.7	1.0	86
310	Si <sub>2</sub> H <sub>5</sub> ·( <sup>2</sup> A')	7	33	53.3	2.0	88	375	(CH <sub>3</sub> ) <sub>2</sub> OH <sup>+</sup>	10	26	132.4	1.9	45
311	H <sub>2</sub> PSiH <sub>3</sub>	7	34	1.8	2.9	57	376	CH <sub>2</sub> =CHCH=CH <sub>2</sub>	10	30	26.3	0.3	56
312	1-H-tetrazole	7	36	80.0	1.1	75	377	CH <sub>3</sub> C≡CCH <sub>3</sub>	10	30	34.8	0.3	56
313	CH <sub>3</sub> COCl	7	40	-58.0	0.2	56	378	Methylenecyclopropane	10	30	47.9	0.4	56
314	H <sub>2</sub> SO <sub>4</sub>	7	50	-175.7	2.0	26	379	Bicyclobutane	10	30	51.9	0.2	56
315	SF <sub>6</sub>	7	70	-291.7	0.2	26	380	Cyclobutene	10	30	37.5	0.4	56
316	CCl <sub>3</sub> CHO	7	72	-47.0	n/a	62	381	CH <sub>3</sub> CH=C=CH <sub>2</sub>	10	30	38.8	0.1	75
317	SF <sub>5</sub> Cl	7	78	-248.3	2.5	26	382	CH <sub>3</sub> COCH <sub>3</sub>	10	32	-51.9	0.2	56
318	H <sub>2</sub> S <sub>5</sub>	7	82	13.8	n/a	62	383	Oxetane	10	32	-19.3	0.2	75
319	CCl <sub>3</sub> COCl	7	88	-57.3	2.1	56	384	(CH <sub>3</sub> ) <sub>2</sub> SiH <sup>-</sup>	10	34	-7.4	2.3	94
320	C <sub>2</sub> Cl <sub>5</sub> ·( <sup>2</sup> A')	7	97	8.1	2.3	89	385	1H-pyrrole	10	36	25.9	0.1	56
321	B <sub>2</sub> H <sub>6</sub>	8	16	9.8	4.0	26	386	cyclo-C <sub>3</sub> H <sub>5</sub> <sup>-</sup>	10	36	22.5	2.0	67
322	C <sub>2</sub> H <sub>6</sub>	8	18	-20.0	0.1	56	387	2-azetidinone	10	38	-22.9	0.2	95
323	Aziridine	8	24	30.2	0.2	56	388	H <sub>2</sub> NCH <sub>2</sub> COOH	10	40	-93.7	0.2	75
324	Cyclo-C <sub>3</sub> H <sub>5</sub> <sup>-</sup>	8	24	58.5	1.0	86	389	Thietane	10	40	14.5	0.3	56
325	CH <sub>2</sub> CHCH <sub>2</sub> <sup>-</sup>	8	24	29.9	2.1	28	390	Na(H <sub>2</sub> O) <sub>3</sub> <sup>+</sup>	10	40	-88.8	n/a	61

TABLE I. (Continued.)

Entry	Species (el state or mult)	Number of		$\Delta H_f^0$ (kcal/mol)		Source	Entry	Species (el state or mult)	Number of		$\Delta H_f^0$ (kcal/mol)		Source
		Nuclei	Elec	Value	Error				Nuclei	Elec	Value	Error	
391	<i>p</i> -benzyne (singlet)	10	40	137.8	2.9	96	456	(CH <sub>2</sub> =CH) <sub>2</sub> CH <sub>2</sub>	13	38	25.2	0.3	56
392	<i>p</i> -benzyne (triplet)	10	40	141.6	2.9	96	457	Cyclopentene	13	38	8.1	0.3	56
393	<i>m</i> -benzyne (singlet)	10	40	121.9	3.1	96	458	Bicyclo[2.1.0]pentane	13	38	37.8	0.2	98
394	<i>m</i> -benzyne (triplet)	10	40	142.9	3.1	96	459	Tetrahydrofuran	13	40	-44.0	0.2	75
395	<i>o</i> -benzyne (singlet)	10	40	105.9	3.3	96	460	(CH <sub>3</sub> ) <sub>3</sub> Al	13	40	-20.9	1.7	75
396	<i>o</i> -benzyne (triplet)	10	40	143.3	3.3	96	461	Si(CH <sub>3</sub> ) <sub>3</sub> ·( <sup>2</sup> A <sub>1</sub> )	13	41	-0.7	1.7	88
397	(CH <sub>3</sub> ) <sub>2</sub> SO	10	42	-36.2	0.2	56	462	(CH <sub>3</sub> ) <sub>3</sub> P	13	42	-22.5	1.2	75
398	Pyridazine	10	42	66.5	0.3	75	463	CH <sub>3</sub> CH(NH <sub>2</sub> )COOH	13	48	-99.1	1.0	106
399	Pyrimidine	10	42	47.0	0.2	75	464	Tetrahydrothiophene	13	48	-8.2	0.3	56
400	Pyrazine	10	42	46.9	0.3	75	465	C <sub>6</sub> H <sub>5</sub> OH	13	50	-23.0	0.2	75
401	HSCH <sub>2</sub> CH <sub>2</sub> SH	10	50	-2.3	0.3	56	466	Na(H <sub>2</sub> O) <sub>4</sub> <sup>+</sup>	13	50	-160.4	n/a	61
402	CH <sub>3</sub> SSCH <sub>3</sub>	10	50	-5.8	0.2	56	467	C <sub>6</sub> H <sub>5</sub> CN	13	54	51.5	0.5	75
403	CH <sub>3</sub> SO <sub>2</sub> CH <sub>2</sub> <sup>-</sup>	10	50	-88.3	2.1	67	468	CH <sub>3</sub> CH(SH)CH <sub>2</sub> SH	13	58	-7.1	0.3	56
404	Thiete sulphone	10	54	-29.7	0.7	75	469	C <sub>6</sub> H <sub>5</sub> SH	13	58	26.9	0.2	56
405	1,3-dithiolan-2-one	10	62	-30.1	1.2	56	470	(CH <sub>2</sub> =CH) <sub>2</sub> SO <sub>2</sub>	13	62	-36.0	0.9	75
406	Dithiooxamide	10	62	19.8	0.4	97	471	Butadiene sulphone	13	62	-61.2	0.7	75
407	1,3-dithiolane-2-thione	10	70	22.4	0.5	56	472	(CH <sub>3</sub> O) <sub>2</sub> SO <sub>2</sub>	13	66	-164.2	0.5	56
408	CH <sub>3</sub> CH <sub>2</sub> CH <sub>3</sub>	11	26	-25.0	0.1	56	473	<i>m</i> -ClC <sub>6</sub> H <sub>4</sub> OH	13	66	-36.6	2.1	56
409	SiH <sub>2</sub> (CH <sub>3</sub> ) <sub>2</sub>	11	34	-22.6	1.0	88	474	<i>p</i> -ClC <sub>6</sub> H <sub>4</sub> OH	13	66	-34.8	2.1	56
410	Cyclopentadiene	11	36	32.1	0.4	56	475	1,3-dithiane-2-thione	13	78	18.8	0.7	75
411	Bicyclo[2.1.0]pentene	11	36	79.8	0.6	98	476	C(NO <sub>2</sub> ) <sub>4</sub>	13	98	19.7	0.5	107
412	Cyclobutanone	11	38	-24.2	0.3	99	477	C(NF <sub>2</sub> ) <sub>4</sub>	13	106	0.2	1.3	75
413	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> Cl	11	42	-31.5	0.3	56	478	C <sub>6</sub> Cl <sub>5</sub> OH	13	130	-53.8	0.9	56
414	Pyridine	11	42	33.6	0.2	56	479	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>2</sub> CH <sub>3</sub>	14	34	-30.0	0.2	56
415	(CH <sub>3</sub> ) <sub>2</sub> CHCl	11	42	-34.6	0.3	56	480	(CH <sub>3</sub> ) <sub>3</sub> CH	14	34	-32.1	0.2	56
416	2,5-dihydrothiophene	11	46	20.8	0.3	56	481	B <sub>5</sub> H <sub>9</sub>	14	34	17.5	1.6	26
417	(CH <sub>3</sub> ) <sub>2</sub> SO <sub>2</sub>	11	50	-89.2	0.7	56	482	Pyrrolidine	14	40	-0.9	0.2	108
418	Si(CH <sub>3</sub> ) <sub>2</sub> HCl	11	50	-67.4	1.7	88	483	SiH(CH <sub>3</sub> ) <sub>3</sub>	14	42	-39.1	1.0	88
419	CH <sub>3</sub> CHClCH <sub>2</sub> Cl	11	58	-38.9	0.3	56	484	Bicyclo[2.2.0]hex-2-ene	14	44	62.4	0.3	98
420	FC(NF <sub>2</sub> ) <sub>3</sub>	11	90	-48.0	0.6	75	485	<i>cyclo</i> -C <sub>7</sub> H <sub>7</sub> <sup>+</sup>	14	48	206.7	0.7	109
421	Cyclobutane	12	32	6.8	0.1	56	486	(CH <sub>3</sub> ) <sub>3</sub> CCl	14	50	-43.5	0.5	56
422	(CH <sub>3</sub> ) <sub>2</sub> C=CH <sub>2</sub>	12	32	-4.0	0.2	56	487	(CH <sub>3</sub> )CHCH <sub>2</sub> Cl	14	50	-38.1	2.0	56
423	CH <sub>3</sub> CH <sub>2</sub> CH=CH <sub>2</sub>	12	32	0.0	0.2	56	488	C <sub>6</sub> H <sub>5</sub> NH <sub>2</sub>	14	50	20.8	0.2	75
424	( <i>Z</i> )-CH <sub>3</sub> CH=CHCH <sub>3</sub>	12	32	-1.7	0.2	56	489	C <sub>6</sub> H <sub>5</sub> CHO	14	56	-8.8	2.0	75
425	( <i>E</i> )-CH <sub>3</sub> CH=CHCH <sub>3</sub>	12	32	-2.7	0.2	56	490	CH <sub>3</sub> COSC <sub>2</sub> H <sub>5</sub>	14	56	-54.5	0.2	56
426	(CH <sub>3</sub> ) <sub>2</sub> CHOH	12	34	-65.2	0.1	56	491	CH <sub>3</sub> SO <sub>2</sub> C <sub>2</sub> H <sub>5</sub>	14	58	-97.7	0.7	56
427	CH <sub>3</sub> CH <sub>2</sub> OCH <sub>3</sub>	12	34	-51.7	0.2	56	492	Si(CH <sub>3</sub> ) <sub>3</sub> Cl	14	58	-84.6	0.7	88
428	Benzene	12	42	19.7	0.2	56	493	Benzotriazole	14	62	80.2	0.3	110
429	Fulvene	12	42	53.6	0.1	90	494	Benzoxazole	14	62	10.8	0.1	111
430	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> SH	12	42	-16.2	0.2	56	495	C <sub>6</sub> H <sub>5</sub> NCO	14	62	-3.5	0.3	112
431	(CH <sub>3</sub> ) <sub>2</sub> CHSH	12	42	-18.2	0.2	56	496	Benzothiazole	14	70	48.8	0.1	111
432	Pyridine-H <sup>+</sup>	12	42	177.0	1.9	45	497	C <sub>6</sub> H <sub>5</sub> COCl	14	72	-24.7	1.0	56
433	1,3,5-trioxane	12	48	-111.3	0.1	100	498	<i>o</i> -ClC <sub>6</sub> H <sub>4</sub> CHO	14	72	-15.0	2.1	56
434	C <sub>6</sub> H <sub>5</sub> F	12	50	-27.8	0.3	75	499	P <sub>4</sub> O <sub>10</sub>	14	140	-694.1	2.1	26
435	C <sub>6</sub> H <sub>5</sub> O <sup>-</sup>	12	50	-37.1	3.1	101	500	1,3,5-cycloheptatriene	15	50	43.2	0.5	56
436	Pyridine- <i>N</i> -oxide	12	50	21.0	0.6	102	501	Norbornadiene	15	50	58.8	0.7	56
437	<i>p</i> -benzoquinone	12	56	-29.3	0.9	75	502	C <sub>6</sub> H <sub>5</sub> CH <sub>3</sub>	15	50	12.0	0.1	75
438	C <sub>6</sub> H <sub>5</sub> S·( <sup>2</sup> B <sub>1</sub> )	12	57	55.8	1.5	103	503	Quadricyclane	15	50	81.0	0.6	56
439	C <sub>6</sub> H <sub>5</sub> Cl	12	58	12.4	0.3	56	504	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub> SH	15	50	-21.1	0.3	56
440	(CH <sub>3</sub> O) <sub>2</sub> SO	12	58	-115.5	0.5	56	505	(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> S	15	50	-20.0	0.2	56
441	Pyrazine-1,4-dioxide	12	58	44.6	0.5	104	506	Si(CH <sub>3</sub> ) <sub>3</sub> OH	15	50	-119.5	0.7	88
442	<i>o</i> -C <sub>6</sub> H <sub>4</sub> Cl <sub>2</sub>	12	74	7.2	0.5	56	507	C <sub>6</sub> H <sub>5</sub> NH <sub>3</sub> <sup>+</sup>	15	50	175.6	1.9	45
443	<i>m</i> -C <sub>6</sub> H <sub>4</sub> Cl <sub>2</sub>	12	74	6.1	0.5	56	508	(CH <sub>3</sub> O)(C <sub>2</sub> H <sub>5</sub> O)SO	15	66	-125.2	0.5	56
444	<i>p</i> -C <sub>6</sub> H <sub>4</sub> Cl <sub>2</sub>	12	74	5.4	0.4	56	509	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> Cl	15	66	4.5	0.7	56
445	C <sub>6</sub> F <sub>6</sub>	12	90	-228.5	0.3	75	510	<i>o</i> -ClC <sub>6</sub> H <sub>4</sub> COOH	15	80	-72.7	0.2	113
446	Perfluorocyclobutane	12	96	-369.5	2.6	75	511	<i>m</i> -ClC <sub>6</sub> H <sub>4</sub> COOH	15	80	-76.9	0.2	113
447	C <sub>6</sub> F <sub>5</sub> Cl	12	98	-194.1	0.7	56	512	<i>p</i> -ClC <sub>6</sub> H <sub>4</sub> COOH	15	80	-77.6	0.2	113
448	Tetrachloro- <i>p</i> -benzoquinone	12	120	-44.4	2.8	56	513	Bicyclopropyl	16	46	30.9	0.9	75
449	C <sub>6</sub> Cl <sub>6</sub>	12	138	-8.6	2.3	75	514	<i>cis</i> -bicyclo[2.2.0]hexane	16	46	29.8	0.3	98
450	N <sub>3</sub> P <sub>3</sub> Cl <sub>6</sub>	12	168	-175.9	n/a	105	515	Cubane	16	56	148.7	1.0	75
451	(CH <sub>3</sub> ) <sub>3</sub> C·( <sup>2</sup> A <sub>1</sub> )	13	33	12.3	0.4	32	516	1,3,5,7-cyclooctatetraene	16	56	70.7	0.4	56
452	(CH <sub>3</sub> ) <sub>3</sub> N	13	34	-5.7	0.2	56	517	C <sub>6</sub> H <sub>5</sub> CH=CH <sub>2</sub>	16	56	35.3	0.4	56
453	Spiropentane	13	38	44.3	0.2	56	518	B(OCH <sub>3</sub> ) <sub>3</sub>	16	56	-214.6	0.7	75
454	( <i>Z</i> )-CH <sub>3</sub> CH=CHCH=CH <sub>2</sub>	13	38	19.5	0.3	56	519	(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> SO	16	58	-49.1	0.4	56
455	( <i>E</i> )-CH <sub>3</sub> CH=CHCH=CH <sub>2</sub>	13	38	18.2	0.2	56	520	Indole	16	62	37.4	0.3	108

TABLE I. (Continued.)

Entry	Species (el state or mult)	Number of		$\Delta H_f^0$ (kcal/mol)		Source	Entry	Species (el state or mult)	Number of		$\Delta H_f^0$ (kcal/mol)		Source
		Nuclei	Elec	Value	Error				Nuclei	Elec	Value	Error	
521	HS(CH <sub>2</sub> ) <sub>4</sub> SH	16	66	-12.0	0.4	56	561	Urotropin	22	76	47.6	0.7	121
522	C <sub>2</sub> H <sub>5</sub> SSC <sub>2</sub> H <sub>5</sub>	16	66	-17.9	0.2	56	562	Acenaphthene	22	82	37.3	0.7	56
523	P(OCH <sub>3</sub> ) <sub>3</sub>	16	66	-168.6	1.5	57	563	Biphenyl	22	82	43.4	0.5	56
524	<i>p</i> -O <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> NH <sub>2</sub>	16	72	13.2	0.4	114	564	Carbazole	22	88	50.0	1.2	108
525	Pyridinium dicyanomethylide	16	74	125.1	3.0	91	565	2,4,6-(CH <sub>3</sub> ) <sub>3</sub> C <sub>6</sub> H <sub>2</sub> CN→O	23	86	32.7	1.0	122
526	C(CH <sub>3</sub> ) <sub>4</sub>	17	42	-40.3	0.3	75	566	Acridine	23	94	65.5	1.0	108
527	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub> CH <sub>3</sub>	17	42	-35.1	0.2	56	567	Phenanthridine	23	94	57.5	1.0	108
528	Piperidine	17	48	-11.3	0.1	108	568	(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> S	23	98	55.3	0.7	56
529	(CH <sub>3</sub> ) <sub>4</sub> Si	17	50	-55.7	0.8	88	569	Phenanthrene	24	94	49.5	1.1	75
530	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>4</sub> Cl	17	58	-41.8	0.5	56	570	Anthracene	24	94	55.2	0.5	56
531	(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> SO <sub>2</sub>	17	66	-102.6	0.6	56	571	( <i>E</i> )-azobenzene	24	96	96.9	0.3	123
532	Quinoline	17	68	47.9	0.3	108	572	( <i>Z</i> )-azobenzene	24	96	107.7	0.5	124
533	Isoquinoline	17	68	48.9	0.3	108	573	(CH <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> SO	24	106	25.5	0.7	56
534	Cyclohexane	18	48	-29.5	0.2	56	574	C <sub>6</sub> H <sub>5</sub> SSC <sub>6</sub> H <sub>5</sub>	24	114	58.2	1.0	56
535	<i>o</i> -C <sub>6</sub> H <sub>4</sub> (CH <sub>3</sub> ) <sub>2</sub>	18	58	4.6	0.3	56	575	Si(CH <sub>3</sub> ) <sub>2</sub> (OC <sub>2</sub> H <sub>5</sub> ) <sub>2</sub>	25	82	-185.7	1.2	88
536	<i>m</i> -C <sub>6</sub> H <sub>4</sub> (CH <sub>3</sub> ) <sub>2</sub>	18	58	4.1	0.2	56	576	P(OC <sub>2</sub> H <sub>5</sub> ) <sub>3</sub>	25	90	-194.4	1.3	57
537	<i>p</i> -C <sub>6</sub> H <sub>4</sub> (CH <sub>3</sub> ) <sub>2</sub>	18	58	4.3	0.2	56	577	( <i>E</i> )-azoxybenzene	25	104	81.7	0.6	125
538	Naphthalene	18	68	36.1	0.3	75	578	(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> SO <sub>2</sub>	25	114	-28.4	0.8	56
539	Azulene	18	68	69.1	0.8	56	579	Si(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> Cl <sub>2</sub>	25	130	-51.5	n/a	126
540	(C <sub>2</sub> H <sub>5</sub> O) <sub>2</sub> SO	18	74	-132.0	0.5	56	580	Adamantane	26	76	-31.8	0.3	127
541	<i>p</i> -ClC <sub>6</sub> H <sub>4</sub> C <sub>2</sub> H <sub>5</sub>	18	74	-0.9	0.6	56	581	( <i>Z</i> )-stilbene	26	96	60.3	0.5	56
542	1-chloronaphthalene	18	84	28.6	2.3	56	582	( <i>E</i> )-stilbene	26	96	56.4	0.3	56
543	2-chloronaphthalene	18	84	32.8	2.4	56	583	(C <sub>2</sub> H <sub>5</sub> O) <sub>3</sub> PO	26	98	-285.8	n/a	128
544	Perfluorocyclohexane	18	144	-566.2	1.8	115	584	Pyrene	26	106	53.9	0.3	56
545	Bicyclo[2.2.1]heptane	19	54	-13.1	1.1	56	585	Fluoranthene	26	106	69.1	0.2	56
546	(CH <sub>3</sub> ) <sub>3</sub> SiNH(CH <sub>3</sub> )	19	58	-54.3	1.0	88	586	[Si(CH <sub>3</sub> ) <sub>3</sub> ] <sub>2</sub> O	27	90	-185.7	1.5	88
547	Cyclohexanethiol	19	64	-23.0	0.2	56	587	[Si(CH <sub>3</sub> ) <sub>3</sub> ] <sub>2</sub> NH	28	90	-114.0	1.2	88
548	(C <sub>2</sub> H <sub>5</sub> O) <sub>2</sub> SO <sub>2</sub>	19	82	-180.8	0.5	56	588	C <sub>6</sub> H <sub>5</sub> SO <sub>2</sub> SO <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	28	146	-114.9	0.9	75
549	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>4</sub> CH <sub>3</sub>	20	50	-39.9	0.2	56	589	Si(C <sub>2</sub> H <sub>5</sub> ) <sub>4</sub>	29	82	-71.0	1.4	88
550	Bullvalene	20	70	79.9	0.8	116	590	Be(CH <sub>3</sub> COCHCOCH <sub>3</sub> ) <sub>2</sub>	29	110	-272.7	0.7	129
551	Triquinacene	20	70	57.5	0.7	117	591	Triphenylene	30	120	65.5	1.0	56
552	2,4,10-trioxadamantane	20	76	-119.3	0.5	118	592	Benzo[ <i>c</i> ]phenanthrene	30	120	69.6	1.1	56
553	Biphenylene	20	80	99.9	0.8	56	593	Benz[ <i>a</i> ]anthracene	30	120	70.0	1.0	56
554	Acenaphthylene	20	80	62.1	1.1	56	594	Chrysene	30	120	64.5	1.6	56
555	1-azabicyclo[2.2.2]octane	21	62	-1.0	0.3	119	595	[Si(CH <sub>3</sub> ) <sub>3</sub> ] <sub>2</sub> NCH <sub>3</sub>	31	98	-107.3	2.0	88
556	Si(CH <sub>3</sub> ) <sub>3</sub> OC <sub>2</sub> H <sub>5</sub>	21	66	-119.0	1.0	88	596	Perylene	32	132	75.4	0.9	130
557	Mg( <i>cyclo</i> -C <sub>3</sub> H <sub>5</sub> ) <sub>2</sub>	21	82	32.9	0.9	120	597	P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub>	34	138	76.5	1.1	57
558	Si(OCH <sub>3</sub> ) <sub>4</sub>	21	82	-281.8	1.0	88	598	[Si(CH <sub>3</sub> ) <sub>3</sub> ] <sub>3</sub> N	40	130	-160.4	3.0	88
559	bicyclo[2.2.2]octane	22	62	-23.7	0.2	119	599	Si(C <sub>6</sub> H <sub>5</sub> ) <sub>4</sub>	45	178	79.8	1.5	88
560	(CH <sub>3</sub> ) <sub>3</sub> SiN(CH <sub>3</sub> ) <sub>2</sub>	22	66	-59.3	1.0	88	600	C <sub>60</sub>	60	360	618.1	3.4	131

of this function is unknown,  $e_2$  is approximated by an empirical expression that involves parameters determined with the aforementioned fitting procedure.

The BDF scheme offers several distinct advantages over other approaches to the estimation of standard enthalpies of formation. First of all, it does not require the knowledge of either the zero-point energy or the thermal correction, eliminating the need for costly vibrational frequency calculations. Second, it is universally applicable to all species composed of a given set of elements, regardless of the presence of particular types of bonds or even the existence of a Lewis structure. Moreover, it is well defined, as the attractor interaction lines and the bond critical points are entirely determined by the properties of electron density. In these respects, the BDF method constitutes a substantial improvement over the bond additivity corrections that, although reducing the errors in the predicted values of  $\Delta H_f^0$ , rely on the identification of chemical bonds by means of "chemical intuition"

and are not applicable to systems with less usual bonding situations.<sup>17</sup>

Performance assessments carried out for various BDF schemes have demonstrated their capability of significantly enhancing the accuracy of the computed standard enthalpies

TABLE II. Parameters of the B3LYP/6-311++G\*\* modified atom-equivalent scheme<sup>a</sup>

Z	$e_1(Z)$ (a.u.)	Z	$e_1(Z)$ (a.u.)	$e_0$ (kcal/mol)	$e_5$ (kcal/mol)
1	0.594 725	11	162.325 944	-2.714	4.006
3	7.551 433	12	200.141 950		
4	14.807 256	13	242.498 552		
5	24.882 548	14	289.543 197		
6	38.127 846	15	341.376 506		
7	54.787 885	16	398.222 170		
8	75.172 827	17	460.204 694		
9	99.784 419				

<sup>a</sup>See Eq. (2).



TABLE III. Members of the test set with large errors in the values of  $\Delta H_f^0$  predicted with the B3LYP/6-311++G\*\* modified atom-equivalent scheme.<sup>a</sup>

Entry	Species (el state or mult)	$\Delta H_f^0$ (kcal/mol)			Entry	Species (el state or mult)	$\Delta H_f^0$ (kcal/mol)		
		Expt	Pred	Error			Expt	Pred	Error
544	Perfluorocyclohexane	-566.2	-601.2	-35.0	331	CH <sub>3</sub> COOH	-103.4	-115.8	-12.4
196	P <sub>4</sub>	14.1	-18.5	-32.6	489	C <sub>6</sub> H <sub>5</sub> CHO	-8.8	-20.8	-12.0
476	C(NO <sub>2</sub> ) <sub>4</sub>	19.7	-11.6	-31.3	318	H <sub>2</sub> S <sub>5</sub>	13.8	2.1	-11.7
129	FPO	-96.7	-126.5	-29.8	102	BO <sub>2</sub> ·( <sup>2</sup> Π <sub>g</sub> )	-68.0	-79.7	-11.7
140	ClPO	-51.4	-77.5	-26.1	342	CF <sub>3</sub> COOH	-246.5	-258.0	-11.5
226	O=C=C=C=O	-22.4	-47.7	-25.3	463	CH <sub>3</sub> CH(NH <sub>2</sub> )COOH	-99.1	-110.4	-11.3
71	P <sub>2</sub>	34.3	9.4	-24.9	543	2-chloronaphthalene	32.8	21.5	-11.3
271	N <sub>2</sub> O <sub>4</sub>	2.2	-22.5	-24.8	120	HOS <sup>-</sup>	-37.8	-49.0	-11.2
346	1,3-dithiole-2-thione	60.5	38.3	-22.2	126	SCN <sup>-</sup>	-5.2	-16.4	-11.2
75	SiCl·( <sup>2</sup> Π <sub>1/2</sub> )	47.4	25.6	-21.8	305	CH <sub>3</sub> NO <sub>2</sub>	-17.8	-28.9	-11.1
73	AlS <sup>-</sup>	-3.0	-24.5	-21.5	498	<i>o</i> -ClC <sub>6</sub> H <sub>4</sub> CHO	-15.0	-26.0	-11.0
338	(COOH) <sub>2</sub>	-175.0	-196.1	-21.1	334	CH <sub>3</sub> COSH	-41.8	-52.7	-10.9
590	Be(CH <sub>3</sub> COCHCOCH <sub>3</sub> ) <sub>2</sub>	-272.7	-292.4	-19.7	420	FC(NF <sub>2</sub> ) <sub>3</sub>	-48.0	-58.8	-10.8
445	C <sub>6</sub> F <sub>6</sub>	-228.5	-248.1	-19.6	185	COCl <sub>2</sub>	-52.6	-63.3	-10.8
70	AlS·( <sup>2</sup> Σ <sup>+</sup> )	57.0	38.8	-18.2	435	C <sub>6</sub> H <sub>5</sub> O <sup>-</sup>	-37.1	-47.8	-10.7
466	Na(H <sub>2</sub> O) <sub>4</sub> <sup>+</sup>	-160.4	-178.4	-18.0	112	FNO	-15.7	-26.2	-10.6
511	<i>m</i> -ClC <sub>6</sub> H <sub>4</sub> COOH	-76.9	-94.7	-17.8	163	HNCO	-24.3	-34.8	-10.5
512	<i>p</i> -ClC <sub>6</sub> H <sub>4</sub> COOH	-77.6	-95.3	-17.7	388	H <sub>2</sub> NCH <sub>2</sub> COOH	-93.7	-104.2	-10.5
109	HOSi <sup>+</sup>	155.2	137.6	-17.6	574	C <sub>6</sub> H <sub>5</sub> SSC <sub>6</sub> H <sub>5</sub>	58.2	47.7	-10.5
448	Tetrachloro- <i>p</i> -benzoquinone	-44.4	-61.5	-17.1	490	CH <sub>3</sub> COSC <sub>2</sub> H <sub>5</sub>	-54.5	-64.9	-10.4
343	1, 3-dithiol-2-one	-3.6	-20.7	-17.1	66	SF <sup>-</sup>	-49.9	-60.3	-10.4
173	FNO <sub>2</sub>	-26.0	-42.8	-16.8	15	Al <sup>+</sup>	216.7	206.3	-10.4
228	B <sub>2</sub> O <sub>3</sub>	-199.8	-216.4	-16.6	267	SiH <sub>2</sub> =SiH <sub>2</sub>	65.7	55.4	-10.3
223	HNO <sub>3</sub>	-32.1	-48.6	-16.5	111	C <sub>3</sub>	34.1	23.8	-10.3
61	SiF·( <sup>2</sup> Π <sub>1/2</sub> )	-4.8	-21.1	-16.3	57	SiO	-24.6	-34.9	-10.3
447	C <sub>6</sub> F <sub>5</sub> Cl	-194.1	-210.3	-16.2	462	(CH <sub>3</sub> ) <sub>3</sub> P	-22.5	-32.7	-10.2
49	F <sub>2</sub> ·( <sup>2</sup> Σ <sub>u</sub> <sup>+</sup> )	-69.3	-85.5	-16.2	116	NO <sub>2</sub> <sup>-</sup>	-44.5	-54.7	-10.2
510	<i>o</i> -ClC <sub>6</sub> H <sub>4</sub> COOH	-72.7	-88.7	-16.0	485	<i>cyclo</i> -C <sub>7</sub> H <sub>7</sub> <sup>+</sup>	206.7	196.6	-10.1
433	1,3,5-trioxane	-111.3	-127.2	-15.9	593	Benz[ <i>a</i> ]anthracene	70.0	59.9	-10.1
286	(COCl) <sub>2</sub>	-80.3	-96.0	-15.7	558	Si(OCH <sub>3</sub> ) <sub>4</sub>	-281.8	-291.9	-10.1
137	CS <sub>2</sub>	28.0	12.3	-15.7	78	CH <sub>2</sub> ( <sup>3</sup> B <sub>1</sub> )	92.8	102.9	10.1
180	ClNO <sub>2</sub>	2.9	-12.6	-15.6	35	N <sub>2</sub>	0.0	10.1	10.1
68	Si <sub>2</sub> ( <sup>3</sup> Σ <sub>g</sub> <sup>-</sup> )	139.9	124.4	-15.5	31	CN·( <sup>2</sup> Σ <sup>+</sup> )	104.9	115.0	10.1
121	COS	-33.1	-48.5	-15.4	440	(CH <sub>3</sub> O) <sub>2</sub> SO	-115.5	-104.8	10.6
518	B(OCH <sub>3</sub> ) <sub>3</sub>	-214.6	-229.8	-15.2	312	1- <i>H</i> -tetrazole	80.0	90.7	10.7
229	N <sub>2</sub> O <sub>3</sub>	19.8	4.6	-15.2	557	Mg( <i>cyclo</i> -C <sub>3</sub> H <sub>5</sub> ) <sub>2</sub>	32.9	43.9	11.0
437	<i>p</i> -benzoquinone	-29.3	-44.1	-14.8	291	PCl <sub>5</sub>	-89.9	-78.5	11.4
165	HCOO <sup>-</sup>	-110.9	-125.7	-14.8	362	CH <sub>3</sub> SOCH <sub>2</sub> <sup>-</sup>	-29.2	-17.8	11.4
350	S <sub>8</sub>	24.0	9.2	-14.8	555	1-azabicyclo[2.2.2]octane	-1.0	10.5	11.5
370	B <sub>3</sub> O <sub>3</sub> Cl <sub>3</sub>	-390.0	-404.8	-14.8	8	B <sup>+</sup>	325.2	336.8	11.6
103	CO <sub>2</sub>	-94.1	-108.8	-14.7	24	NH( <sup>3</sup> Σ <sup>-</sup> )	85.2	96.8	11.6
233	F <sub>3</sub> NO	-39.0	-53.5	-14.5	580	Adamantane	-31.8	-19.1	12.6
330	HCOOCH <sub>3</sub>	-85.0	-99.5	-14.5	587	[Si(CH <sub>3</sub> ) <sub>3</sub> ] <sub>2</sub> NH	-114.0	-100.8	13.1
264	(CHO) <sub>2</sub>	-50.7	-64.9	-14.2	198	SiCl <sub>3</sub> ·( <sup>2</sup> A <sub>1</sub> )	-93.3	-79.9	13.4
309	B(OH) <sub>3</sub>	-237.2	-251.3	-14.1	560	(CH <sub>3</sub> ) <sub>3</sub> SiN(CH <sub>3</sub> ) <sub>2</sub>	-59.3	-45.3	14.0
497	C <sub>6</sub> H <sub>5</sub> COCl	-24.7	-38.7	-14.0	132	ClO <sub>2</sub> ·( <sup>2</sup> B <sub>1</sub> )	25.0	39.0	14.0
224	HOCO <sub>2</sub> <sup>-</sup>	-177.8	-191.8	-14.0	589	Si(C <sub>2</sub> H <sub>5</sub> ) <sub>4</sub>	-71.0	-55.9	15.1
134	Al <sub>2</sub> O	-34.7	-48.7	-14.0	114	NaCN	22.5	38.6	16.1
176	FOOF	4.6	-9.3	-13.9	595	[Si(CH <sub>3</sub> ) <sub>3</sub> ] <sub>2</sub> NCH <sub>3</sub>	-107.3	-90.8	16.5
405	1,3-dithiolan-2-one	-30.1	-44.0	-13.9	236	SiF <sub>4</sub>	-386.0	-368.9	17.1
597	P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub>	76.5	62.7	-13.9	347	Al <sub>2</sub> F <sub>6</sub>	-629.5	-611.1	18.4
390	Na(H <sub>2</sub> O) <sub>3</sub> <sup>+</sup>	-88.8	-102.5	-13.7	243	SF <sub>4</sub>	-182.4	-163.8	18.6
446	Perfluorocyclobutane	-369.5	-383.2	-13.7	404	Thiete sulphone	-29.7	-10.2	19.5
273	C <sub>2</sub> F <sub>4</sub>	-157.4	-171.0	-13.6	365	C(CN) <sub>4</sub>	160.8	180.5	19.7
441	Pyrazine-1, 4-dioxide	44.6	31.0	-13.6	417	(CH <sub>3</sub> ) <sub>2</sub> SO <sub>2</sub>	-89.2	-69.1	20.1
130	SiF <sub>2</sub> (singlet)	-140.5	-153.9	-13.4	179	SO <sub>3</sub>	-94.6	-72.7	21.9
339	ClCH <sub>2</sub> COOH	-104.0	-117.2	-13.2	531	(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> SO <sub>2</sub>	-102.6	-80.4	22.1
216	HCOOH	-90.5	-103.4	-12.9	548	(C <sub>2</sub> H <sub>5</sub> O) <sub>2</sub> SO <sub>2</sub>	-180.8	-158.6	22.1
60	PO·( <sup>2</sup> Π <sub>1/2</sub> )	-5.6	-18.5	-12.9	472	(CH <sub>3</sub> O) <sub>2</sub> SO <sub>2</sub>	-164.2	-141.9	22.3
524	<i>p</i> -O <sub>2</sub> NO <sub>6</sub> H <sub>4</sub> NH <sub>2</sub>	13.2	0.4	-12.8	470	(CH <sub>2</sub> =CH) <sub>2</sub> SO <sub>2</sub>	-36.0	-13.4	22.6
97	PH <sub>2</sub> <sup>-</sup>	6.4	-6.3	-12.7	561	Urotropin	47.6	70.3	22.8
360	$\beta$ -propiolactone	-67.6	-80.3	-12.7	491	CH <sub>3</sub> SO <sub>2</sub> C <sub>2</sub> H <sub>5</sub>	-97.7	-74.9	22.8
74	SiS (singlet)	25.3	12.7	-12.6	578	(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> SO <sub>2</sub>	-28.4	-5.5	22.9
167	OBBO	-109.0	-121.6	-12.6	246	SO <sub>2</sub> Cl <sub>2</sub>	-84.8	-61.7	23.1

TABLE III. (Continued.)<sup>a</sup>

Entry	Species (el state or mult)	$\Delta H_f^0$ (kcal/mol)			Entry	Species (el state or mult)	$\Delta H_f^0$ (kcal/mol)		
		Expt	Pred	Error			Expt	Pred	Error
598	[Si(CH <sub>3</sub> ) <sub>3</sub> ] <sub>3</sub> N	-160.4	-136.9	23.5	499	P <sub>4</sub> O <sub>10</sub>	-694.1	-656.1	38.0
403	CH <sub>3</sub> SO <sub>2</sub> CH <sub>2</sub> <sup>-</sup>	-88.3	-64.8	23.5	284	SF <sub>5</sub> ( <sup>2</sup> A <sub>1</sub> )	-218.1	-172.8	45.3
471	Butadiene sulphone	-61.2	-36.2	25.0	450	N <sub>3</sub> P <sub>3</sub> Cl <sub>6</sub>	-175.9	-130.5	45.4
481	B <sub>5</sub> H <sub>9</sub>	17.5	43.9	26.4	600	C <sub>60</sub>	618.1	665.8	47.7
314	H <sub>2</sub> SO <sub>4</sub>	-175.7	-148.2	27.5	239	FCIO <sub>3</sub>	-5.1	45.5	50.5
282	PF <sub>5</sub>	-381.1	-353.4	27.8	315	SF <sub>6</sub>	-291.7	-240.3	51.4
279	HSO <sub>4</sub> <sup>-</sup>	-231.9	-203.5	28.4	317	SF <sub>5</sub> Cl	-248.3	-192.0	56.3
277	HOSO <sub>2</sub> F	-180.0	-149.7	30.3	588	C <sub>6</sub> H <sub>5</sub> SO <sub>2</sub> SO <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	-114.9	-51.0	64.0
125	FAIO	-139.0	-107.1	31.9	369	Cl <sub>2</sub> O <sub>7</sub>	65.0	156.4	91.4
237	SO <sub>2</sub> F <sub>2</sub>	-181.3	-148.4	32.9					

<sup>a</sup>See Eq. (2) and Table II. Only the species with absolute errors in the predicted  $\Delta H_f^0$  greater than 10 kcal/mol are listed.

of formation.<sup>6</sup> For example, at the B3LYP/6-311G\*\* level of theory, the average absolute error of 6.6 kcal/mol in the values of  $\Delta H_f^0$  obtained with the modified atom-equivalent scheme,

$$\Delta H_f^0(X) = E(X) + e_Q Q(X) + e_S N_S(X) + \sum_I e_1(Z_I), \quad (2)$$

is almost halved to 3.4 kcal/mol upon the inclusion of a five-term BDF. The main contributors to this residual error are anions with localized charges, which are poorly described by the basis set that lacks diffuse functions, and several species with inaccurate experimental data that were included in the original 300-member training set.

These encouraging results have prompted us to develop a more accurate B3LYP/6-311++G\*\* scheme, with the present compilation of standard enthalpies of formation being employed as the training set. Accordingly, total energies of the 600 species listed in Table I were computed at their optimized geometries with the GAUSSIAN 94 suite of programs.<sup>133</sup> The fitting process and the forms of the BDFs were identical to those described previously.<sup>6</sup> The resulting parameters of the modified atom-equivalent scheme [Eq. (2)] are listed in Table II. As expected,<sup>6,22,23,134</sup> stabilities of hypervalent species are grossly underestimated, whereas the computed standard enthalpies of formation of polyhalogenated compounds with normal valences are often too low (Table III). The overall average absolute error and the standard deviation equal 7.7 and 11.8 kcal/mol, respectively. The errors for individual species range from -35.0 to 91.4 kcal/mol, the largest absolute deviation between the computed and experimental values of  $\Delta H_f^0$  being observed for Cl<sub>2</sub>O<sub>7</sub>. One out of four predictions suffers from an absolute error in excess of 10 kcal/mol (Table IV).

These errors reflect three deficiencies of the B3LYP/6-311++G\*\* modified atom equivalent scheme, namely the semiempirical inclusion of zero-point energies and thermal corrections, the modest size of the basis set, and the inaccuracy of the B3LYP functional itself. In light of the previously published study, the elimination of the first deficiency is expected to improve the computed standard enthalpies of formation only marginally.<sup>6</sup> On the other hand, there is some evidence that the inclusion of more polarization functions in the basis sets may lead to substantially better

(although still not sufficiently accurate) predictions for hypervalent species.<sup>17,22,23</sup> However, such calculations are presently not feasible for larger systems, including many of those listed in Table I.

Inspection of Table IV reveals that a practical route to improving the accuracy of the computed values of  $\Delta H_f^0$  is offered by the BDF approach. Both the average absolute error and the standard deviation decrease steadily with the number of terms in BDF. In particular, the five-term BDF,

$$\begin{aligned}
 &e_2(\rho_{IJ}, R_{IJ}, Z_{IJ}, \alpha_{IJ}, \beta_{IJ}) \\
 &= -8.612 \times 31 \times 10^{-1} \rho_{IJ}^{4/3} R_{IJ}^{-1/3} Z_{IJ} \alpha_{IJ}^{-2/3} \beta_{IJ}^{1/3} \\
 &+ 5.22004 \times 10^2 \rho_{IJ}^3 R_{IJ}^{2/3} Z_{IJ}^{-2/3} \alpha_{IJ}^{-1} \beta_{IJ}^{1/3} \\
 &- 4.40326 \times 10^{-4} \rho_{IJ}^3 R_{IJ}^{-3} Z_{IJ}^3 \alpha_{IJ}^{2/3} \beta_{IJ}^{-4/3} \\
 &+ 1.91731 \times 10^{-7} \rho_{IJ}^3 R_{IJ}^3 Z_{IJ}^3 \alpha_{IJ}^{-2} \beta_{IJ} \\
 &- 3.27319 \times 10^{-3} \rho_{IJ}^{-3} R_{IJ}^3 \alpha_{IJ}^3 \beta_{IJ}^{-1/2}, \quad (3)
 \end{aligned}$$

affords standard enthalpies of formation with the average absolute error of 3.3 kcal/mol and the standard deviation of 5.1 kcal/mol (Table IV). The parameters  $e_Q$  and  $e_S$  are much smaller in magnitude than those of the modified atom equivalent scheme (Table V), reflecting an improved handling of ions and radicals. Out of the 600 species, 270 (45%

TABLE IV. Error statistics for the B3LYP/6-311++G\*\* BDF schemes.<sup>a</sup>

$N_{\text{BDF}}^b$	Av. abs. err.	Std. dev.	Max. abs. err. <sup>c</sup>	Error range	$M^d$
0	7.7	11.8	91.4 (Cl <sub>2</sub> O <sub>7</sub> )	-35.0-91.4	147 (24.5%)
1	4.6	7.1	67.6 (Cl <sub>2</sub> O <sub>7</sub> )	-25.3-67.6	56 (9.3%)
2	3.9	6.1	54.7 (Cl <sub>2</sub> O <sub>7</sub> )	-22.6-54.7	45 (7.5%)
3	3.6	5.4	35.8 (FAIO)	-21.7-35.8	37 (6.2%)
4	3.5	5.2	34.9 (FAIO)	-21.9-34.9	29 (4.8%)
5	3.3	5.1	36.0 (FAIO)	-21.6-36.0	26 (4.3%)

<sup>a</sup>See Eq. (1). All errors are in kcal/mol.

<sup>b</sup>The number of terms in BDF.  $N_{\text{BDF}}=0$  corresponds to the modified atom-equivalent scheme of Eq. (2).

<sup>c</sup>The species with the largest absolute error in the predicted  $\Delta H_f^0$  is given in parentheses.

<sup>d</sup>The number of species with absolute errors in the predicted  $\Delta H_f^0$  greater than 10 kcal/mol.

TABLE V. Parameters of the B3LYP/6-311++G\*\* five-term BDF scheme.<sup>a</sup>

Z	$e_1(Z)$ (a.u.)	Z	$e_1(Z)$ (a.u.)	$e_Q$ (kcal/mol)	$e_S$ (kcal/mol)
1	0.586 789	11	162.323 050	0.284	-0.345
3	7.546 572	12	200.147 133		
4	14.798 838	13	242.509 075		
5	24.877 331	14	289.574 486		
6	38.132 726	15	341.418 336		
7	54.792 149	16	398.249 566		
8	75.193 391	17	460.220 360		
9	99.797 820				

<sup>a</sup>See Eq. (1).

of the total) have their enthalpies predicted within 2 kcal/mol from the experimental values, while the predictions for 356 (59% of the total) species fall within 3 kcal/mol. The errors exceed 5 kcal/mol only in 123 (21% of the total) cases.

The set of systems for which the five-term BDF scheme fares poorly, yielding enthalpies with errors greater than 10 kcal/mol, comprises 26 species (Table VI). It is dominated by molecules containing either aluminum atoms and/or multiple fluorines. It is unclear at present whether these systems represent cases where the BDF methodology fails or, more probably, instances of grossly inaccurate experimental values of  $\Delta H_f^0$ . Resolution of these discrepancies calls for revisiting the published thermochemical data and thus new calorimetric experiments.

#### IV. DISCUSSION AND CONCLUSIONS

The comprehensive set of experimental standard enthalpies of formation presented in this paper is certain to facilitate benchmarking, calibration, and parametrization of electronic structure methods. With its diverse molecules, many possessing unusual geometries and bonding situations, the present set is capable of uncovering deficiencies in approaches of quantum chemistry that are not detectable with smaller compilations of data. These deficiencies can often be alleviated with additional/revised parameterization.

An example of such a methodology is provided by the development of the B3LYP/6-311++G\*\* bond density functional (BDF) scheme. The set of atoms, molecules, and ions listed in Table III, for which the original B3LYP/6-311++G\*\* level of theory produces unacceptably large errors in the predicted values of  $\Delta H_f^0$ , contains the species that are poorly handled by a typical hybrid density functional used in conjunction with a moderate-size basis set. As such, it is suitable for a rigorous testing of new functionals.

The B3LYP/6-311++G\*\* BDF method, defined by Eqs. (1), (3), and the parameters listed in Table V, affords accurate estimates of  $\Delta H_f^0$  for a majority of the members of the test set. It is sufficiently inexpensive in terms of computer time and memory to allow predictions of standard enthalpies of formation even for molecules as large as the C<sub>60</sub> fullerene. It requires only single point calculations at optimized geometries, yielding values of  $\Delta H_f^0$  with the average-absolute error of 3.3 kcal/mol and thus rivaling more expensive methods in accuracy (especially for larger systems).

TABLE VI. Members of the test set with large errors in the values of  $\Delta H_f^0$  predicted with the B3LYP/6-311++G\*\* five-term (BDF) scheme.<sup>a</sup>

Entry	Species (el state or mult)	$\Delta H_f^0$ (kcal/mol)		
		Expt	Pred	Error
557	Mg( <i>cyclo</i> -C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub>	32.9	11.3	-21.6
129	FPO	-96.7	-117.4	-20.7
420	FC(NF <sub>2</sub> ) <sub>3</sub>	-48.0	-65.9	-17.9
477	C(NF <sub>2</sub> ) <sub>4</sub>	0.2	-16.4	-16.6
137	CS <sub>2</sub>	28.0	13.9	-14.1
140	CIPO	-51.4	-65.4	-14.0
346	1,3-dithiole-2-thione	60.5	46.6	-13.9
544	Perfluorocyclohexane	-566.2	-579.8	-13.6
73	AlS <sup>-</sup>	-3.0	-15.7	-12.7
70	AlS· ( <sup>2</sup> Σ <sup>+</sup> )	57.0	45.2	-11.8
49	F <sub>2</sub> <sup>-</sup> · ( <sup>2</sup> Σ <sub>u</sub> <sup>+</sup> )	-69.3	-80.4	-11.1
351	Al <sub>2</sub> Cl <sub>6</sub>	-309.7	-319.9	-10.1
8	B <sup>+</sup>	325.2	336.5	11.3
291	PCl <sub>5</sub>	-89.9	-78.0	11.9
236	SiF <sub>4</sub>	-386.0	-374.0	12.0
391	<i>p</i> -benzynes (singlet)	137.8	150.9	13.1
315	SF <sub>6</sub>	-291.7	-278.4	13.3
114	NaCN	22.5	35.9	13.4
281	NCSSCN	83.6	97.7	14.1
198	SiCl <sub>3</sub> · ( <sup>2</sup> A <sub>1</sub> )	-93.3	-78.0	15.3
600	C <sub>60</sub>	618.1	634.8	16.7
588	C <sub>6</sub> H <sub>5</sub> SO <sub>2</sub> SO <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	-114.9	-94.9	20.0
284	SF <sub>5</sub> · ( <sup>2</sup> A <sub>1</sub> )	-218.1	-197.8	20.3
365	C(CN) <sub>4</sub>	160.8	182.3	21.5
317	SF <sub>5</sub> Cl	-248.3	-224.2	24.1
125	FAIO	-139.0	-103.0	36.0

<sup>a</sup>See Eqs. (1), (3), and Table V. Only the species with absolute errors in the predicted  $\Delta H_f^0$  greater than 10 kcal/mol are listed.

Still, this scheme could possibly be refined even further, especially in order to reduce errors observed for molecules such as H<sub>2</sub>, N<sub>2</sub>, C<sub>2</sub>H<sub>2</sub>, and H<sub>2</sub>F<sub>2</sub>.

It appears that the experimental data for at least some of the 26 species listed in Table VI are of suspect quality. As such, they may be omitted from the test set, although at the expense of a reduced diversity in the remaining systems.

#### ACKNOWLEDGMENTS

The research described in this publication has been supported by the Office of Energy Research, Office of Basic Energy Sciences, Division of Chemical Sciences, US Department of Energy under Grant No. DE-FG02-97ER14758. M.S. acknowledges a Feodor-Lynen Research Fellowship from the Alexander von Humboldt Foundation.

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