

# Heats of Formation of Beryllium, Boron, Aluminum, and Silicon Re-examined by Means of W4 Theory

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Received: March 1, 2007; In Final Form: April 12, 2007

Benchmark total atomization energies (TAE<sub>0</sub> values) were obtained, by means of our recent W4 theory [Karton, A.; Rabinowitz, E.; Martin, J. M. L.; Ruscic, B. *J. Chem. Phys.* **2006**, *125*, 144108], for the molecules Be<sub>2</sub>, BeF<sub>2</sub>, BeCl<sub>2</sub>, BH, BF, BH<sub>3</sub>, BHF<sub>2</sub>, B<sub>2</sub>H<sub>6</sub>, BF<sub>3</sub>, AlF, AlF<sub>3</sub>, AlCl<sub>3</sub>, SiH<sub>4</sub>, Si<sub>2</sub>H<sub>6</sub>, and SiF<sub>4</sub>. We were then able to deduce “semi-experimental” heats of formation for the elements beryllium, boron, aluminum, and silicon by combining the calculated TAE<sub>0</sub> values with experimental heats of formation obtained from reactions that do not involve the species Be(g), B(g), Al(g), and Si(g). The elemental heats of formation are fundamental thermochemical quantities that are required whenever a molecular heat of formation has to be derived from a calculated binding energy. Our recommended  $\Delta H_{f,0}^\circ[A(g)]$  values are Be  $76.4 \pm 0.6$  kcal/mol, B  $135.1 \pm 0.2$  kcal/mol, Al  $80.2 \pm 0.4$  kcal/mol, and Si  $107.2 \pm 0.2$  kcal/mol. (The corresponding values at 298.15 K are 77.4, 136.3, 80.8, and 108.2 kcal/mol, respectively.) The Be value is identical to the CODATA recommendation (but with half of the uncertainty), while the B, Al, and Si values represent substantial revisions from established earlier reference data. The revised B and Si values are in agreement with earlier semi-ab initio derivations but carry much smaller uncertainties.

## I. Introduction

From an experimentalist’s perspective, the most basic thermodynamic property of a polyatomic molecule is its heat of formation. From a theoretician’s perspective (or, in the case of diatomic molecules, a spectroscopist’s perspective), the most basic quantity is the total atomization energy, that is, the energy required to break the molecule up into its constituent gas-phase atoms in their respective ground states. The two are related by the equation

$$\begin{aligned} \Delta H_{f,T}^\circ(X_k Y_l Z_m \dots) - k\Delta H_{f,T}^\circ(X) - l\Delta H_{f,T}^\circ(Y) - \\ m\Delta H_{f,T}^\circ(Z) - \dots \\ = -\text{TAE}_0[X_k Y_l Z_m \dots] + \text{hcf}_T[X_k Y_l Z_m \dots] - k\text{hcf}_T(X) - \\ l\text{hcf}_T(Y) - m\text{hcf}_T(Z) - \dots \quad (1) \end{aligned}$$

where  $\text{hcf}_T \equiv H_T - H_0$  is the heat content function, and the total atomization energy at absolute zero, TAE<sub>0</sub>, is defined as

$$\begin{aligned} \text{TAE}_0[X_k Y_l Z_m \dots] = kE_e[X] + lE_e[Y] + mE_e[Z] - \dots \\ - E_e[X_k Y_l Z_m \dots] - \text{ZPVE}[X_k Y_l Z_m \dots] \quad (2) \end{aligned}$$

where  $E_e$  represents the absolute energy in the hypothetical motionless state (at the bottom of the well) and ZPVE is the molecular zero-point vibrational energy.

For diatomic or small polyatomic molecules, TAE<sub>0</sub> can be determined spectroscopically as (the sum of) bond dissociation energies. For theoretical thermochemistry methods, be they ab initio or semiempirical, the primary calculated thermochemical quantity is TAE<sub>0</sub>, which needs to be translated into a heat of

formation through eq 1. This equation requires accurate values of the heats of formation of the gas-phase atoms.

Most studies use JANAF<sup>1</sup> or CODATA<sup>2</sup> standard values, although for the {H,C,N,O,F} elements, revised values with smaller uncertainties have very recently been obtained through the ATcT (active thermochemical tables) project of Ruscic and co-workers.<sup>3–8</sup>

For four elements with  $Z \leq 20$ , beryllium, boron, aluminum, and silicon, the atomic heat of formation is associated with uncertainties greater than or equal to about 1 kcal/mol (Table 1). Clearly, this is not a very desirable state of affairs.

The accurate ab initio calculation of vaporization energies of solid metals is presently not an option (we note that for these elements, the heat of formation is equivalent to the heat of vaporization or sublimation). However, assuming that, for some compounds of a given element A, (1) accurate molecular heats of formation are available experimentally *without involvement of the atomic heat of formation of A*, (2) accurate ab initio total atomization energies can be calculated, and (3) all other elements in these compounds have precisely known atomic heats of formation, the atomic heat of formation of A can be obtained semi-experimentally from a thermochemical cycle.

This is precisely the approach that was followed in the pioneering 1995 paper of Ochterski, Petersson, and Wiberg (OPW).<sup>9</sup> These authors combined experimental heats of formation for Be<sub>2</sub>, BeF<sub>2</sub>, BHF<sub>2</sub>, BF<sub>3</sub>, SiH<sub>4</sub>, and Si<sub>2</sub>H<sub>6</sub> with ab initio calculations using the CBS/APNO method<sup>10</sup> of Petersson and co-workers. (For a recent review of computational thermochemistry methods, see ref 11.) As shown in Table 1, OPW (a) proposed a minor downward revision by 0.6 kcal/mol for Be, (b) found corroboration for an earlier statement by Grev and Schaefer<sup>12</sup> that the experimental heats of formation of Si and SiH<sub>4</sub> are incompatible and proposed an upward revision by 1.6 kcal/mol for Si, and (c) proposed that an earlier measurement of  $\Delta H_{f,0}^\circ[B(g)]$  by Storms and Mueller<sup>14</sup> — 2.4 kcal/mol above

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**TABLE 1: Gas-Phase Atomic Heats of Formation at 0 K (kcal/mol) of the First 20 Elements**

element	JANAF <sup>a</sup>	CODATA	ATcT	OPW <sup>9</sup>	this work
H		51.634 ± 0.001	51.633 ± 0.000		
Li		37.70 ± 0.24			
Be		76.42 ± 1.20		75.8 ± 0.8	76.4 ± 0.6
B	132.6	133.82 ± 1.20		136.2 ± 0.2	135.1 ± 0.2
C		169.98 ± 0.11	170.055 ± 0.026		
N		112.53 ± 0.10	112.469 ± 0.006		
O		58.985 ± 0.024	58.997 ± 0.000		
F		18.47 ± 0.07	18.456 ± 0.036		
Na	25.71	25.76 ± 0.17			
Mg		34.87 ± 0.19			
Al	78.23	78.30 ± 0.96			80.2 ± 0.4
Si		106.5 ± 1.9		108.1 ± 0.5	107.15 ± 0.2
P	75.42	75.45 ± 0.24			
S	65.66	65.709 ± 0.036			
Cl		28.590 ± 0.002	28.590 ± 0.000		
K		21.48 ± 0.19			
Ca		42.39 ± 0.19			

<sup>a</sup> JANAF entries identical to CODATA have been left blank.

the CODATA value and 3.6 kcal/mol above the JANAF value, and which had been rejected by the JANAF compilers as an outlier, is in fact the correct one.

Collins and Grev,<sup>13</sup> upon inclusion of relativistic corrections in a SiH<sub>4</sub> calculation, found corroboration of the OPW number for silicon.

The hybrid empirical correction-extrapolation nature of CBS-APNO constituted a potential Achilles's Heel of the OPW predictions. Much more elaborate benchmark calculations amounting to W2 theory<sup>15,16</sup> in everything but name were carried out by Bauschlicher, Martin, and Taylor<sup>17</sup> (BMT; see also ref 18) for BF<sub>3</sub> and by Martin and Taylor<sup>19</sup> (MT) for SiF<sub>4</sub>. W2 theory, essentially a layered extrapolation to the relativistic CCSD(T) basis set limit, is entirely devoid of empirical parameters and can reach mean absolute errors in the kJ/mol range for molecules dominated by dynamical correlation, as these perfluoro systems are. These studies confirmed that revisions for B and Si were in order but seemed to indicate that the OPW numbers represent overcorrections; BMT proposed 136.1 ± 0.75 kcal/mol for boron and 107.15 ± 0.38 kcal/mol for silicon.

The importance of post-CCSD(T) correlation effects is an open question and the one most fundamental weakness in those studies. The dangers of relying on "handwaving" arguments about why a contribution is not important are best illustrated by the scalar relativistic contribution. It was received wisdom at the time that scalar relativistic contributions to atomization energies would not be important for first-row or even second-row compounds, yet BMT and MT found quite nontrivial relativistic corrections, -0.7 kcal/mol for BF<sub>3</sub> and -1.9 kcal/mol for SiF<sub>4</sub>.

Recently, post-CCSD(T) calculations for small molecules have become drastically simplified by the development of general coupled cluster codes such as MRCC.<sup>20</sup> Consequently, successors to W2 theory that include post-CCSD(T) corrections have been developed. W3 theory<sup>21</sup> has similar accuracy to W2 theory but is much more robust to nondynamical correlation effects; the most recently developed W4 theory<sup>22</sup> incorporates additional improvements and boasts, for about two dozen molecules with experimentally very precisely known total atomization energies, a mean absolute error of 0.06 kcal/mol, a rms error of 0.08 kcal/mol, and a 95% confidence interval of 0.16 kcal/mol. While precise reference data obtained by the novel ATcT (active thermochemical tables) approach of Ruscic

and co-workers were invaluable in validating the W4 protocol, it still does not involve any parameters derived from experiment and is thus perfectly suited for the present application.

In the present work, we will re-examine the heats of vaporization of boron and silicon and will additionally consider beryllium and aluminum.

## II. Computational Methods

All calculations reported in the present work were carried out on the Linux cluster of the Martin group, which consists of machines custom-built by Access Technologies of Rehovot, Israel. We relied very heavily on two machines in particular, which each have four dual-core AMD Opteron 870 CPUs, 16 gigabytes of RAM, and 2 terabytes of scratch disk space (eight 250 GB Serial-ATA disks striped 8-way on a hardware RAID controller).

All post-CCSD(T) calculations were carried out using a prerelease OpenMP-parallel version of Mihály Kállay's general coupled cluster code MRCC<sup>20</sup> interfaced to the Austin-Mainz-Budapest version of the ACES II program system.<sup>23</sup> All large-scale CCSD and CCSD(T) calculations<sup>24,25</sup> were carried out using versions 2002.6 and 2006.1 of the MOLPRO<sup>26</sup> program system. A few anharmonic force field calculations for the purpose of zero-point vibrational energies (ZPVEs) were carried out using a locally modified version of GAUSSIAN 03 revision C.01.<sup>27</sup> Anharmonic ZPVEs were obtained by the expression of Allen and co-workers.<sup>28</sup>

The computational protocols of W4 theory, of the simplified variants W4lite, W3.2, and W2.2, and of the post-W4 methods W4.2 and W4.3 theory, have been specified and rationalized in great detail in ref 22. We will not repeat these details here, but will just briefly summarize.

All basis sets employed, except for the simple Dunning-Hay double- $\zeta$  basis set employed for some post-CCSD(T) contributions, belong to the correlation-consistent family of Dunning and co-workers.<sup>29-33</sup>

All reference geometries were optimized at the CCSD(T)/cc-pV(Q+d)Z level with only valence electrons correlated. They are available as Supporting Information to the present paper.

W2.2 theory includes the following contributions, each extrapolated to the basis set limit: SCF, valence CCSD correlation energy, valence (T) correlation energy, inner-shell CCSD(T) correlation, scalar relativistic effects (CCSD(T) within the second-order Douglas-Kroll approximation<sup>34,35</sup>), first-order spin-orbit corrections, and SCF-level diagonal Born-Oppen-

TABLE 2: Overview of Convergence of Different Contributions (in kcal/mol)<sup>a</sup>

	valence																	inner shell
	SCF		CCSD		(T)		$\hat{T}_3$ -(T)		(Q)		$\hat{T}_4$ -(Q)		(5)		$\hat{T}_5$ -(5)		$\hat{T}_3$ -(T)	
	(a)	(b)	(a)	(b)	(c)	(a)	(d)	(e)	(f)	(g)	(h)	(i)	(j)	(k)	(f)	(k)	(f)	(l)
H <sub>2</sub>	83.84	83.85	25.62	25.63	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
F <sub>2</sub>	-31.08	-31.08	61.79	61.91	7.62	7.63	-0.35	-0.30	0.93	1.00	0.98	-0.12	-0.12	0.04	0.05	-0.01	0.00	0.03
CH	57.22	57.22	25.85	25.83	0.89	0.89	0.10	0.10	0.03	0.03	0.03	0.00	0.00	0.00	0.00	0.00	0.00	0.01
CF	83.62	83.62	43.57	43.65	5.03	5.03	-0.15	-0.16	0.30	0.31	0.31	-0.06	-0.06	-0.06	-0.07	0.05	0.05	0.01
CH <sub>4</sub>	331.54	331.55	84.73	84.72	2.92	2.89	-0.08	-0.10	0.08	0.08	0.09	0.00	0.00	0.00	0.01	0.00	0.00	0.01
CF <sub>4</sub>	330.48	330.49	133.89	134.31	13.30	13.25	-1.02	N/A	0.86	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
Be <sub>2</sub>	-6.79	-6.79	6.04	6.04	2.58	2.61	0.47	0.41	0.12	0.18	0.17	0.08	0.06	0.00	0.00	0.00	0.00	-0.01
BeF <sub>2</sub>	247.81	247.81	53.27	53.44	5.78	5.77	-0.32	-0.49	0.45	0.30	N/A	-0.07	N/A	-0.02	-0.05	0.03	N/A	0.00
BeCl <sub>2</sub>	194.13	194.11	25.02	24.58	4.85	4.94	-0.32	N/A	0.23	0.34	N/A	-0.03	N/A	-0.04	N/A	0.02	N/A	N/A
BH	64.31	64.31	20.01	20.01	0.41	0.41	0.00	0.00	0.03	0.05	0.04	0.01	0.01	0.00	0.00	0.00	0.00	0.01
BF	143.09	143.09	34.67	34.76	3.99	4.00	-0.30	-0.32	0.30	0.29	0.29	-0.04	-0.03	-0.06	-0.06	0.06	0.04	0.01
BH <sub>3</sub>	234.36	234.35	44.97	44.97	0.80	0.79	0.00	-0.02	0.02	0.03	0.03	0.00	0.00	0.00	N/A	0.00	N/A	0.00
B <sub>2</sub> H <sub>6</sub>	490.60	490.60	108.81	108.85	4.53	4.47	0.02	N/A	0.11	0.17	N/A	0.01	N/A	0.00	N/A	0.00	N/A	N/A
BHF <sub>2</sub>	329.85	329.85	73.35	73.54	6.13	6.11	-0.48	N/A	0.43	0.33	N/A	-0.06	N/A	-0.02	N/A	0.03	N/A	N/A
BF <sub>3</sub>	374.63	374.64	86.11	86.41	8.30	8.28	-0.72	N/A	0.65	0.48	N/A	-0.08	N/A	-0.02	N/A	0.04	N/A	N/A
AlH	55.07	55.09	18.52	18.52	0.07	0.07	-0.09	-0.06	0.02	0.03	0.03	0.01	0.01	0.00	0.00	0.00	0.00	0.03
AlF	125.36	125.45	34.68	34.72	3.25	3.27	-0.41	-0.41	0.29	0.23	0.23	-0.05	-0.03	-0.02	-0.06	0.03	0.05	0.06
AlH <sub>3</sub>	171.21	171.26	42.38	42.39	0.18	0.17	-0.06	-0.02	0.02	0.03	0.03	0.01	0.01	0.00	0.00	0.00	0.00	0.05
AlF <sub>3</sub>	334.18	334.44	88.83	88.98	7.84	7.91	-0.78	N/A	0.74	0.47	N/A	-0.10	N/A	0.00	N/A	0.03	N/A	N/A
AlCl	98.81	98.81	20.72	20.57	2.92	2.97	-0.37	-0.38	0.19	0.28	0.29	-0.02	0.00	-0.03	-0.02	0.02	0.02	0.02
AlCl <sub>3</sub>	258.14	258.16	48.54	47.94	7.01	7.17	-0.83	N/A	0.38	0.55	N/A	-0.03	N/A	-0.03	N/A	0.02	N/A	N/A
SiH	52.23	52.26	21.14	21.12	0.38	0.39	0.00	0.04	0.01	0.01	0.02	0.00	0.05	0.00	0.00	0.00	0.00	0.02
SiF	102.17	102.24	36.54	36.55	3.52	3.55	-0.37	-0.34	0.28	0.22	0.23	-0.06	0.00	-0.02	-0.05	0.04	0.04	0.05
SiH <sub>4</sub>	259.76	259.83	64.22	64.18	0.80	0.81	-0.06	0.04	0.02	0.03	-0.04	0.00	0.05	0.00	0.00	0.00	0.00	0.06
Si <sub>2</sub> H <sub>6</sub>	424.01	424.14	109.03	108.85	2.87	2.90	-0.13	N/A	0.09	0.16	N/A	0.00	N/A	0.00	N/A	0.00	N/A	N/A
SiF <sub>4</sub>	448.14	448.41	118.96	119.07	10.00	10.12	-1.14	N/A	0.93	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A

<sup>a</sup> Basis sets: (a) AV{Q,5}+dZ, (b) AV{5,6}+dZ, (c) AV{T,Q}+dZ, (d) V{D,T}Z, (e) V{T,Q}Z, (f) PVDZ, (g) 1.10\*PVTZ, (h) PVQZ, (i) 1.10\*[RCCSDTQ/PVDZ-UCCSDT(Q)/PVDZ], (j) UCCSDTQ/PVTZ-UCCSDT(Q)/PVTZ, (k) DZ, (l) CVTZ, core{CCSDT,ACES} - core{CCSDT(T),molpro}.

heimer corrections.<sup>36</sup> The largest basis sets employed are of aug-cc-pV(5+d)Z quality; the “+d” indicates the addition of an extra high-exponent d function in second-row compounds<sup>31</sup> to accommodate “inner polarization”.<sup>37,38</sup>

W3.2 theory includes all W2.2 contributions plus two post-CCSD(T) valence correlation contributions, (a) a correction for higher-order  $T_3$  effects, estimated as the CCSDT-CCSD(T) difference extrapolated from cc-pVDZ and cc-pVTZ basis sets and (b) a correction for connected quadruple excitations,  $T_4$ , estimated as the CCSDT(Q)/cc-pVDZ - CCSDT/cc-pVDZ difference.

W4lite theory includes all W3.2 contributions, except that the SCF, valence CCSD, and valence (T) contributions are extrapolated from basis sets as large as aug-cc-pV(6+d)Z.

In full W4 theory, the  $T_4$  contribution is estimated as CCSDTQ/cc-pVDZ-CCSDT(Q)/cc-pVDZ+CCSDT(Q)/cc-pVTZ-CCSDT/cc-pVTZ, scaled by 1.10. A connected quintuples,  $T_5$ , contribution is computed within a double- $\zeta$  basis set. For the W4 systems, for which accurate ATcT atomization energies were available, W4 theory has a rms error of only 0.08 kcal/mol and a 95% confidence interval of 0.16 kcal/mol.<sup>22</sup>

In W4.2 theory, a higher-order  $T_3$  correction is additionally added to the inner-shell correlation contribution, while in W4.3 theory, the treatment of post-CCSD(T) valence correlation effects is made much more rigorous (at great computational expense); (a) the higher order  $T_3$  effects (also known as “T-(T)”) and quasiperturbative  $T_4$  effects, that is, CCSDT(Q)-CCSDT, are extrapolated from cc-pVTZ and cc-pVQZ basis sets; (b) higher order connected quadruples, that is, CCSDTQ-CCSDT(Q), are obtained with the cc-pVTZ basis set; (c) a cc-pVDZ basis set is employed for  $T_5$ ; and (d) a correction for connected sextuple excitations is computed at the CCSDTQ5-(6)/DZ level.

Zero-point vibrational energies for the diatomics were obtained from harmonic frequencies and anharmonic corrections given in Huber and Herzberg,<sup>39</sup> while those for polyatomic molecules will be discussed individually below.

### III. Results and Discussion

Our results are gathered in the following tables. Table 2 gives an overview of basis set convergence of the various components. Diagnostics for the importance of nondynamical correlation, including our own %[(T)] diagnostic proposed in ref 22, are gathered in Table 3. A component breakdown of the final W4 data is given in Table 4. The final results at various  $W_n$  levels are compared in Table 5, while our recommended heats of formation for atomic beryllium, boron, and silicon are compared with earlier values in Table 6.

**A. Beryllium Compounds.** Only two beryllium compounds were considered in this work, BeF<sub>2</sub> and Be<sub>2</sub>.

Earlier studies on the pathological multireference beryllium dimer have been reviewed in refs 40 and 41. Martin,<sup>40</sup> in a combined coupled cluster/multireference ACPF study, found  $D_e = 944 \pm 25 \text{ cm}^{-1}$ , considerably higher than the Bondybey-English<sup>42</sup> experimental value of  $790 \pm 30 \text{ cm}^{-1}$ . Gdanitz,<sup>43</sup> using explicitly correlated MRACPF-R12 techniques (rather than extrapolation of conventional one-particle basis sets like those in ref 40 and the present work), found a lower  $D_e = 899 \text{ cm}^{-1}$  (corresponding to  $D_0 = 2.20 \text{ kcal/mol}$ ); the Martin and Gdanitz studies disagree primarily in the contribution of inner-shell correlation. Roeggen and Veseth,<sup>41</sup> using Gaussian geminal methods, confirmed the earlier study<sup>40</sup> but with a smaller error bar,  $D_e = 945 \pm 15 \text{ cm}^{-1}$  (corresponding to  $D_0 = 2.33 \pm 0.04$

TABLE 3: Diagnostics for Importance of Nondynamical Correlation

	%TAE[SCF] <sup>a</sup>	-CCSD(T)/cc-pVTZ-			%TAE[(T)] <sup>a</sup>	%TAE [post-CCSD(T)] <sup>a</sup>	%TAE[T <sub>4</sub> + T <sub>5</sub> ] <sup>a</sup>	NO occupations	
		T <sub>1</sub> diagnostic	D <sub>1</sub>	largest T <sub>2</sub> amplitudes				HDOMO <sup>c</sup>	LUMO
H <sub>2</sub>	76.6	0.006	0.008	0.056	0	0	0	1.964	0.020
F <sub>2</sub>	-81.5	0.011	0.029	0.169	20.00	1.493	2.408	1.904	0.096
CH	68.1	0.008	0.017	0.091 (×2)	1.05	0.160	0.040	1.940	0.020
CF	63.2	0.020	0.052	0.100	3.80	0.061	0.176	1.965	0.040
CH <sub>4</sub>	78.9	0.007	0.011	0.035 (×2)	0.69	-0.001	0.019	1.958	0.022
CF <sub>4</sub>	69.3 <sup>b</sup>	0.011	0.030	0.024 (×2)	2.78 <sup>b</sup>	-0.034 <sup>b</sup>	0.180 <sup>b</sup>	1.961	0.037
Be <sub>2</sub>	-246.1	0.03	0.047	0.23	94.54	26.36	9.261	1.745	0.148
BeF <sub>2</sub>	80.5	0.013	0.031	0.016	1.87	-0.025	0.078	1.969	0.023
BeCl <sub>2</sub>	87.0	0.008	0.020	0.023	2.21	-0.020	0.123	1.949	0.027
BH	75.8	0.013	0.026	0.107 (×2)	0.49	0.072	0.068	1.866	0.060
BF	78.6	0.016	0.031	0.097 (×2)	2.20	-0.029	0.136	1.900	0.050
BH <sub>3</sub>	83.3	0.006	0.009	0.038	0.28	0.013	0.012	1.958	0.017
B <sub>2</sub> H <sub>6</sub>	80.8	0.010	0.018	0.039	0.74	0.034	0.030	1.949	0.027
BHF <sub>2</sub>	80.5	0.016	0.053	0.029	1.49	-0.050	0.067	1.962	0.030
BF <sub>3</sub>	79.8 <sup>b</sup>	0.012	0.043	0.018 (×2)	1.76 <sup>b</sup>	-0.016 <sup>b</sup>	0.137 <sup>b</sup>	1.968	0.031
AlF	77.0	0.015	0.029	0.109 (×2)	2.01	-0.139	0.115	1.874	0.052
AlH	75.3	0.013	0.024	0.094 (×2)	0.09	-0.064	0.054	1.891	0.048
AlH <sub>3</sub>	80.6	0.008	0.014	0.030	0.08	-0.012	0.015	1.950	0.026
AlF <sub>3</sub>	78.1	0.013	0.035	0.013 (×2)	1.85	-0.093	0.088	1.969	0.028
AlCl	81.5	0.007	0.020	0.100 (×2)	2.45	-0.107	0.199	1.889	0.048
AlCl <sub>3</sub>	83.6	0.011	0.027	0.017	2.32	-0.110	0.159	1.948	0.033
SiH	71.2	0.012	0.022	0.080	0.53	0.011	0.017	1.921	0.040
SiF	72.2	0.016	0.035	0.103	2.50	-0.139	0.121	1.966	0.039
SiH <sub>4</sub>	80.3	0.011	0.017	0.028	0.25	-0.011	-0.007	1.952	0.023
Si <sub>2</sub> H <sub>6</sub>	79.5	0.013	0.023	0.029 (×2)	0.54	0.006	0.030	1.935	0.030
SiF <sub>4</sub>	78.1 <sup>b</sup>	0.011	0.028	0.015	1.76 <sup>b</sup>	-0.035 <sup>b</sup>	0.163 <sup>b</sup>	1.968	0.032

<sup>a</sup> Percentages of the total atomization energy relate to nonrelativistic, clamped-nuclei values with inner-shell electrons constrained to be doubly occupied. (from W4 theory). <sup>b</sup> From W4lite. <sup>c</sup> Highest doubly occupied molecular orbital.

kcal/mol). Very recently, Spirko<sup>44</sup> reanalyzed the experimental data of Bondybey and English<sup>42</sup> with the aid of the calculated potential of Gdanitz and found  $D_e = 923 \text{ cm}^{-1}$  (2.64 kcal/mol), corresponding to  $D_0 = 2.27 \text{ kcal/mol}$ .

The pathological multireference character of Be<sub>2</sub> expresses itself in the highest %[(T)] diagnostic we have thus far encountered; in fact, this molecule is only bound at all when T<sub>3</sub> is introduced. Higher-order T<sub>3</sub> effects contribute almost 0.5 kcal/mol to the binding energy (over 20% of the total!), while valence T<sub>4</sub> effects are about half as important. Under the circumstances, it is not surprising that W2.2, which neglects post-CCSD(T) correlation effects entirely, underbinds the molecule by about 0.75 kcal/mol. W3.2 and W4lite are very close to the Spirko number, somewhat below the Roeggen and Veseth value. W4 and W4.2 are near the upper edge of the uncertainty band of the Martin number, while W4.3 is just 0.02 kcal/mol (7 cm<sup>-1</sup>) above Spirko. The difference between W4 and W4.3 results basically entirely from basis set extension effects in the post-CCSD(T) contributions, divided about evenly between T<sub>4</sub> and higher-order T<sub>3</sub> effects.

In contrast, the BeF<sub>2</sub> and BeCl<sub>2</sub> molecules are remarkably uncomplicated from an electronic structure point of view. Hartree-Fock accounts for about 80% of the atomization energy of BeF<sub>2</sub>, among the highest percentages we have observed, and this fraction reaches 87% in BeCl<sub>2</sub>, the highest we have thus far encountered. The %[(T)] diagnostics of only about 2% likewise indicate systems dominated by dynamical correlation. For BeF<sub>2</sub>, W4 and W4.2 agree to within 0.02 kcal/mol. Our best values are TAE<sub>0</sub>[BeF<sub>2</sub>] = 303.64 ± 0.16 kcal/mol and TAE<sub>0</sub>[BeCl<sub>2</sub>] = 220.20 ± 0.16 kcal/mol, where the quoted uncertainties are a 95% confidence band for the W4 systems. W4lite somewhat overestimates TAE<sub>0</sub>[BeF<sub>2</sub>] but slightly underestimates TAE<sub>0</sub>[BeCl<sub>2</sub>], which is primarily due to the limitations of the T<sub>4</sub> correction used. The zero-point vibrational energy of 4.27 kcal/mol for BeF<sub>2</sub> was obtained from the

experimental harmonic frequencies and anharmonicity constants from ref 45, while the corresponding value for BeCl<sub>2</sub> was derived from observed fundamental frequencies in ref 46.

The JANAF Tables<sup>1</sup> list  $\Delta H_{f,0}^\circ[\text{BeF}_2(\text{g})] = -190.25 \pm 1 \text{ kcal/mol}$ , while the highly respected Gurvich compilation<sup>47</sup> recommends  $\Delta H_{f,0}^\circ[\text{BeF}_2(\text{g})] = -190.41 \pm 0.93 \text{ kcal/mol}$  and  $\Delta H_{f,0}^\circ[\text{BeCl}_2(\text{g})] = -86.64 \pm 0.76 \text{ kcal/mol}$ . These values were obtained by combining heats of formation of the solid halides with sublimation enthalpies of said halides averaged over many measurements by a variety of techniques (see pp 364–368 and 370–374 of Vol. 3 of ref 47 for details). At no point is the sought quantity  $\Delta H_{f,0}^\circ[\text{Be}(\text{g})]$  involved. From the Gurvich data, the ATcT dissociation energies<sup>22</sup> of F<sub>2</sub> and Cl<sub>2</sub>, and our calculations, we derive  $\Delta H_{f,0}^\circ[\text{Be}(\text{g})] = 76.38 \pm 0.78 \text{ kcal/mol}$  via the chloride and  $76.31 \pm 0.95 \text{ kcal/mol}$  via the fluoride. The weighted average (weighing by inverse uncertainties, as customary) is  $76.35 \pm 0.61 \text{ kcal/mol}$ . Using the CODATA heat content functions for gas and metal, we obtain  $\Delta H_{f,298}^\circ[\text{Be}(\text{g})] = 77.37 \pm 0.61 \text{ kcal/mol}$ . This is basically identical to the CODATA-recommended value,  $77.4 \pm 1.2 \text{ kcal/mol}$ , but has half the uncertainty.

**B. Boron Compounds.** The two boron compounds that have the best-established experimental heats of formation would appear to be BF<sub>3</sub> and B<sub>2</sub>H<sub>6</sub>. The CODATA reference value<sup>2</sup> for  $\Delta H_{f,0}^\circ[\text{BF}_3(\text{g})] = -271.51 \pm 0.19 \text{ kcal/mol}$  is an average of many different measurements (none of which involve the boron atom in the gas phase), but the final number (because of weighting by inverse uncertainties) almost entirely derives from fluorine bomb combustion calorimetry data for the reaction B(cr) + (3/2)F<sub>2</sub>(g) → BF<sub>3</sub>(g). CODATA has no entry for B<sub>2</sub>H<sub>6</sub>; the Gurvich<sup>47</sup> reference value for  $\Delta H_{f,298}^\circ[\text{B}_2\text{H}_6(\text{g})] = 8.75 \pm 0.48 \text{ kcal/mol}$  derives mostly from enthalpy measurements of diborane thermolysis to 2B(am) + 3H<sub>2</sub>(g) on the one hand,<sup>48</sup> and hydrolysis of diborane in water near infinite dilution on the other

**TABLE 4: Component Breakdown of the Final W4 Total Atomization Energies at the Bottom of the Well (in kcal/mol)**

	SCF	valence CCSD	valence (T)	$\hat{T}_3$ -(T)	$\hat{T}_4^g$	$\hat{T}_5$	inner shell	relativ.	spin-orbit	DBOC	<i>h</i>	<i>i</i>	$\Delta$ DBOC	TAE <sub>c</sub>
H <sub>2</sub>	83.85	25.63	0	0	0	0	0	-0.002	0	0.05 <sup>d</sup>	0	0.00	-0.04	109.53
D <sub>2</sub>										0.03			-0.02	109.51
B <sub>2</sub>	20.49	34.96	9.77	0.18	1.37	0.08	0.79	-0.06	-0.06	0.01	0.00	-0.01	0.00	67.52
F <sub>2</sub>	-31.08	61.91	7.63	-0.35	0.89	0.03	-0.10	-0.03	-0.77	0.00	0.01	0.00	0.00	38.14
CH	57.22	25.83	0.89	0.10	0.03	0.00	0.14	-0.04	-0.04	-0.08	0.02	0.00	-0.02	84.06
CF	83.62	43.65	5.03	-0.15	0.24	-0.01	0.32	-0.16	-0.36	0.01	0.02	0.00	0.00	132.21
CH <sub>4</sub>	331.55	84.72	2.89	-0.08	0.08	0.00	1.27	-0.19	-0.08	0.10	0.02	0.00	-0.04	420.26
CF <sub>4</sub>	330.49	134.31	13.25	-1.02	N/A <sup>b</sup>	N/A	1.07	-0.85	-1.63	0.07	0.04	0.00	N/A	N/A <sup>c</sup>
Be <sub>2</sub>	-6.79	6.04	2.61	0.47	0.26	0.00	0.19	-0.01	0.00	0.00	0.00	0.00	0.00	2.76
BeF <sub>2</sub>	247.81	53.44	5.77	-0.32	0.23	0.01	2.17	-0.46	-0.77	0.04	0.01	0.00	-0.01	307.92
BeCl <sub>2</sub>	194.11	24.58	4.94	-0.32	0.31	-0.02	1.66	-0.52	-1.68	0.02	0.02	0.00	N/A	223.09
BH	64.31	20.01	0.41	0.00	0.06	0.00	0.19	-0.02	-0.03	-0.10 <sup>e</sup>	0.00	0.00	-0.03	84.84
BD										-0.05			-0.02	84.89
BF	143.09	34.76	4.00	-0.30	0.25	-0.01	0.72	-0.16	-0.41	0.01	0.01	0.00	-0.01	181.95
BH <sub>3</sub>	234.35	44.97	0.79	0.00	0.03	0.00	1.14	-0.07	-0.03	-0.02	0.00	0.00	-0.05	281.18
BD <sub>3</sub>										0.00			-0.03	281.20
B <sub>2</sub> H <sub>6</sub>	490.60	108.85	4.47	0.02	0.18	0.00	2.90	-0.18	-0.06	0.04	0.01	0.00	-0.07	606.83
B <sub>2</sub> D <sub>6</sub>										0.05			-0.04	606.84
BHF <sub>2</sub>	329.85	73.54	6.11	-0.48	0.27	0.01	1.66	-0.47	-0.80	0.04	0.02	0.00	-0.02	409.75
BF <sub>3</sub>	374.64	86.41	8.28	-0.72	0.39	N/A <sup>a</sup>	1.94	-0.69	-1.18	0.06	0.02	0.00	N/A	469.15
AlH	55.09	18.52	0.07	-0.09	0.04	0.00	-0.12	-0.08	-0.21	-0.06	0.00	0.00	-0.02	73.15
AlF	125.45	34.72	3.27	-0.41	0.18	0.01	0.50	-0.29	-0.60	0.01	0.01	0.00	0.00	162.83
AlH <sub>3</sub>	171.26	42.39	0.17	-0.06	0.03	0.00	-0.73	-0.42	-0.21	-0.02	0.00	0.00	-0.05	212.43
AlF <sub>3</sub>	334.44	88.98	7.91	-0.78	0.37	0.04	0.00	-1.31	-1.37	0.03	0.02	0.00	N/A	428.32
AlCl	98.81	20.57	2.97	-0.87	0.27	-0.01	0.32	-0.24	-1.05	0.00	0.01	0.00	0.00	121.27
AlCl <sub>3</sub>	256.16	47.94	7.17	-0.83	0.52	-0.01	-0.31	-1.28	-2.74	0.02	0.03	0.00	N/A	308.65
SiH	52.26	21.12	0.39	0.00	0.01	0.00	0.00	-0.11	-0.22	-0.05	0.00	0.00	N/A	73.40
SiF	102.24	36.55	3.55	-0.37	0.17	0.01	0.40	-0.29	-0.58	0.00	0.01	0.00	N/A	141.69
SiH <sub>4</sub>	259.83	64.18	0.81	-0.06	0.02	0.00	-0.08	-0.67	-0.43	0.00	0.01	0.00	-0.06	323.62
Si <sub>2</sub> H <sub>6</sub>	424.14	108.85	2.90	-0.13	0.16	0.00	-0.04	-1.32	-0.86	0.01	0.01	0.00	-0.07	533.72
SiF <sub>4</sub>	448.41 <sup>f</sup>	119.07	10.12	-1.14	N/A <sup>b</sup>	N/A	0.84	-1.90	-1.97	0.05	0.03	0.00	N/A	N/A <sup>c</sup>

<sup>a</sup> RCCSDTQ(P)/DZ-RCCSDTQ/DZ is -0.01 kcal/mol; RCCSDTQ(P)<sub>A</sub>/DZ-RCCSDTQ/DZ is +0.02 kcal/mol. <sup>b</sup> RCCSDT(Q)/PVDZ-RCCSDT/PVDZ is 0.93 kcal/mol for SiF<sub>4</sub> and 0.86 kcal/mol for CF<sub>4</sub>. <sup>c</sup> W4lite TAE is 574.43 kcal/mol for SiF<sub>4</sub> and 476.58 kcal/mol for CF<sub>4</sub>. <sup>d</sup> Inclusion of correlation in DBOC reduces it by 0.04 kcal/mol.<sup>70</sup> <sup>e</sup> CISD/AVTZ: -0.13 kcal/mol. <sup>f</sup> SCF/AV5Z+2d1f and SCF/AV6Z+2d1f atomization energies are both 448.42 kcal/mol. <sup>g</sup> UHF reference; for RCCSDTQ-UCCSDTQ, see *i*. <sup>h</sup> The difference between the ACES II and MOLPRO definitions of the valence ROCCSD(T). <sup>i</sup> RCCSDTQ/PVDZ-UCCSDTQ/PVDZ.

hand.<sup>49,62</sup> The final adopted value is basically identical to the thermolysis value, except for the smaller uncertainty.

For those reasons, we will mostly be concerned with BF<sub>3</sub> and B<sub>2</sub>H<sub>6</sub>. However, we carried out post-W4 calculations on some additional boron compounds such that we could estimate post-W4 corrections for BF<sub>3</sub> and B<sub>2</sub>H<sub>6</sub> by means of isodesmic reactions.

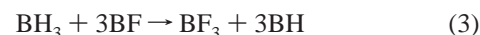
All of the boron compounds considered are dominated by dynamical correlation. In the highly polar-bonded BF, HBF<sub>2</sub>, and BH<sub>3</sub> systems, considerable differences are seen between W3.2 and W4lite results, which almost entirely result from basis set expansion in the CCSD correlation energy.

While in BF we see nearly perfect cancellation between *T*<sub>4</sub> and higher-order *T*<sub>3</sub> effects, in both HBF<sub>2</sub> and BF<sub>3</sub>, the higher-order *T*<sub>3</sub> correction (which decreases the TAE) is significantly larger in absolute magnitude than the *T*<sub>4</sub> correction (which increases the TAE), and as a result, the CCSD(T) limit binding energy is an overestimate. We were unable to compute an iterative *T*<sub>5</sub> correction for BF<sub>3</sub>, but both the CCSDTQ(5) and CCSDTQ(5)<sub>A</sub> methods<sup>50</sup> find negligible *T*<sub>5</sub> corrections. Note that the W4 TAEs are considerably lower than their W4lite counterparts; the CCSDT(Q)/cc-pVDZ estimate of *T*<sub>4</sub> clearly overshoots the connected quadruples correction in this case.

As for the hydrides, W2.2, W3.2, W4lite, and W4 all yield remarkably similar results there; the one exception is diborane, for which we find a nontrivial *T*<sub>4</sub> contribution. As such, a contribution is completely absent in BH<sub>3</sub>; it seems to represent an intriguing manifestation of the diborane bridge.

BH diatomic has a nontrivial negative DBOC contribution to the dissociation energy of -0.10 kcal/mol, which actually increases (in absolute value) to -0.13 kcal/mol when electron correlation is accounted for in this contribution.

Post-W4 contributions in BF<sub>3</sub> and B<sub>2</sub>H<sub>6</sub> can be estimated by assuming that they leave the reaction energies of the following reactions constant



In refs 17 and 18, the zero-point vibrational energy (ZPVE) of BF<sub>3</sub> was taken from an earlier accurate anharmonic force field calculation.<sup>51</sup> As very recently a complete set of high-resolution fundamental frequencies was reported for the first time, however,<sup>52</sup> we were able to introduce a correction for the difference between the calculated and observed fundamental frequencies. The resulting ZPVE, 7.83 kcal/mol, is slightly lower.

The one for B<sub>2</sub>H<sub>6</sub> was obtained by combining CCSD(T)/cc-pVQZ harmonic frequencies with an anharmonic force field<sup>53</sup> obtained at the B3LYP density functional level<sup>54</sup> with a pc-2 basis set.<sup>55</sup> In addition, a correction of +0.04 kcal/mol for the isotopic average ZPVE (relative to pure <sup>11</sup>B<sub>2</sub>H<sub>6</sub>) was obtained from B3LYP/pc-2 anharmonic ZPVEs for the <sup>11</sup>B<sub>2</sub>H<sub>6</sub>, <sup>10</sup>B<sup>11</sup>BH<sub>6</sub>, and <sup>10</sup>B<sub>2</sub>H<sub>6</sub> isotopomers.

**TABLE 5: Comparison between W4 Total Atomization Energies at 0 K, Active Thermochemical Tables Benchmarks, and Earlier Reference Data (kcal/mol)**

	ZPVE	W2.2	W3.2	W4lite	W4	W4.2	W4.3	ATcT <sup>a</sup>	uncert.	earlier ref <sup>b</sup>	uncert.	CCCBDB <sup>c</sup>	uncert.
H <sub>2</sub>	6.23	103.28	103.28	103.30	103.30	103.30	103.30	103.27	0.00	103.27	0.00	103.27	0.00
F <sub>2</sub>	1.30	36.14	36.72	36.85	36.84	36.87	36.97	36.91	0.07	36.94	0.10	36.9	0.1
CH	4.04	79.89	80.02	80.01	80.02	80.02	80.03	79.98	0.05	79.90	0.23	79.6	0.3
CF	1.86	130.17	130.33	130.41	130.35	130.35	130.36			128.8 <sup>l</sup>	3.5	128.3	1.9
CH <sub>4</sub>	27.74	392.55	392.56	392.52	392.52	392.52	392.53	392.50	0.03	392.51	0.14	392.4	0.1
CF <sub>4</sub>	10.86	465.48	465.34	465.72	465.40 <sup>m</sup>	465.39 <sup>m</sup>	465.41 <sup>m</sup>	465.58	0.18	465.48 <sup>k</sup>	0.23	465.5	0.4
Be <sub>2</sub>	0.37	1.64	2.24	2.26	2.39	2.38	2.29					2	2.9
BeF <sub>2</sub>	4.27 <sup>f</sup>	303.56	303.71	303.87	303.65	303.64	N/A					—	—
BeCl <sub>2</sub>	2.89	220.60	220.52	220.14	220.20	N/A	N/A					—	—
BH	3.35	81.43	81.47	81.47	81.49	81.50	81.49			81.5	0.5 <sup>g</sup>	80.4	2.3
BF	2.00	179.91	179.92	180.01	179.95	179.96	179.96					178.6	2.7
BH <sub>3</sub>	16.36	264.79	264.82	264.80	264.82	264.82	264.80					262.3	2.7
B <sub>2</sub> H <sub>6</sub>	39.25 <sup>j</sup>	567.34	567.48	567.46	567.53	567.53 <sup>d</sup>	567.51 <sup>d</sup>					564.9	2.4
BHF <sub>2</sub>	11.02 <sup>o</sup>	398.74	398.70	398.89	398.73	398.72 <sup>e</sup>	398.71 <sup>e</sup>					398.3	1.7
BF <sub>3</sub>	7.83 <sup>i</sup>	461.33	461.27	461.55	461.32	461.32 <sup>p</sup>	461.31 <sup>p</sup>					460.1	1.2
AlF	1.14	161.78	161.66	161.79	161.69	161.74	161.76					160.3	1.2
AlH	2.38	70.79	70.73	70.75	70.77	70.80	70.83					70.3	1.3
AlH <sub>3</sub>	11.61	200.79	200.75	200.80	200.82	200.87	200.92					70.3	1.3
AlF <sub>3</sub>	4.84	423.36	423.34	423.81	423.47	423.58 <sup>s</sup>	423.58 <sup>s</sup>					421.9	1.1
AlCl	0.69	120.78	3120.61	120.51	120.58	120.60	120.64					119.2	1.8
AlCl <sub>3</sub>	3.05	306.32	305.88	305.46	305.59	N/A	N/A					303.4	1.2
SiH	2.89	70.48	70.49	70.50	70.50	70.52	70.65 <sup>f</sup>					70.4	2.7
SiF	1.22	140.54	140.46	140.57	140.46	140.51	140.62 <sup>f</sup>			137.8	2.2	131.5	3.3
SiH <sub>4</sub>	19.69	303.92	303.88	303.92	303.93	303.98	304.03					302.6	1.9
Si <sub>2</sub> H <sub>6</sub>	30.63 <sup>o</sup>	503.07	503.04	503.02	503.09	N/A	N/A					508.7	3.8
SiF <sub>4</sub>	8.04	566.08	565.90	566.39	565.95 <sup>n</sup>	566.09 <sup>n</sup>	566.04 <sup>n</sup>					565.1	1.9

<sup>a</sup> Ref 3; the adjunct uncertainties correspond to 95% confidence intervals, as customary in experimental thermochemistry, which were obtained by utilizing the full covariance matrix computed by ATcT; see also refs 5–7. <sup>b</sup> Ref 21 and references therein. <sup>c</sup> Experimental data section of ref 71. <sup>d</sup> Difference with W4 estimated from the dimerization reaction 2BH<sub>3</sub> → B<sub>2</sub>H<sub>6</sub>. <sup>e</sup> Difference with W4 estimated from the isodesmic reaction BHF<sub>2</sub> + 2BH → BH<sub>3</sub> + 2BF. <sup>f</sup> From experimental harmonic frequencies and anharmonicity constants in ref 45. <sup>g</sup> Difference with W4 estimated from the isodesmic reaction AlH<sub>3</sub> + 3AlF → AlF<sub>3</sub> + 3AlH. <sup>h</sup> Derived from the anharmonic force field in ref 65. <sup>i</sup> Derived from the anharmonic force field in ref 51, corrected for the difference between the computed and observed<sup>52</sup> fundamentals. <sup>j</sup> Combination of CCSD(T)/cc-pVQZ harmonic frequencies and B3LYP/pc2 quartic force field,<sup>53</sup> using the Allen expression<sup>28</sup> for the ZPVE, plus a correction of 0.04 kcal/mol for the difference between the isotopic average and the most abundant isotopomer. <sup>k</sup> Gurvich heat of formation combined with ATcT heats of elements, 711.51 ± 0.11 and 77.22 ± 0.15 kJ/mol for C and F, respectively. <sup>l</sup> Derived by deducting 3RT/2 from D<sub>298</sub> = 129.7 ± 3.5 kcal/mol in Jesinger, R. A.; Squires, R. R. *Int. J. Mass Spectrom.* **1999**, *185*, 745; [http://dx.doi.org/10.1016/S1387-3806\(98\)14182-9](http://dx.doi.org/10.1016/S1387-3806(98)14182-9). <sup>m</sup> Difference with W4lite estimated from the homodesmic reaction CH<sub>4</sub> + 4BF → CF<sub>4</sub> + 4BH. <sup>n</sup> Difference with W4lite estimated from the isodesmic reaction SiH<sub>4</sub> + 4SiF → SiF<sub>4</sub> + 4SiH. <sup>o</sup> Combining CCSD(T)/cc-pVTZ harmonic frequencies calculated by Puzzarini and Taylor<sup>59</sup> with experimental fundamentals compiled in that reference and the  $-\sum X_{ii}d_i/4 + G_0$  correction term of 0.11 kcal/mol calculated at the MP2/cc-pVTZ level in the present work. <sup>p</sup> Difference with W4 estimated from the isodesmic reaction BH<sub>3</sub> + 3BF → BF<sub>3</sub> + 3BH. <sup>q</sup> Ref 72.

**TABLE 6: Derived Heats of Formation at 0 and 298 K of Be, B, Al, and Si Compared to the Literature and Earlier Computationally Derived Values**

	Be		B		Si		Al	
	0 K	298 K	0 K	298 K	0 K	298 K	0 K	298 K
from the best AF <sub>n</sub>	76.31 ± 0.95		135.10 ± 0.27		107.35 ± 0.37		80.06 ± 0.63	
from AlCl <sub>n</sub>	76.38 ± 0.78		—		—		80.33 ± 0.46	
from the best A <sub>2</sub> H <sub>6</sub> average	—	—	135.11 ± 0.25		107.12 ± 0.18		80.22 ± 0.38	
from AH <sub>n</sub>	—	—	136.31 ± 2.40		107.03 ± 0.34			
from BHF <sub>2</sub>	—	—	134.26 ± 1.21		—	—		
weighted average	76.35 ± 0.61		135.08 ± 0.23		107.15 ± 0.15		80.22 ± 0.38	
<b>recommended</b>	<b>76.4 ± 0.6</b>	<b>77.4 ± 0.6</b>	<b>135.1 ± 0.2</b>	<b>136.3 ± 0.2</b>	<b>107.2 ± 0.15</b>	<b>108.2 ± 0.15</b>	<b>80.2 ± 0.4</b>	<b>80.8 ± 0.4</b>
CODATA	76.4 ± 1.2	77.4 ± 1.2	133.8 ± 1.2	135.0 ± 1.2	106.5 ± 1.9	107.5 ± 1.9	78.30 ± 0.96	78.87 ± 0.96
Gurvich			133.8 ± 1.2	135.0 ± 1.2	106.6 ± 1.9	107.6 ± 1.9		
Ochterski et al. <sup>a</sup>	75.8 ± 0.8	76.8 ± 0.8	136.2 ± 0.2	137.4 ± 0.2	108.1 ± 0.5	109.1 ± 0.5		
BMT			135.1 ± 0.75	136.3 ± 0.75	107.15 ± 0.38	108.19 ± 0.38		

<sup>a</sup> Ochterski et al.<sup>9</sup> <sup>b</sup> BF<sub>3</sub>: ref 17; SiF<sub>4</sub>: ref 19. <sup>c</sup> For auxiliary thermodynamic data, see (b). ( $\Delta H_{f,298}^\circ - \Delta H_{f,0}^\circ$ )[A(g)] from CODATA:<sup>2</sup> 1.217 ± 0.002 kcal/mol for B, 1.036 ± 0.002 kcal/mol for Si, 1.015 ± 0.005 kcal/mol for Be, 0.569 ± 0.005 kcal/mol for Al.

We thus obtain best-estimate TAE<sub>0</sub> values of 567.51 ± 0.16 and 461.31 ± 0.16 kcal/mol, respectively, for B<sub>2</sub>H<sub>6</sub> and BF<sub>3</sub>. Combination with the best available heats of formation,  $\Delta H_{f,0}^\circ$ [B<sub>2</sub>H<sub>6</sub>(g)] = 12.52 ± 0.48 kcal/mol from Gurvich and  $\Delta H_{f,0}^\circ$ [BF<sub>3</sub>(g)] = 270.84 ± 0.19 kcal/mol from CODATA, we find derived values for  $\Delta H_{f,0}^\circ$ [B(g)] of 135.11 ± 0.25 and 135.10 ± 0.27 kcal/mol, respectively. Averaging the two, we get 135.11 ± 0.18 kcal/mol. If we include values derived from

BH<sub>3</sub> and BHF<sub>2</sub> as well and assign weights by inverse uncertainty, we obtain a weighted average of 135.08 ± 0.23 kcal/mol.

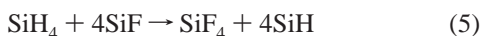
Our final recommended values,  $\Delta H_{f,0}^\circ$ [B(g)] = 135.1 ± 0.2 kcal/mol and  $\Delta H_{f,298}^\circ$ [B(g)] = 136.3 ± 0.2 kcal/mol, are identical to the revised values recommended by Bauschlicher, Martin, and Taylor but with a much smaller uncertainty. It again confirms, in our opinion beyond reasonable doubt, that the

accepted CODATA value should be revised upward, albeit not by as large of an amount as that suggested by earlier work.<sup>9,18</sup>

**C. Silicon Compounds.** For three silicon compounds, accurate experimental heats of formation are available, SiH<sub>4</sub>, Si<sub>2</sub>H<sub>6</sub>, and SiF<sub>4</sub>, the uncertainty per silicon atom being the smallest in the latter two. The hydride data derive from explosive decomposition of silane and disilane,<sup>62</sup> while the perfluoro data<sup>61</sup> derive from direct combination of the elements in their standard states in a fluorine bomb calorimeter.

While we have no trouble carrying out W4 calculations on silane and disilane, we were only able to carry out a W4lite calculation on SiF<sub>4</sub>; bridging the gap to full W4 would require a fully iterative CCSDTQ/cc-pVDZ calculation with  $9.2 \times 10^9$  amplitudes and a quasiperturbative CCSDT(Q)/cc-pVTZ calculation involving no less than  $589 \times 10^9$  determinants in the (Q) stage, calculations simply beyond the realm of feasibility with the available hardware.

As we have seen above, W4lite by itself is liable to overestimate TAE<sub>0</sub> in perfluoro systems; we have resorted to estimating the W4.3 – W4lite difference by assuming the reaction energy of the following homodesmotic reaction to remain constant



We obtained very similar results from other reactions, such as (W4 – W4lite differences) SiH<sub>4</sub> + 2BHF<sub>2</sub> → SiF<sub>4</sub> + 2BH<sub>3</sub> and SiH<sub>4</sub> + (4/3)AlF<sub>3</sub> → SiF<sub>4</sub> + (4/3)AlH<sub>3</sub>. (A two-stage W4.3 – W4lite correction is possible for the latter reaction, first correcting AlF<sub>3</sub> to W4.3 with reactions involving AlH, AlH<sub>3</sub>, and AlF.)

As expected for such a polarly bound molecule, we note a hefty 0.5 kcal/mol change between W3.2 and W4lite (0.3 kcal/mol at the SCF level, the remainder from CCSD correlation). Because of the presence of a second-row element in a high oxidation state, which was previously observed<sup>19</sup> to cause serious inner polarization effects (see ref 38 and references therein), we carried out SCF/AV5Z+2d1f and SCF/AV6Z+2d1f calculations to verify proper basis set convergence of the SCF component. These two basis sets yield a SCF-limit binding energy within 0.01 kcal/mol of our extrapolated answer from AV(5+d)Z and AV(6+d)Z basis sets.

Because of an error compensation between neglect of post-CCSD(T) correlation effects and post-W3 basis set expansion effects, the W2.2 number is in excellent agreement with our estimated W4 result, which is also surprisingly close to the earlier W2-level calculation of Martin and Taylor.<sup>19</sup>

The zero-point vibrational energy in this case, 8.04 kcal/mol, was taken from an earlier anharmonic force field study by Wang, Sibert, and Martin<sup>56</sup> (not explicitly given in that paper). Our best estimate is TAE<sub>0</sub> = 566.04 ± 0.16 kcal/mol.

An indirect check on our results for SiF<sub>4</sub> can be carried out by performing a W4lite calculation on CF<sub>4</sub>, for which an ATcT value for TAE<sub>0</sub> of 465.58 ± 0.18 kcal/mol is available.<sup>57</sup> An additional experimental data point can be obtained by combining the Gurvich heat of formation with the ATcT heats of formation of atomic C and F, which leads to a somewhat lower value of 465.48 kcal/mol. Comparison suggests that our calculation for SiF<sub>4</sub>, if anything, might err a little on the low side. (Here too, the ZPVE was taken from ref 56.)

Because of the uncertainties introduced by our post-W4lite corrections, we have arbitrarily increased the uncertainty on TAE<sub>0</sub>[SiF<sub>4</sub>(g)] to 0.32 kcal/mol.

In the case of Si<sub>2</sub>H<sub>6</sub>, for want of a proper anharmonic force field, we approximated the zero-point vibrational energy by

means of the following equation (e.g., eq 2.11 in ref 58, with  $l_i = 0$  for nondegenerate frequencies)

$$\text{ZPVE}_{\text{anharm}} = (\text{ZPVE}_{\text{harm}} + \text{ZPVE}_{\text{fund}})/2 - \frac{1}{4} \sum_i (X_{ii} + G_{ii}^2) d_i + G_0 \quad (6)$$

where we evaluated ZPVE<sub>fund</sub> from the experimental fundamental frequencies compiled by Puzzarini and Taylor<sup>59</sup> and ZPVE<sub>harm</sub> from CCSD(T)/cc-pVQZ harmonic frequencies calculated in the present work. The remaining terms, which add up to only 0.10 kcal/mol and are weakly dependent on the level of theory, are calculated at the MP2/cc-pVTZ level using Gaussian 03. (Attempts to calculate this difference at the B3LYP/pc-2 level ran into symmetry issues that we were unable to resolve.) We will assign an (conservative) estimated 0.12 kcal/mol uncertainty to the zero-point energy. Treating the constituent uncertainties as multipliers of standard deviations, our best value was TAE<sub>0</sub> = 503.09 ± 0.20 kcal/mol.

The heat content function of SiF<sub>4</sub> was taken from Martin and Taylor,<sup>19</sup> while that of Si<sub>2</sub>H<sub>6</sub> was calculated at the B3LYP/pc-2 level, treating the internal rotation using the Ayala–Schlegel method.<sup>60</sup>

Combining the TAE<sub>0</sub> values with the best available experimental heats of formation at 298 K, ΔH<sub>f,298</sub><sup>o</sup>[SiF<sub>4</sub>] = –386.18 ± 0.11 kcal/mol from Johnson<sup>61</sup> and ΔH<sub>f,298</sub><sup>o</sup>[Si<sub>2</sub>H<sub>6</sub>] = 17.1 ± 0.3 kcal/mol from Gunn and Green,<sup>62</sup> we obtain the following values of ΔH<sub>f,0</sub><sup>o</sup>[Si(g)]: 107.12 ± 0.18 kcal/mol via Si<sub>2</sub>H<sub>6</sub> and 107.35 ± 0.37 kcal/mol via SiF<sub>4</sub>. Their weighted average is 107.20 ± 0.17 kcal/mol. Via SiH<sub>4</sub>, we would obtain 107.03 ± 0.34 kcal/mol, again using the Gunn and Green experimental heat of formation. (Like the earlier calculations of Feller and Dixon,<sup>63</sup> our results are incompatible with a putative 1 kcal/mol/(Si atom) correction<sup>64</sup> of the Gunn and Green data for a transition between amorphous and solid silicon.) A weighted average of all three values yields our final recommended ΔH<sub>f,0</sub><sup>o</sup>[Si(g)] = 107.15 ± 0.15 and ΔH<sub>f,298</sub><sup>o</sup>[Si(g)] = 108.19 ± 0.15 kcal/mol, identical to the earlier revised value of Martin and Taylor but with a much smaller uncertainty.

**D. Aluminum Compounds.** The aluminum compounds we will consider here are AlF<sub>3</sub> and AlCl<sub>3</sub>, for both of which tolerably good experimental heats of formation are available that do not depend on the heat of formation of the metal, ΔH<sub>f,0</sub><sup>o</sup>[AlF<sub>3</sub>(g)] = –288.15 ± 0.60 and ΔH<sub>f,0</sub><sup>o</sup>[AlCl<sub>3</sub>(g)] = –139.30 ± 0.69 kcal/mol.<sup>1</sup> A more recent value for AlCl<sub>3</sub> (the JANAF data having last been reviewed in 1979) can be found in Konings and Booiij,<sup>66</sup> ΔH<sub>f,298</sub><sup>o</sup>[AlCl<sub>3</sub>(g)] = –139.99 ± 0.43 kcal/mol. From the difference between the JANAF room-temperature value, ΔH<sub>f,298</sub><sup>o</sup>[AlCl<sub>3</sub>(g)] = –139.72 kcal/mol, and its counterpart at absolute zero, we find from Konings and Booiij that ΔH<sub>f,0</sub><sup>o</sup>[AlCl<sub>3</sub>(g)] = –139.57 ± 0.43 kcal/mol.

Like the isovalent BF and BF<sub>3</sub>, AlF, AlF<sub>3</sub>, AlCl, and AlCl<sub>3</sub> are entirely dominated by a single reference configuration, and hence, post-CCSD(T) corrections are rather small. In the case of AlF<sub>3</sub> and AlCl<sub>3</sub>, post-W4 corrections were estimated by means of an isodesmotic reaction involving AlH<sub>3</sub>, AlX, and AlH. They were found to be quite small. We do note fairly substantial differences between W2.2, W3.2, W4lite, and W4 for AlCl<sub>3</sub>, which mostly reflect slow basis set convergence.

The zero-point vibrational energy for AlF<sub>3</sub> was obtained from an anharmonic force field calculation by Pak, Sibert, and Woods,<sup>65</sup> corrected for differences between computed and observed fundamentals compiled in that reference. The ZPVE for AlCl<sub>3</sub> was obtained from experimental fundamental frequen-

cies compiled by Hargitai,<sup>67</sup> corrected by a  $ZPVE_{\text{anhar}} - ZPVE_{\text{fund}}$  difference of 0.021 kcal/mol calculated in this work from a B3LYP/aug-cc-pV(T+d)Z quartic force field.

The  $\Delta H_{f,0}^{\circ}[\text{Al}(\text{g})]$  obtained via  $\text{AlF}_3$  and  $\text{AlCl}_3$  are  $80.06 \pm 0.63$  and  $80.33 \pm 0.46$  kcal/mol, respectively. The weighted average,  $80.22 \pm 0.38$  kcal/mol, is about 2 kcal/mol higher than JANAF and nearly 2 kcal/mol higher than the CODATA recommendation. It was previously suggested by Feller and Dixon<sup>68</sup> that the established heat of formation of  $\text{Al}(\text{g})$  might be in error.

#### IV. Conclusions

By means of benchmark W4 theory calculations on  $\text{Be}_2$ ,  $\text{BeF}_2$ ,  $\text{BeCl}_2$ ,  $\text{BH}$ ,  $\text{BF}$ ,  $\text{BH}_3$ ,  $\text{BHF}_2$ ,  $\text{B}_2\text{H}_6$ ,  $\text{BF}_3$ ,  $\text{AlF}$ ,  $\text{AlF}_3$ ,  $\text{SiH}_4$ ,  $\text{Si}_2\text{H}_6$ , and  $\text{SiF}_4$ , and combining our theoretical total atomization energies with available experimental heats of formation, we were able to derive heats of formation in the gas phase for the elements beryllium, boron, aluminum, and silicon. These are fundamental thermochemical quantities that are required whenever a molecular heat of formation has to be derived from a calculated binding energy. Our recommended  $\Delta H_{f,0}^{\circ}[\text{A}(\text{g})]$  values are  $\text{Be } 76.4 \pm 0.6$  kcal/mol,  $\text{B } 135.1 \pm 0.2$  kcal/mol,  $\text{Al } 80.2 \pm 0.4$  kcal/mol, and  $\text{Si } 107.15 \pm 0.15$  kcal/mol. (The corresponding values at 298.15 K are 77.4, 136.3, 80.8, and 108.2 kcal/mol, respectively.) The Be value is identical to the CODATA recommendation (but with half of the uncertainty), while the B, Al, and Si values represent substantial revisions from experiment. The revised B and Si values are in agreement with earlier semi-ab initio derivations but carry much smaller uncertainties.

**Note Added in Proof:** In the context of a very recent basis set convergence study on higher-order correlation effects (Karton, A.; Taylor, P. R.; Martin, J. M. L. *J. Chem. Phys.*, accepted), it was found that the use of valence-only-correlated reference geometries causes small but noticeable underestimates of binding energies in second-row molecules with several A–B bonds. We recalculated the total atomization energies of  $\text{SiH}_4$ ,  $\text{Si}_2\text{H}_6$ , and  $\text{SiF}_4$  at CCSD(T)/cc-pwCVQZ and CCSD(T)/aug-cc-pwCVQZ reference geometries, respectively, and found them to go up by 0.01, 0.04, and 0.15 kcal/mol, respectively. After proper weighting, our best heat of vaporization at absolute zero for silicon is found to go up by 0.05 kcal/mol, which leaves the rounded best estimate unchanged at  $107.2 \pm 0.15$  kcal/mol. For similar reasons, our best estimate for aluminum should be adjusted upward by 0.1 kcal/mol.

**Acknowledgment.** Research was supported by the Israel Science Foundation (Grant 709/05), the Minerva Foundation (Munich, Germany), and the Helen and Martin Kimmel Center for Molecular Design. J.M.L.M. is the incumbent of the Baroness Thatcher Professorial Chair of Chemistry and a member ad personam of the Lise Meitner-Minerva Center for Computational Quantum Chemistry. The authors would like to thank Dr. Branko Ruscic (Argonne National Laboratory) for helpful discussions, for early communication of ref 57, and for assistance in locating the nearly unobtainable third volume of ref 47. Furthermore, the authors gratefully acknowledge Dr. Mihály Kállay (Budapest) for early access to a new version of MRCC and kind assistance with the code. The research presented in this paper is part of ongoing work in the framework of a Task Group of the International Union of Pure and Applied Chemistry on “Selected free radicals and critical intermediates: thermodynamic properties from theory and experiment”

(2000-013-2-100, renewal 2003-024-1-100). See ref 69 for further details.

**Supporting Information Available:** CCSD(T)/cc-pV-(Q+d)Z-optimized reference geometries used for the calculations in this work. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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