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AM1* parameters for aluminum, silicon, titanium and zirconium

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Abstract Our extension of the AM1 semiempirical molecular orbital technique, AM1*, has been parameterized for the elements Al, Si, Ti and Zr. The basis sets for all four metals contain a set of *d*-orbitals. Thus, AM1* parameters are now available for H, C, N, O and F (which use the original AM1 parameters), Al, Si, P, S, Cl, Ti, Mo and Zr. Special attention was paid to reproducing homolytic and heterolytic bond-dissociation energies correctly. Such bond-energy data help to avoid eccentricities in the parameterization caused by inaccurate experimental heats of formation. The performance and typical errors of AM1* for the newly parameterized elements are discussed. Generally, the new method performs less well than established techniques for heats of formation but considerably better for the heats of reaction.

Keywords AM1* · Parameterization · Aluminum · Silicon · Titanium · Zirconium · Semiempirical MO-theory

Introduction

We recently [1] introduced an extension of AM1 molecular orbital theory [2], named AM1*, which uses *d*-orbitals for the elements P, S, Cl and a slight modification of Voityuk and Rösch's AM1(d) parameters for Mo [3]. AM1* performs significantly better than AM1 for P-containing, S-containing and Cl-containing compounds but retains its advantages (good energies for hydrogen bonds, higher rotation barriers for π -systems

than MNDO [4, 5] or PM3 [6–8]) for the elements H, C, N, O and F. We now report AM1* parameters for aluminum, silicon, titanium and zirconium, which are important in zeolite [9] and olefin polymerization chemistry [10]. Because the experimental data for heats of formation of compounds of the four metals are relatively sparse and prone to errors, we have for the first time paid special attention to reproducing homolytic and heterolytic bond-dissociation energies as closely as possible in order to produce a robust parameterization. Using such bond energies should ensure the correct chemical behavior for most reactions, although the error in calculated heats of formation compared to experiment may become higher.

Theory

AM1* for the four new elements uses the same basic theory as outlined previously [1] with the exception that the core–core repulsion potential for the Ti–H interaction used a distance-dependent term δ_{ij} , rather than the constant term used for core–core potentials for all other interactions in AM1* [1]. A distance-dependent δ_{ij} was also used for the Mo–H interaction in AM1(d) [3]. The core–core terms for Ti–H and Zr–H are thus:

$$E^{\text{core}}(i-j) = Z_i Z_j \rho_{ss}^0 [1 + r_{ij} \delta_{ij} \exp(-\alpha_{ij} r_{ij})] \quad (1)$$

where all terms have the same meaning as given in Ref. [1].

The parameterization techniques were those reported in Ref. [1] and will not be described further here.

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Parameterization Data

Parameterization data for silicon and aluminum were taken largely from the MNDO/d parameterization dataset [11, 12], but were extended with data from the PM3 [7] and AM1 [13, 14] datasets. Since these sets are

dominated by the heats of formation, we have added a series of geometrical parameters based on DFT geometries to give greater coverage to a number of underrepresented bond types, such as Al–Al, Al–S, Al–P, Si–S and Si–P bonds.

The data set for compounds involving Ti was based on the MSINDO parameterization for third-row transition metals [15]. However, this data is based predominantly on very small molecules ($\text{Ti}(\text{Cp})_2\text{Cl}_2$ is the only compound larger than five atoms). Because of this, we

expanded the data set to include titanium compounds with heats of formation in the NIST WebBook database [16] and used calculated geometrical values. Since no previous data sets for Zr compounds existed, we have based our parameterization on available heats of formation from the NIST WebBook and calculated geometries.

In addition to the standard parameterization target values, we have added a series of calculated reaction energies (dimerization, adiabatic ionization potentials,

Table 1 AM1* parameters for the elements Al, Si, Ti and Zr

Parameter	Al	Si	Ti	Zr
U_{ss} [eV]	-24.5602105	-35.1025011	-10.1084773	-9.9546468
U_{pp} [eV]	-13.7049056	-27.4557671	-2.4462081	-2.2195281
U_{dd} [eV]	-6.8179405	-12.7115757	-23.9034044	-20.2935796
ζ_s [bohr ⁻¹]	1.5808063	1.5486715	1.5696034	1.6607978
ζ_p [bohr ⁻¹]	1.5598372	1.346864	1.5696034	1.6607978
ζ_d [bohr ⁻¹]	0.1050463	0.2979484	2.7348707	3.0064733
β_s [eV]	-7.4011762	-3.9886239	-10.1909308	-11.3107916
β_p [eV]	-2.2331537	-2.5760327	-2.8704589	-3.0054726
β_d [eV]	-0.4441486	-0.457257	-0.8523629	-0.7912566
g_{ss} [eV]	9.726034	14.6307585	3.078831	2.7135314
g_{pp} [eV]	7.0181635	7.6410202	12.549291	13.8163511
g_{sp} [eV]	3.9277121	4.667435	25.4165018	22.895573
g_{p2} [eV]	5.9450316	8.8079605	20.3430761	17.9306483
h_{sp} [eV]	0.5830777	0.6711716	0.5863918	0.6997347
z_{sn} [bohr ⁻¹]	2.3115349	4.7072332	14.4314615	12.3091799
z_{pn} [bohr ⁻¹]	1.5740136	1.6790098	6.6592598	7.0226726
z_{dn} [bohr ⁻¹]	0.4796566	0.5564688	1.1708127	1.0850375
$\square(\text{core})$ [bohr ⁻¹]	1.3127952	1.0001556	2.3830131	2.6422529
$\Delta H_f^\circ(\text{atom})$ [kcal mol ⁻¹]	79.49	108.39	112.3	145.5
F_{sd}^0 [eV]	4.496379	6.3386046	1.4582843	1.3979775
G_{sd}^2 [eV]	6.9241222	14.5719405	1.3237728	1.644892
α_{ij} [\AA^{-1}]				
H	3.3050075	2.7069137	2.8366207	2.8186298
C	2.8051511	2.6612219	2.6583073	2.4664812
N	2.7291355	3.1765503	2.6399847	2.5734504
O	2.8693214	3.4253695	2.5623795	2.4752289
F	2.1741552	2.7852557	3.1991591	3.0002541
Al	2.4030559	2.8539528	2.4560418	2.3835763
Si	2.8539528	2.3452252	2.2545275	2.2220888
P	1.6942589	2.2061477	3.7754720	3.3027486
S	1.8406946	2.7078528	2.1732697	2.6575520
Cl	2.0611639	2.9030226	2.8990097	5.4791068
Ti	2.4560418	2.2545275	2.7149128	1.0700289
Zr	2.3835763	2.2220888	1.0700289	2.4980342
δ_{ij}				
H	10.9172770	2.3321311	3.3024430^a	3.2885959^a
C	7.6622796	4.1397608	4.7058331	5.4225345
N	5.1321889	9.5779805	3.6239466	4.4817796
O	4.7014268	8.9075202	2.4868107	2.3617297
F	1.3582859	2.6676348	7.0863573	6.6146056
Al	8.8461475	9.7389477	18.4753536	18.5000120
Si	9.7389477	1.8296180	3.9075768	4.0818782
P	1.5246045	2.7227698	8.5297153	9.9851281
S	1.4176441	6.9100579	2.7018956	9.8466777
Cl	1.5267651	5.2459739	5.3612679	5.2262751
Ti	18.4753536	3.9075768	9.7712491	1.0000047
Zr	18.5000120	4.0818782	1.0000047	10.1338549

^aDistance-dependent δ [\AA^{-1}] according to Equation (1)

Table 2 Experimental and calculated heats of Formation, dipole moments and vertical ionization potentials for the aluminum training set. Calculated ionization potentials are those given by Koopmans' theorem. The errors are ^a (< 5 kcal mol⁻¹), ^c (5–10 kcal mol⁻¹), ^d (10–20 kcal mol⁻¹) and ^b (> 20 kcal mol⁻¹). The color codes for dipole moments (in Debye) are ^a < 0.5, ^c 0.5–1, ^d > 1 and for ionization potentials (eV) ^a < 0.5, ^c 0.5–1, ^d 1–2 and ^b > 2

Compound	Heat of Formation (kcal mol ⁻¹)						Error (kcal mol ⁻¹)				
	Exper.	AMI	PM3	PM5	MNDO/d	AMI*	AMI	PM3	PM5	MNDO/d	AMI*
Al ⁺	218.10	213.33	279.75	224.59	218.10	227.83	4.77	-61.65	-6.49	0.00	-9.73
Al ₂	116.40	117.51	97.80	117.51	117.87	132.70	-1.11	18.60	-1.11	-1.47	-16.30
AlH	57.70	52.89	70.06	56.84	62.98	64.83	4.81	-12.36	0.86	-5.28	-7.13
AlH ₂	63.00	45.03	4.24	50.32	50.91	62.19	17.97	58.76	12.68	12.09	0.81
AlH ₃	29.10	13.62	84.46	16.77	26.95	25.49	15.48	-55.36	12.33	2.15	3.61
Al ₂ H ₆	24.60	-15.49	6.65	-48.94	27.63	23.08	40.09	17.95	73.54	-3.03	1.52
AlC	164.80	164.72	134.12	167.80	192.41	209.02	0.08	30.68	-3.00	-27.61	-44.22
(CH ₃) ₃ Al	-20.90	-27.50	-5.74	-37.68	-20.52	-18.88	6.60	-15.16	16.78	-0.38	-2.02
(C ₂ H ₅) ₂ AlH	-35.00	-27.98	10.79	-28.14	-18.70	-20.90	-7.02	-45.79	-6.86	-16.30	-14.10
(C ₂ H ₅) ₃ Al	-39.10	-46.27	-23.83	-48.25	-39.37	-42.48	7.17	-15.27	9.15	0.27	3.38
(<i>n</i> -C ₃ H ₇) ₃ Al	-57.10	-65.88	-47.03	-65.30	-51.69	-63.45	8.78	-10.07	8.20	-5.41	6.35
(<i>i</i> -C ₄ H ₉) ₃ Al	-78.23	-80.08	-59.64	-84.17	-52.80	-79.48	1.85	-18.59	5.94	-25.43	1.25
AlO ⁺	237.30	234.61	202.36	224.20	219.38	237.22	2.69	34.94	13.10	17.92	0.08
AlO	16.00	7.76	-28.38	10.45	3.07	14.49	8.24	44.38	5.55	12.93	1.51
AlO ⁻	-64.40	-52.86	-50.87	-49.02	-24.49	-60.83	-11.54	-13.53	-15.38	-39.91	-3.57
AlO ₂ ⁺	155.90	147.04	179.75	146.74	137.69	126.35	8.86	-23.85	9.16	18.21	29.55
AlO ₂	-20.60	-17.25	-54.92	-31.60	-25.60	-28.09	-3.35	34.32	11.00	5.00	7.49
AlO ₂ ⁻	-116.00	-95.47	-117.09	-116.00	-127.48	-102.37	-20.53	1.09	0.00	11.48	-13.63
Al ₂ O	-34.70	-39.16	-28.58	-47.91	-34.03	-53.99	4.46	-6.12	13.21	-0.67	19.29
Al ₂ O ₂ ⁺ (linear)	126.00	126.81	59.10	113.42	87.89	110.22	-0.81	66.90	12.58	38.11	15.70
Al ₂ O ₂ ⁻ (linear)	-94.30	-75.40	-124.00	-97.28	-101.47	-90.79	-18.90	29.70	2.98	7.17	-3.51
H-Al=O	-8.00	-21.89	2.19	-22.10	-21.12	-17.33	13.89	-10.19	14.10	13.12	9.33
HAIO ⁻	-55.00	-44.83	-109.27	-31.55	-14.90	-62.45	-10.17	54.27	-23.45	-40.10	7.45
AlOH ⁺	130.00	157.53	118.53	158.62	141.63	142.90	-27.53	11.47	-28.62	-11.63	-12.90
AlOH	-43.00	-38.91	-24.08	-51.29	-34.51	-55.31	-4.09	-18.92	8.29	-8.49	12.31
HO-Al=O	-110.00	-79.53	-105.09	-92.13	-101.31	-95.23	-30.47	-4.91	-17.87	-8.69	-14.77
(C ₂ H ₅) ₂ AlOC ₂ H ₅	-113.40	-103.61	-101.18	-108.96	-98.10	-115.62	-9.79	-12.22	-4.44	-15.30	2.22
(C ₂ H ₅) ₂ AlOCH(CH ₃) ₂	-144.10	-110.47	-106.19	-114.62	-102.66	-123.53	-33.63	-37.91	-29.48	-41.44	-20.57
Aluminum <i>tris</i> (acetylacetonate)	-399.40	-308.13	-371.01	-429.95	-307.45	-410.41	-91.27	-28.39	30.55	-91.95	11.01
AlF ⁺	165.40	126.69	244.57	156.29	126.86	118.65	38.71	79.17	9.11	38.54	46.75
AlF	-63.50	-77.87	-50.13	-65.11	-65.69	-87.80	14.37	-13.37	1.61	2.19	24.30
AlF ₂ ⁺	22.00	18.38	29.04	36.69	22.96	6.25	3.62	-7.04	-14.69	-0.96	15.75
AlF ₂	-166.00	-169.55	-164.29	-153.17	-171.31	-170.71	3.55	-1.71	-12.83	5.31	4.71
AlF ₂ ⁻	-217.00	-210.87	-229.60	-208.12	-201.03	-212.95	-6.13	12.60	-8.88	-15.97	-4.05
AlF ₃	-289.00	-285.85	-291.49	-280.36	-291.87	-295.71	-3.15	2.49	-8.64	2.87	6.71
AlF ₄ ⁻	-476.00	-427.69	-469.18	-453.80	-458.48	-433.19	-48.31	-6.82	-22.20	-17.82	-42.81
Al ₂ F ₆	-629.50	-645.98	-631.36	-648.90	-628.33	-636.82	16.48	1.86	19.40	-1.17	7.32
F-Al=O	-139.00	-110.15	-124.71	-110.47	-126.65	-115.15	-28.85	-14.29	-28.53	-12.35	-23.85
F ₂ AlO ⁻	-311.56	-257.16	-285.97	-279.85	-287.25	-264.27	-54.40	-25.59	-31.71	-24.31	-47.29
AlCl ⁺	206.00	179.66	197.53	198.00	169.61	198.34	26.34	8.47	8.00	36.39	7.66
AlCl	-12.30	-20.85	-5.48	-9.57	-12.74	-10.06	8.55	-6.82	-2.73	0.44	-2.24
AlCl ₂ ⁺	115.00	104.18	124.33	111.27	93.93	140.27	10.82	-9.33	3.73	21.07	-25.27
AlCl ₂	-67.00	-74.69	-69.90	-55.02	-72.87	-58.17	7.69	2.90	-11.98	5.87	-8.83
AlCl ₂ ⁻	-115.00	-119.95	-144.84	-113.61	-108.96	-122.34	4.95	29.84	-1.39	-6.04	7.34
AlCl ₃	-139.70	-140.31	-122.09	-135.81	-149.18	-125.34	0.61	-17.61	-3.89	9.48	-14.36
Al ₂ Cl ₆	-309.70	-318.96	-311.24	-309.70	-296.02	-330.84	9.26	1.54	0.00	-13.68	21.14
<i>n</i> -C ₈ H ₁₈ AlCl ₂ Al(<i>i</i> -C ₄ H ₉) ₂	-99.12	-101.68	-83.58	-107.36	-87.71	-105.64	2.56	-15.54	8.24	-11.41	6.52
AlClF ⁺	66.00	60.75	74.95	70.79	58.07	67.45	5.25	-8.95	-4.79	7.93	-1.45
Cl-Al=O	-83.20	-66.44	-72.42	-67.05	-78.58	-50.26	-16.76	-10.78	-16.15	-4.62	-32.94
AlClF	-117.00	-121.19	-117.85	-104.29	-121.24	-126.59	4.19	0.85	-12.71	4.24	9.59
AlClF ₂	-238.80	-236.20	-234.59	-232.81	-242.95	-254.99	-2.60	-4.21	-5.99	4.15	16.19
AlCl ₂ F	-189.00	-186.69	-177.98	-184.16	-195.36	-198.18	-2.31	-11.02	-4.84	6.36	9.18

electron affinities and homo-lytic and heterolytic bond cleavage) to supplement the data sets. This is somewhat inconsistent with using heats of formation rather than Born–Oppenheimer energies, however the near atom-additivity of thermal corrections [17] allows minimization of these quantities simultaneously. The use of

reaction energetics increases the scope of the parameterization data, particularly in the case of transition metals, where heats of formation are sparse. In addition, the use of feasible chemical processes (rather than the rather contrived, but convenient, heat of formation) in the optimization procedure should increase the appli-

Table 2 (Contd.)

AIS	48.00	48.01	21.95	40.31	5.37	41.29	-0.01	26.05	7.69	42.63	6.71
Statistics, Heats of Formation (N=53)											
Mean Signed Error							-2.45	0.48	-0.21	-1.58	-0.81
Mean Unsigned Error							13.88	20.98	12.20	14.66	12.99
Dipole Moments (Debye)											
AlH	0.17	0.97	0.66	1.02	0.21	0.40	-0.80	-0.49	-0.85	-0.04	-0.23
H-Al=O	1.50	2.10	0.45	1.73	1.57	1.52	-0.60	1.05	-0.23	-0.07	-0.02
AlF	1.53	1.00	3.29	0.03	0.59	1.18	0.53	-1.76	1.50	0.94	0.35
Statistics, Dipole Moments (N=3)											
Mean Signed Error							-0.29	-0.40	0.14	0.28	0.03
Mean Unsigned Error							0.64	1.10	0.86	0.35	0.20
Ionization Potentials (eV)											
Al ₂	6.20	6.37	9.22	6.42	6.27	6.66	-0.17	-3.02	-0.22	-0.07	-0.46
AlH	8.40	7.98	9.69	8.24	7.50	7.47	0.42	-1.29	0.16	0.90	0.93
(CH ₃) ₃ Al	9.76	10.31	10.10	9.26	10.57	10.18	-0.55	-0.34	0.50	-0.81	-0.42
H-Al=O	7.50	8.67	8.60	9.66	7.83	8.92	-1.17	-1.10	-2.16	-0.33	-1.42
AlF	9.80	8.90	9.29	9.97	8.44	9.32	0.90	0.51	-0.17	1.36	0.48
AlF ₃	16.10	13.77	15.20	14.10	15.26	14.34	2.33	0.90	2.00	0.84	1.76
AlCl	8.50	8.75	9.08	9.71	8.29	9.39	-0.25	-0.58	-1.21	0.21	-0.89
AlCl ₃	12.01	12.49	11.40	11.63	11.59	11.84	-0.48	0.61	0.38	0.42	0.17
(CH ₃) ₂ AlCl	10.25	10.39	10.17	9.63	10.61	10.22	-0.14	0.08	0.62	-0.36	0.03
Cl-Al=O	12.00	11.65	11.01	10.98	12.07	11.10	0.35	0.99	1.02	-0.07	0.90
Statistics, Ionization Potentials (N=10)											
Mean Signed Error							0.12	-0.32	0.09	0.21	0.11
Mean Unsigned Error							0.68	0.94	0.84	0.54	0.75

capability of semiempirical methods to chemical applications. While reaction enthalpies are often used to evaluate the appropriateness of a particular parameter minimum they are not generally included in the parameterization procedure.

While the NIST WebBook makes a large amount of data available, many data points are of uncertain accuracy, particularly for transition metal complexes. For example, the heats of formation of large titanium complexes are calculated relative to Ti(Cp)₂Cl₂, which may not be consistent with data with the smaller compounds.

To avoid having our parameterization skewed by possibly erroneous data, heats of formation, dipole moments and geometries were checked using the following DFT-based scheme with the exception of tetraphenylsilane and ((CH₃)₃Si)₃N. Geometries were optimized using the Becke gradient corrected exchange functional [18] in conjunction with the Lee–Yang–Parr correlation functional [19] with three parameters (B3LYP [20]), as implemented in Gaussian 98 [21]. For compounds which contained Ti or Zr the LANLdz basis set [22–24] was used for and for all of the other compounds the 6-31+G(d) [25–29] basis set. Harmonic vibrational frequencies were also calculated at this level and used for extrapolation to 298 K. Single point B3LYP/LANLdz++//B3LYP/LANLdz and B3LYP/6-311+G(2d,f)//B3LYP/6-31G(d) calculations [30, 31] were used to refine the energies and dipole moments. Heats of formation were calculated using these Born–Oppenheimer energies and the thermodynamic corrections derived from the smaller basis set by optimizing the atomic parameters through

a multi-linear least squares analysis. This method has been demonstrated to give more accurate results than the a priori atomic values [17].

We will draw special attention to some molecules for which the situation is unclear.

We removed four molecules from the training set, disobutylaluminum hydride, aluminum nitride, AlOF₂ and Al(Cl)₂(i-Bu).

Rather than attempting to gather a comprehensive set of reactions, we have chosen a representative series. In doing so, we have relied exclusively on calculated energies, rather than reactions where heats of formation exist for all the compounds involved. In addition to allowing greater coverage as to the nature of the bonds being broken and formed, this method has the advantage that the systematic nature of the DFT calculations helps us to create a consistent parameterization.

The final set contains 234 heats of formation 284 reaction energies, 27 ionization potentials, 23 dipole moments, 351 bond lengths and 112 bond angles. The individual datasets and the values used for parameterization are outlined in the tables and supplementary material. These and other parameterization data will soon be made available as a freely accessible web-based dataset [32, 33].

Parameterization

The only change to the parameterization procedure from that reported previously [1] was that we determined appropriate weighting factors for each of the components in the error function. Despite numerous additions

Table 3 DFT and semiempirical calculated energies for the reactions used in the aluminum training set. The errors are indicated as for Table 2

Reaction	ΔE_R (kcal mol ⁻¹)						Error (kcal mol ⁻¹)				
	DFT	AM1	PM3	PM5	MNDO/d	AM1*	AM1	PM3	PM5	MNDO/d	AM1*
AlH ₃ → H ⁺ + AlH ₂ ⁺	247.72	281.41	272.83	269.49	263.43	256.91	-33.68	-25.11	-21.77	-15.77	-9.19
AlH ₃ → H ⁺ + AlH ₂ [*]	87.05	83.519	-28.122	85.65	76.06	88.803	3.53	115.17	1.40	10.99	-1.75
AlH ₃ → H ⁺ + AlH ₂ ⁻	378.31	318.18	197.36	331.00	353.97	338.08	60.13	180.95	47.31	24.34	40.23
CH ₃ AlH ₂ → CH ₃ ⁺ + AlH ₂ ⁺	244.92	268.73	263.40	259.40	262.67	244.72	-23.81	-18.48	-14.48	-17.75	0.20
CH ₃ AlH ₂ → CH ₃ ⁻ + AlH ₂ ⁻	285.16	270.80	131.18	293.64	287.34	291.18	14.36	153.98	-8.48	-2.18	-6.02
AlH ₂ OH → OH ⁺ + AlH ₂ ⁺	253.06	258.48	269.44	227.65	266.56	255.76	-5.42	-16.38	25.41	-13.50	-2.70
AlH ₂ OH → OH ⁻ + AlH ₂ ⁻	479.43	419.65	282.48	443.06	442.17	461.33	59.78	196.95	36.37	37.26	18.10
NH ₂ AlH ₂ → NH ₂ ⁺ + AlH ₂ ⁺	568.58	545.70	524.11	535.64	530.50	510.20	22.88	44.47	32.94	38.09	58.38
NH ₂ AlH ₂ → NH ₂ ⁻ + AlH ₂ ⁻	68.74	96.02	-60.42	89.00	102.27	104.92	-27.28	129.16	-20.26	-33.53	-36.18
AlH ₂ F → F ⁺ + AlH ₂ ⁺	242.81	304.39	270.45	246.78	283.63	291.78	-61.57	-27.64	-3.97	-40.82	-48.97
AlH ₂ F → F ⁻ + AlH ₂ ⁻	542.80	465.80	361.33	545.58	516.38	497.58	77.00	181.47	-2.78	26.42	45.22
AlH ₂ Cl → Cl ⁺ + AlH ₂ ⁺	197.87	211.84	198.39	183.97	196.14	205.24	-13.97	-0.52	13.91	1.73	-7.37
AlH ₂ Cl → Cl ⁻ + AlH ₂ ⁻	394.88	367.15	194.40	362.38	370.65	341.06	27.73	200.48	32.50	24.24	53.82
AlH ₂ SH → AlH ₂ ⁺ + HS ⁻	206.04	197.48	206.05	179.63	233.23	172.37	8.56	-0.01	26.41	-27.19	33.67
AlH ₂ SH → AlH ₂ ⁻ + HS ⁺	311.50	259.46	133.61	304.85	313.63	300.12	52.04	177.89	6.65	-2.13	11.38
AlH ₂ SiH ₃ → PH ₂ ⁺ + AlH ₂ ⁺	206.06	180.69	285.18	200.77	224.94	190.67	25.37	-79.12	5.29	-18.88	15.39
AlH ₂ SiH ₃ → PH ₂ ⁻ + AlH ₂ ⁻	273.78	252.47	178.00	295.93	285.57	270.53	21.31	93.78	-22.15	-11.79	3.25
SiH ₃ AlH ₂ → SiH ₃ ⁺ + AlH ₂ ⁺	200.95	187.03	174.07	203.64	215.24	182.03	13.92	26.88	-2.69	-14.29	18.92
SiH ₃ AlH ₂ → SiH ₃ ⁻ + AlH ₂ ⁻	231.09	219.18	62.90	238.89	249.86	228.23	11.91	168.19	-7.80	-18.77	2.86
ZrH ₃ AlH ₂ → ZrH ₃ ⁺ + AlH ₂ ⁺	205.71	426.65	273.78	802.83		137.35	-220.94	-68.07	-597.12		68.36
ZrH ₃ AlH ₂ → ZrH ₃ ⁻ + AlH ₂ ⁻	202.33	265.83	235.05	626.35		143.56	-63.49	-32.71	-424.02		58.77
H ₂ + CH ₃ AlH ₂ → AlH ₃ + CH ₄	-7.19	11.58	31.22	0.91	3.50	12.07	-18.77	-38.41	-8.10	-10.68	-19.26
CH ₄ + CH ₃ AlH ₂ → C ₂ H ₆ + AlH ₃	12.86	6.54	25.72	14.39	8.39	7.02	6.32	-12.86	-1.53	4.47	5.84
H ₂ + AlH ₂ OH → AlH ₃ + H ₂ O	28.60	22.70	65.86	19.22	21.00	44.49	5.90	-37.26	9.38	7.60	-15.88
CH ₄ + AlH ₂ OH → AlH ₃ + CH ₃ OH	58.05	28.50	67.03	44.07	37.25	50.29	29.55	-8.98	13.98	20.80	7.76
H ₂ + NH ₂ AlH ₂ → AlH ₃ + NH ₃	18.50	38.18	67.84	17.48	20.59	27.18	-19.68	-49.34	1.02	-2.09	-8.68
CH ₄ + NH ₂ AlH ₂ → AlH ₃ + CH ₃ NH ₂	45.64	41.68	65.34	40.45	32.09	30.67	3.96	-19.70	5.20	13.55	14.98
H ₂ + AlH ₂ F → AlH ₃ + HF	41.05	36.02	71.28	26.00	50.64	47.90	5.03	-30.23	15.05	-9.59	-6.85
CH ₄ + AlH ₂ F → AlH ₃ + CH ₃ F	67.98	52.86	79.84	55.36	62.13	64.75	15.12	-11.86	12.62	5.85	3.23
H ₂ + AlH ₂ Cl → AlH ₃ + HCl	35.21	34.24	61.50	12.48	48.55	40.47	0.98	-26.29	22.73	-13.34	-5.26
CH ₄ + AlH ₂ Cl → AlH ₃ + CH ₃ Cl	57.90	43.49	66.90	44.19	53.57	42.69	14.41	-9.00	13.71	4.33	15.21
H ₂ + AlH ₂ SH → AlH ₃ + H ₂ S	23.32	19.90	53.34	16.60	48.89	41.11	3.42	-30.02	6.72	-25.57	-17.79
CH ₄ + AlH ₂ SH → AlH ₃ + CH ₃ SH	44.18	17.95	48.35	34.02	57.03	34.28	26.23	-4.16	10.16	-12.85	9.90
Electron Affinity Al	3.22	4.07	-87.34	72.33	54.78	13.65	-0.85	90.56	-69.11	-51.56	-10.43
Electron Affinity AlO	-58.12	-60.63	-22.50	-59.47	-27.56	-75.31	2.51	-35.62	1.35	-30.56	17.19
Electron Affinity AlO ₂	111.42	-78.21	-62.17	-84.40	-101.88	-74.27	-33.21	-49.25	-27.02	-9.54	-37.15
Electron Affinity AlF ₂	-46.91	-41.33	-65.31	-54.94	-29.72	-42.24	-5.58	18.40	8.03	-17.19	-4.67
Electron Affinity AlCl ₂	-54.34	-45.26	-74.93	-58.59	-36.10	-64.17	-9.08	20.59	4.25	-18.24	9.83
AlH ₂ [*] + AlH ₂ [*] → Al ₂ H ₄	-59.06	-63.82	153.99	-85.90	-56.41	-51.61	4.76	-213.05	26.83	-2.65	-7.45
CH ₃ AlH ₂ → AlH ₂ [*] + CH ₃ [*]	80.57	76.55	-21.41	80.35	64.74	82.32	4.02	101.98	0.22	15.83	-1.75
AlH ₂ [*] + CH ₃ AlH ₂ [*] → CH ₃ AlHAlH ₂	-57.82	-59.40	73.84	-81.61	-58.76	-52.49	1.58	-131.66	23.79	0.94	-5.33
CH ₃ AlH [*] + CH ₃ AlH [*] → CH ₃ AlHAlHCH ₃	-56.02	-54.77	-6.99	-77.51	-59.31	-52.69	-1.25	-49.03	21.49	3.29	-3.33
AlH ₂ OH → AlH ₂ [*] + OH [*]	128.11	108.82	28.52	120.27	106.85	135.88	19.29	99.60	7.84	21.26	-7.77
CH ₃ OAlH ₂ → CH ₃ O [*] + AlH ₂ [*]	112.35	96.30	14.05	105.61	96.88	121.66	16.05	98.30	6.74	15.47	-9.31
NH ₂ AlH ₂ → AlH ₂ [*] + NH ₂ [*]	108.31	109.44	12.50	106.43	88.04	103.72	-1.13	95.81	1.88	20.27	4.59
AlH ₂ F → AlH ₂ [*] + F [*]	157.01	155.42	59.30	154.32	153.94	172.59	1.59	97.71	2.69	3.07	-15.58
CF ₃ AlH ₂ → AlH ₂ [*] + CF ₃ [*]	76.04	51.30	-23.97	79.00	58.65	65.68	24.74	100.01	-2.96	17.39	10.36
AlH ₂ Cl → AlH ₂ [*] + Cl [*]	117.29	114.07	17.34	114.16	112.80	113.09	3.22	99.95	3.13	4.49	4.20
AlH ₂ SH → AlH ₂ [*] + HS [*]	93.97	84.38	-1.80	95.40	108.03	108.46	9.59	95.77	-1.42	-14.06	-14.49
CH ₃ SAIH ₂ → AlH ₂ [*] + CH ₃ S [*]	87.71	75.93	42.26	86.59	103.86	98.96	11.78	45.45	1.12	-16.15	-11.25

to the parameterization data, the weighting factors used have remained constant since MNDO. As Dewar and Holder noted in the parameterization of AM1 for aluminum, the choice of weighting factors was originally developed by trial and error based on “chemical acceptability of the results for as many additional molecules and properties as the available data will allow”. As we have observed previously [1], the current com-

position of data sets and weighting factors emphasizes heats of formation (as a larger number of data of this type has been added relative to the others) at the expense of the other factors. The new weighting factors were determined so that the error function at the minimum was composed of approximately one-third each of the heats of formation and reaction energetics. The remaining third consisted of errors in dipole moments,

Table 3 (Contd.)

$\text{AlH}_2\text{PH}_2 \rightarrow \text{AlH}_2^+ + \text{PH}_2^+$	68.85	59.84	67.49	90.51	74.25	72.48	9.01	1.36	-21.66	-5.40	-3.63
$\text{SiH}_3\text{AlH}_2 \rightarrow \text{AlH}_2^+ + \text{SiH}_3^+$	66.89	48.92	-42.28	76.94	67.04	72.24	17.97	109.17	-10.05	-0.15	-5.35
$\text{SiF}_3\text{AlH}_2 \rightarrow \text{AlH}_2^+ + \text{SiF}_3^+$	72.64	31.98	-75.23	62.10	60.06	48.63	40.66	147.87	10.54	12.58	24.01
$\text{TiH}_3\text{AlH}_2 \rightarrow \text{AlH}_2^+ + \text{TiH}_3^+$	27.56	238.82	66.50	331.72			62.85	-211.26	-38.94	-304.16	-35.29
$\text{ZrH}_3\text{AlH}_2 \rightarrow \text{AlH}_2^+ + \text{ZrH}_3^+$	44.58	180.81	56.35	545.21			46.94	-136.23	-11.77	-500.63	-2.36
Adiabatic Ionization Potential Al	138.86	133.84	233.73	145.10	140.11	148.55	5.03	-94.87	-6.24	-1.24	-9.69
Adiabatic Ionization Potential AlO	238.94	226.85	230.74	213.75	216.30	222.73	12.09	8.20	25.19	22.63	16.21
Adiabatic Ionization Potential AlF	224.67	204.57	294.70	221.40	192.55	206.44	20.10	70.03	3.27	32.12	18.23
Adiabatic Ionization Potential AlF ₂	205.11	187.92	193.33	189.86	194.27	176.96	17.19	11.78	15.25	10.84	28.15
Adiabatic Ionization Potential AlCl	213.37	200.51	203.01	207.57	182.35	208.40	12.86	10.36	5.81	31.02	4.97
Adiabatic Ionization Potential AlCl ₂	182.72	178.87	194.23	166.30	166.79	198.44	3.85	-11.51	16.43	15.93	-15.72
Adiabatic Ionization Potential AlClF	192.68	181.94	192.80	175.09	179.32	194.04	10.74	-0.12	17.59	13.36	-1.36
$2\text{AlH}_3 \rightarrow \text{Al}_2\text{H}_6$	-33.56	-42.72	-162.27	-82.48	-26.27	-27.91	9.16	128.71	48.92	-7.29	-5.65
$2\text{Al}(\text{CH}_3)_3 \rightarrow \text{Al}_2(\text{CH}_3)_6$	-9.45	17.17	-11.72	-45.01	-0.87	-7.09	-26.62	2.27	35.56	-8.58	-2.36
$2\text{AlF}_3 \rightarrow \text{Al}_2\text{F}_6$	-46.16	-74.28	-48.37	-88.18	-44.58	-45.41	28.12	2.21	42.02	-1.58	-0.75
$2\text{AlCl}_3 \rightarrow \text{Al}_2\text{Cl}_6$	-22.74	-38.33	-67.07	-38.07	-26.27	-80.15	15.59	44.33	15.33	-25.08	57.41
$\text{AlH}_2\text{TiH}_3 \rightarrow \text{AlH}_2^+ + \text{TiH}_3^+$	194.78	450.611	236.728	573.044		149.932	-255.83	-41.95	-378.26		44.85
$\text{AlH}_2\text{TiH}_3 \rightarrow \text{AlH}_2^+ + \text{TiH}_3^+$	161.25	392.644	313.55	451.836		214.184	-231.39	-152.3	-290.59		-52.93
Statistics, Heats of Reaction (N=68, N=62 for MNDO/d)											
Mean Signed Error							-8.68	24.32	-30.34	-0.64	4.06
Mean Unsigned Error							35.53	66.85	50.46	15.49	17.28

ionization potentials and geometries. This led to the choice of 1 mol kcal⁻¹ for the reaction, whereas the MNDO values were retained for the rest of the error function.

Results

The optimized AM1* parameters are shown in Table 1. Most of the parameters are quite consistent along the second row. Above all, the *d*-type polarization functions on Al and Si have the expected diffuse exponents.

Geometries were optimized with the new AM1* parameterization using VAMP 8.1, [34] while the AM1, PM3 and PM5 calculations used LinMOPAC2.0 [35]. The two programs give essentially identical results for the Hamiltonians that are available in both.

Aluminum

The results for aluminum are summarized in Table 2. The overall MUE is approximately equal to that of the DFT-based methods (MUE = 12–15.3 kcal mol⁻¹, depending on the basis set).

Particularly large errors in AM1* occur in fluorinated compounds such as AlF₂O⁻ (-47.3), AlF⁺ (46.8), AlC (-44.2) and AlF₄⁻ (-42.8). The MUE for compounds containing fluorine is 18.6 kcal mol⁻¹, significantly higher than overall. In addition, oxygenated compounds are represented by Al₂O⁺ (29.6) and AlO (-33). Both the fluorine-containing and oxygen-containing compounds have mean signed errors (MSE) near zero, indicating that there is no residual systematic error. Generally, AM1* performs comparably to AM1 and PM5 for the heats of formation and very well for the three available dipole moments. The four semiempirical methods are comparable for the ionization potentials.

However, our parameterization set also consisted of a series of reactions, as outlined above. Table 3 shows the results obtained.

For the reactions examined, the seven adiabatic ionization potentials have an MUE of 13.5 kcal mol⁻¹, and the five electron affinities are in error by 15.9 kcal mol⁻¹. This indicates that in the errors in the ions and the neutral compounds are consistent. The dimerization energies are well predicted, about 5 kcal mol⁻¹, with the exception of AlCl₃, where the dimer is too strongly bound despite relatively accurate predictions of the heat of formation of the monomer and the dimer. The bond homolysis energies are particularly well predicted with an MUE of 9.3 kcal mol⁻¹. The Al–O and Al–S bonds are predicted to be too strong, while Al–C and Al–Si bonds are slightly too weak. Bond heterolysis is less accurate, an MUE of 28.9 kcal mol⁻¹, with the largest errors coming from cases resulting in a negatively charged aluminum, with H⁺, F⁺, and Cl⁺ as the other products. These errors are a direct result of the incorrect ionization potential of those species, and are seen in all of the reactions examined here.

The geometric parameters used for the parameterization and the results obtained with the four semiempirical methods are shown in Table S1 of the supplementary material. A statistical analysis of the results is shown in Table S2. For aluminum compounds, the AM1* bond lengths are systematically too short by 0.13 Å. This is primarily a result of Al–halogen bonds, where F–Al bonds and Al–Cl are 0.15 and 0.24 Å in error, respectively. This systematic error in chlorine bonds was noted previously [1] in our parameterization for chlorine, and is seen for the other metals as well. The errors in bond distances with Al for the other first row elements are quite small, less than 0.05 Å. The corresponding errors with second-row elements are also fairly large, although they are typically based on only one or two observations.

Table 4 Experimental and calculated heats of Formation, dipole moments and vertical ionization potentials for the silicon training set. Calculated ionization potentials are those given by Koopmans' theorem. The errors are color coded as for Table 2

Compound	Heat of Formation (kcal mol ⁻¹)						Error (kcal mol ⁻¹)				
	Exper.	AM1	PM3	PM5	MNDO/d	AM1*	AM1	PM3	PM5	MNDO/d	AM1*
Si ⁻	75.50	111.14	110.36	96.07	123.49	81.09	-35.64	-34.86	-20.57	-47.99	-5.59
Si ₂ ⁻	139.90	159.89	143.21	155.97	145.91	164.49	-19.99	-3.31	-16.07	-6.01	-24.59
Si ₂ ⁻	87.90	85.71	54.02	103.80	111.60	107.93	2.19	33.88	-15.90	-23.70	-20.03
Si ₃ ⁻	152.20	184.88	152.79	151.74	161.78	151.81	-32.68	-0.59	0.46	-9.58	0.39
Si ₃ ⁻	100.30	114.99	80.75	100.82	111.73	99.23	-14.69	19.55	-0.52	-11.43	1.07
Si ₄ ⁻	120.20	188.93	83.88	105.89	112.93	117.89	-68.73	36.32	14.31	7.27	2.31
Si ₅ ⁻	106.50	146.14	62.52	96.02	107.85	137.18	-39.64	43.98	10.48	-1.35	-30.68
HSiSiH	90.00	89.40	93.98	89.44	88.06	72.91	0.60	-3.98	0.56	1.94	17.09
H ₂ Si (singlet)	65.20	67.83	72.79	67.88	63.21	46.67	-2.63	-7.59	-2.68	1.99	18.53
H ₂ Si (triplet)	86.20	39.94	68.15	71.63	78.53	82.18	46.26	18.05	14.57	7.67	4.02
SiH ₃ ⁻	234.10	222.90	223.29	212.42	224.26	217.28	11.20	10.81	21.68	9.84	16.82
SiH ₃ ⁺	47.90	24.48	42.11	41.24	44.79	47.76	23.42	5.79	6.66	3.11	0.14
SiH ₃ ⁻	14.00	-1.82	-2.80	13.82	27.27	22.92	15.82	16.80	0.18	-13.27	-8.92
SiH ₄	8.20	4.12	12.48	10.53	10.41	7.23	4.08	-4.28	-2.33	-2.21	0.97
H ₂ Si=SiH ₂	65.70	54.50	56.80	50.68	74.94	63.70	11.20	8.90	15.02	-9.24	2.00
H ₂ SiSiH (singlet)	74.60	79.93	72.65	66.28	75.18	41.21	-5.33	1.95	8.32	-0.58	33.39
Si ₂ H ₅ ⁺	53.30	34.45	45.08	39.52	52.89	51.03	18.85	8.22	13.78	0.41	2.27
Si ₂ H ₆	19.10	16.15	17.85	11.70	24.42	32.77	2.95	1.25	7.40	-5.32	-13.67
Si ₂ H ₈	28.90	24.62	21.71	11.76	27.66	-26.20	4.28	7.19	17.14	1.24	55.10
C ₂ Si	147.00	151.61	155.32	148.68	168.99	200.62	-4.61	-8.32	-1.68	-21.99	-53.62
H ₂ Si=CH ₂	37.00	21.75	40.21	39.53	46.59	80.75	15.25	-3.21	-2.53	-9.59	-43.75
CH ₃ SiH (singlet)	44.00	45.10	49.09	43.84	42.99	40.38	-1.10	-5.09	0.16	1.01	3.62
CH ₃ SiH ₂ ⁺	30.60	7.10	22.30	22.27	24.39	38.06	23.50	8.30	8.33	6.21	-7.46
CH ₃ SiH ₃	-7.00	-11.14	-4.21	-6.17	-8.30	-5.09	4.14	-2.79	-0.83	1.30	-1.91
CH ₃ SiH=SiH ₂	21.00	5.81	21.59	22.75	25.85	69.97	15.19	-0.59	-1.75	-4.85	-48.97
(CH ₃) ₂ Si (singlet)	26.00	24.71	25.54	20.36	23.76	34.26	1.29	0.46	5.64	2.24	-8.26
CH ₂ =CHSiH ₃	1.00	11.41	19.67	15.01	12.34	13.25	-10.41	-18.67	-14.01	-11.34	-12.25
(CH ₃) ₂ SiH ⁺	14.60	-9.25	2.95	4.17	4.43	28.55	23.85	11.65	10.43	10.17	-13.95
(CH ₃) ₂ SiH ₂	-22.60	-25.68	-20.79	-22.53	-26.45	-16.53	3.08	-1.81	-0.07	3.85	-6.07
C ₂ H ₅ SiH ₃	-15.00	-16.51	-10.20	-11.04	16.28	-18.41	1.51	-4.80	-3.96	1.28	3.41
(CH ₃) ₂ Si=CH ₂	5.00	-9.26	3.40	6.99	5.90	59.72	14.26	1.60	-1.99	-0.90	-54.72
(CH ₃) ₂ Si ⁺	-0.70	-24.65	-16.11	-12.96	-14.95	19.35	23.95	15.41	12.26	14.25	-20.05
(CH ₃) ₂ SiH	-39.10	-39.38	-37.30	-38.52	-43.90	-27.05	0.28	-1.80	-0.58	4.80	-12.05
(C ₂ H ₅) ₂ SiH ₂	-43.60	-36.41	-32.62	-32.26	-41.74	-43.19	-7.19	-10.98	-11.34	-1.86	-0.41
(CH ₃) ₂ Si	-55.70	-52.16	-53.75	-53.96	-60.51	-36.66	-3.54	-1.95	-1.74	4.81	-19.04
1,1-Dimethylsilacyclobutane	-33.70	-37.23	-35.65	-38.54	-46.89	-25.78	3.53	1.95	4.84	13.19	-7.92
1,1-Dimethylsilacyclopentane	-43.40	-57.08	-54.43	-57.24	-65.37	-52.19	13.68	11.03	13.84	21.97	8.79
(C ₂ H ₅) ₂ SiH	-39.50	-54.92	-55.38	-52.58	-64.52	-66.82	15.42	15.88	13.08	25.02	27.32
(C ₂ H ₅) ₂ Si	-71.00	-71.95	-78.02	-72.26	-84.40	-88.86	0.95	7.02	1.26	13.40	17.86
Si(C ₆ H ₅) ₄	79.80	74.58	76.04	63.97	62.59	7.95	5.22	3.76	15.83	17.21	71.85
SiH ₃ SiH ₂ CH ₃	2.10	1.25	0.77	-4.41	3.53	15.21	0.85	1.33	6.51	-1.43	-13.11
CH ₃ SiH ₂ SiH ₂ CH ₃	-14.90	-13.35	-16.20	-20.34	-17.00	7.97	-1.55	1.30	5.44	2.10	-22.87
SiH ₃ SiH(CH ₃) ₂	-14.90	-12.89	-16.10	-20.17	-16.77	-1.04	-2.01	1.20	5.27	1.87	-13.86
SiH ₃ Si(CH ₃) ₃	-31.90	-26.12	-32.81	-35.56	-36.29	-16.10	-5.78	0.91	3.66	4.39	-15.80
Si(CH ₃) ₂ HSi(CH ₃) ₂ H	-49.00	-40.91	-49.83	-51.60	-55.63	-16.42	-8.09	0.83	2.60	6.63	-32.58
Si ₂ (CH ₃) ₂ H	-66.00	-53.72	-66.54	-66.85	-73.62	-31.78	-12.28	0.54	0.85	7.62	-34.22
1,1,3,3-Tetramethyl-1,3-disilacyclobutane	-72.00	-75.37	-78.12	-78.31	-90.63	-74.23	3.37	6.12	6.31	18.63	2.23
(CH ₃) ₂ SiSi(CH ₃) ₃	-83.00	-66.38	-83.26	-81.95	-91.00	-40.77	-16.62	0.26	-1.05	8.00	-42.23
SiO	-24.60	-2.08	-26.03	-18.60	-20.63	19.94	-22.52	1.43	-6.00	-3.97	-44.54
SiO ₂	-73.00	-67.49	-88.93	-66.64	-96.90	-12.60	-5.51	15.93	-6.36	23.90	-60.40
H ₂ SiO	-23.50	-19.06	-21.54	-16.00	-32.41	2.50	-4.44	-1.96	-7.50	8.91	-26.00
trans-HSiOH	-23.70	-21.68	-31.41	-29.53	-25.02	-39.02	-2.02	7.71	5.83	1.32	15.32
SiH ₂ OH	-67.50	-64.16	-62.85	-58.59	-66.21	-78.16	-3.34	-4.65	-8.91	-1.29	10.66
Si(OH) ₂ (singlet)	-117.50	-113.72	-134.39	-142.22	-116.33	-124.08	-3.78	16.89	24.72	-1.17	6.58
HSiO(OH)	-110.60	-99.96	-113.25	-106.66	-112.33	-84.11	-10.64	2.65	-3.94	1.73	-26.49
H ₂ Si(OH) ₂	-149.00	-137.90	-144.08	-139.47	-143.00	-164.70	-11.10	-4.92	-9.53	-6.00	15.70
(CH ₃) ₂ SiOH	-119.50	-110.34	-115.50	-113.86	-116.84	-109.50	-9.16	-4.00	-5.64	-2.66	-10.00
Si(CH ₃) ₂ OC ₂ H ₅	-119.00	-112.21	-119.27	-115.88	-117.02	-122.54	-6.79	0.27	-3.12	-1.98	3.54
Si(CH ₃) ₂ (OC ₂ H ₅) ₂	-185.70	-174.93	-184.51	-183.05	-173.88	-211.01	-10.77	-1.19	-2.65	-11.82	25.31
Si(OCH ₃) ₄	-263.27	-273.14	-305.72	-284.12	-268.57	-336.45	9.87	42.45	20.85	5.30	73.18
(CH ₃) ₂ SiOSi(CH ₃) ₃	-185.70	-167.66	-176.54	-179.80	-186.42	-210.17	-18.04	-9.16	-5.90	0.72	24.47
SiN	89.00	77.04	92.62	95.18	118.79	175.26	11.96	-3.62	-6.18	-29.79	-86.26
(CH ₃) ₂ SiNHCH ₃	-54.30	-60.54	-62.01	-56.27	-59.21	-44.17	6.24	7.71	1.97	4.91	-10.13
(CH ₃) ₂ SiN(CH ₃) ₂	-59.30	-55.38	-65.94	-53.41	-55.94	-47.75	-3.92	6.64	-5.89	-3.36	-11.55
(CH ₃) ₂ SiNHSi(CH ₃) ₃	-114.00	-117.96	-119.69	-113.95	-115.86	-107.95	3.96	5.69	-0.05	1.86	-6.05

Most significantly, however, the methods (AM1, PM3 and PM5) that were parameterized using only heats of formation for energies show significant weaknesses when calculating heats of reaction. Thus, although AM1* is no improvement on the other methods for heats of formation, it provides a very important

improvement in heats of reaction, suggesting a generally more robust parameterization. We will return to this point in the discussion. As noted previously [1], the MNDO/d parameterization is particularly robust. MNDO/d gives comparable results to AM1* for the heats of reaction.

Table 4 (Contd.)

Mean unsigned error								16.04	9.38	12.33	7.50	22.94
DIPOLE MOMENTS (Debye)												
CH ₃ SiH ₃	0.73	0.37	0.44	0.11	0.95	0.01	0.36	0.29	0.62	-0.22	0.72	
HCCSiH ₃	0.32	0.69	0.04	0.30	1.72	0.76	-0.37	0.28	0.02	-1.40	-0.44	
CH ₂ =CHSiH ₃	0.66	0.55	0.23	0.12	1.44	0.43	0.11	0.43	0.54	-0.78	0.23	
(CH ₃) ₂ SiH ₂	0.71	0.44	0.46	0.07	1.04	0.07	0.27	0.25	0.64	-0.33	0.64	
C ₂ H ₅ SiH ₂	0.81	0.37	0.36	0.02	0.96	0.03	0.44	0.45	0.79	-0.15	0.78	
(CH ₃) ₃ SiH	0.53	0.39	0.37	0.03	0.85	0.11	0.14	0.16	0.50	-0.32	0.42	
SiO	3.10	1.76	0.74	2.27	2.34	1.02	1.34	2.36	0.83	0.76	2.08	
(CH ₃) ₃ SiNHSi(CH ₃) ₃	0.37	0.55	0.21	0.17	0.46	0.17	-0.18	0.16	0.20	-0.09	0.20	
SiF ₂	1.23	0.95	0.04	1.43	1.17	0.41	0.28	1.19	-0.20	0.06	0.82	
SiH ₃ F	1.30	1.30	1.03	2.29	0.69	1.50	0.00	0.27	-0.99	0.61	-0.20	
SiH ₂ F ₂	1.54	1.57	1.41	3.11	0.99	2.15	-0.03	0.13	-1.57	0.55	-0.61	
SiF ₃ H	1.26	1.53	1.51	3.34	1.08	2.31	-0.27	-0.25	-2.08	0.18	-1.05	
CH ₃ SiH ₂ F	1.71	1.52	1.30	2.42	1.42	1.50	0.19	0.41	-0.71	0.29	0.21	
CH ₃ SiF ₂ H	2.11	2.02	1.72	3.26	1.90	2.23	0.09	0.39	-1.15	0.21	-0.12	
SiH ₃ Cl	1.30	1.63	2.29	2.47	0.60	2.56	-0.33	-0.99	-1.17	0.70	-1.26	
SiH ₂ Cl ₂	1.13	1.75	2.70	2.60	0.44	3.15	-0.62	-1.57	-1.47	0.69	-2.02	
SiCl ₃ H	0.86	1.40	2.38	2.08	0.21	3.27	-0.54	-1.52	-1.22	0.65	-2.41	
CH ₃ SiCl ₃	1.91	2.51	3.15	2.75	1.46	3.62	-0.60	-1.24	-0.84	0.45	-1.71	
SiH ₃ SO	0.24	1.95	2.74	3.40	2.38	3.07	-1.71	-2.50	-3.16	-2.14	-2.83	
Statistics, Dipole Moments												
Mean signed error								-0.08	-0.07	-0.55	-0.01	-0.34
Mean unsigned error								0.41	0.78	0.98	0.56	0.99
IONIZATION POTENTIALS (eV)												
SiH ₄	12.82	12.35	11.79	11.23	13.69	12.96	0.47	1.03	1.59	-0.87	-0.14	
CH ₂ =CHSiH ₃	10.40	10.39	10.01	9.75	10.78	10.86	0.01	0.39	0.65	-0.38	-0.46	
(CH ₃) ₂ SiH ₂	11.20	11.18	10.65	10.13	11.96	11.57	0.02	0.55	1.07	-0.76	-0.37	
C ₂ H ₅ SiH ₃	10.95	11.07	10.63	9.98	11.85	10.97	-0.12	0.32	0.97	-0.90	-0.02	
(CH ₃) ₃ SiH	10.80	10.95	10.51	9.94	11.74	11.48	-0.15	0.29	0.86	-0.94	-0.68	
(CH ₃) ₄ Si	10.23	10.91	10.42	9.73	11.54	11.39	-0.68	-0.19	0.50	-1.31	-1.16	
(CH ₃) ₃ SiNHSi(CH ₃) ₃	8.66	9.49	8.29	7.89	10.60	9.98	-0.83	0.37	0.77	-1.94	-1.32	
SiF ₄	16.46	14.72	15.19	14.29	16.65	15.31	1.74	1.27	2.17	-0.19	1.15	
SiH ₃ F	12.80	11.75	11.17	10.85	13.85	12.77	1.05	1.63	1.95	-1.05	0.03	
SiH ₂ F ₂	12.90	11.61	10.82	10.72	14.07	12.95	1.29	2.08	2.18	-1.17	-0.05	
SiCl ₄	12.03	12.98	11.22	11.83	12.00	12.37	-0.95	0.81	0.20	0.03	-0.34	
SiH ₃ Cl	11.61	11.55	10.24	10.55	12.48	11.10	0.06	1.37	1.06	-0.87	0.51	
SiH ₂ Cl ₂	11.70	11.57	10.27	10.56	12.16	11.33	0.13	1.43	1.14	-0.46	0.37	
SiCl ₃ H	11.94	11.97	10.62	10.91	12.00	11.75	-0.03	1.32	1.03	-0.06	0.19	
(CH ₃) ₂ SiCl ₂	10.79	11.49	10.27	10.25	11.53	11.26	-0.70	0.52	0.54	-0.74	-0.47	
Statistics, Ionization Potentials												
Mean signed error								0.09	0.88	1.11	-0.78	-0.18
Mean unsigned error								0.55	0.90	1.11	-0.78	0.48

Silicon

The results obtained for heats of formation, dipole moments and ionization potentials for silicon compounds are shown in Table 4.

The AM1* errors in heats of formation for silicon compounds are larger than for aluminum compounds and significantly larger for the other semiempirical methods. This is unlikely to be an experimental problem as the errors given by the DFT calculations for this dataset are smaller than those for aluminum (MUE = 5.6–10 kcal mol⁻¹). In particular, compounds with Si–Si bonds are predicted poorly with dominant errors due to the alkyl substituted disilanes, such as hexamethyldisilane (–42.2), pentamethyldisilane (–34.22), and 1,1,2,2-tetramethyldisilane (–32.6). While these errors are fairly large, they are systematic and the trends observed on methylation are reproduced correctly. This systematic error is introduced by corre-

sponding large positive errors in hexachlorodisilane (71.6) and trisilane (55.1).

Extremely small compounds such as silicon nitride (–86.3) and silicon dicarbide (–53.6) also exhibit large errors, but are not expected to be important for the typical silicon chemistry to be treated by AM1*.

The large errors for Si(OCH₃)₄, silicon tetrafluoride (–32.9) and SiOF₂ can be attributed to the limitations in oxygen and fluorine parameters that noted previously [1] and above.

Despite the relatively large errors in the heats of formation, those for the series of reactions is on a par with those for aluminum. Table 5 shows the calculated heats of reaction for silicon compounds.

The ionization potentials and electron affinities have MUEs of 18.7 and 16.4 kcal mol⁻¹, comparable with those for aluminum. The bond homolysis energies have an MUE of 8.3 kcal mol⁻¹, indicating a high degree of accuracy. The largest errors are found for the Si–Si bond

Table 5 DFT and semiempirical calculated energies for the reactions used in the silicon training set. The errors are color coded as for Table 2

Reaction	ΔE_R (kcal mol $^{-1}$)						Error (kcal mol $^{-1}$)				
	DFT	AMI	PM3	PM5	MNDO/d	AMI*	AMI	PM3	PM5	MNDO/d	AMI*
H ₃ TiSiH ₃ → SiH ₃ ⁺ + TiH ₃ ⁻	-12.95	-159.98	-68.36	-171.06		36.84	147.03	55.41	158.11		-49.78
H ⁺ + SiH ₄ → SiH ₅	-157.57	-115.84	-184.60	-121.60	-114.08	-128.87	-41.73	27.03	-35.97	-43.89	-28.7
SiH ₄ → SiH ₃ + H	278.34	304.34	302.60	283.71	287.68	295.63	-26.01	-24.26	-5.37	-9.34	-17.29
SiH ₄ → H ⁺ + SiH ₃	410.23	335.27	383.22	337.39	361.06	355.44	74.96	27.01	72.85	49.18	54.79
(CH ₃)SiH ₃ → CH ₃ ⁺ + SiH ₃ ⁺	273.90	291.75	279.01	270.70	289.41	280.12	-17.85	-5.11	3.20	-15.51	-6.22
(CH ₃)SiH ₃ → CH ₃ ⁺ + SiH ₃ ⁻	283.99	261.67	257.96	269.68	279.45	280.38	22.32	26.03	14.31	4.54	3.61
(HO)SiH ₃ → SiH ₃ ⁺ + OH ⁻	268.2	272.94	268.64	229.36	284.70	281.33	-4.74	-0.44	38.84	-16.50	-13.13
(HO)SiH ₃ → SiH ₃ ⁻ + OH ⁺	495.87	428.26	437.76	436.93	443.21	465.54	67.61	58.11	58.94	52.66	30.33
(NH ₂)SiH ₃ → SiH ₃ ⁺ + NH ₂ ⁺	583.63	550.25	514.23	533.42	544.10	532.14	33.38	69.4	50.21	39.53	51.49
(NH ₂)SiH ₃ → SiH ₃ ⁺ + NH ₂ ⁻	85.09	94.72	85.78	78.95	98.78	105.50	-9.63	-0.69	6.14	-13.69	-20.41
SiH ₃ F → F ⁺ + SiH ₃ ⁺	256.58	312.15	269.47	248.35	297.99	307.91	-55.57	-12.89	8.23	-41.41	-51.33
SiH ₃ F → F ⁺ + SiH ₃ ⁻	557.87	467.71	516.43	539.30	513.65	492.36	90.16	41.44	18.57	44.23	65.51
(F ₃ Si)SiH ₃ → SiH ₃ ⁺ + SiF ₃ ⁻	208.11	190.21	181.61	165.73	176.39	185.11	17.90	26.51	42.38	31.73	23.00
(F ₃ Si)SiH ₃ → SiH ₃ ⁺ + SiF ₃ ⁺	290.91	205.40	218.69	245.28	270.83	280.35	85.51	72.22	45.63	20.08	10.56
SiH ₃ Cl → SiH ₃ ⁺ + Cl ⁻	208.62	222.92	199.69	188.15	201.40	232.34	-14.30	8.93	20.47	7.22	-23.72
SiH ₃ Cl → SiH ₃ + Cl ⁺	406.93	372.38	351.79	358.72	358.81	346.81	34.55	55.14	48.21	48.12	60.12
(HS)SiH ₃ → SiH ₃ ⁺ + HS ⁻	218.94	209.24	204.79	181.90	230.11	193.48	9.70	14.15	37.04	-11.17	25.46
(HS)SiH ₃ → SiH ₃ ⁻ + HS ⁺	325.69	265.36	288.44	299.28	293.41	299.88	60.33	37.25	26.41	32.28	25.81
P(SiH ₃)H ₂ → SiH ₃ ⁺ + PH ₂ ⁻	228.09	198.32	202.21	199.44	232.41	228.18	29.77	25.88	28.65	-4.32	-0.09
P(SiH ₃)H ₂ → SiH ₃ ⁻ + PH ₂ ⁺	297.11	264.26	253.12	286.77	275.93	286.70	32.85	44.00	10.34	21.18	10.41
(AlH ₂)SiH ₃ → SiH ₃ ⁻ + AlH ₂ ⁺	200.95	187.03	174.07	203.64	215.24	182.03	13.92	26.88	-2.69	-14.29	18.92
(AlH ₂)SiH ₃ → SiH ₃ ⁺ + AlH ₂ ⁻	231.09	219.18	62.90	238.89	249.86	228.23	11.91	168.19	-7.80	-18.77	2.86
H ₃ TiSiH ₃ → SiH ₃ ⁺ + TiH ₃ ⁺	415.42	315.26	418.17	312.10		315.12	100.16	-2.75	103.32		100.30
(ZrH ₃)SiH ₃ → SiH ₃ ⁺ + ZrH ₃ ⁺	421.3	650.66	688.37	565.76		336.26	-229.36	-267.07	-144.46		85.04
(ZrH ₃)SiH ₃ → SiH ₃ ⁻ + ZrH ₃ ⁻	23.08	72.56	86.28	27.34		-0.07	-49.48	-63.2	-4.26		23.15
Electron affinity Si	-7.85	-13.14	1.97	-12.32	16.32	-27.25	5.29	-9.82	4.47	-24.17	19.40
Adiabatic electron affinity SiH	-9.78	-4.87	-6.85	1.54	13.33	-38.24	-4.91	-2.93	-11.32	-23.11	28.46
Adiabatic electron affinity SiH ₂	-46.81	-10.23	-50.77	-35.48	-26.93	-35.87	-36.58	3.96	-11.33	-19.88	-10.94
Adiabatic electron affinity SiH ₃	-31.44	-26.30	-44.91	-27.42	-17.52	-24.85	-5.14	13.47	-4.02	-13.92	-6.60
SiH ₄ → H + SiH ₃	95.12	72.46	81.74	82.81	86.49	92.64	22.66	13.38	12.31	8.63	2.48
H ₃ SiSiH ₃ → SiH ₃ + SiH ₃	73.41	32.82	66.37	70.78	65.17	62.76	40.59	7.04	2.63	8.24	10.65
(CH ₃)SiH ₃ → CH ₃ + SiH ₃	86.99	65.57	74.28	74.58	77.72	82.83	21.42	12.71	12.41	9.27	4.16
(CH ₃)SiH ₃ → H + (CH ₃)SiH ₂	95.59	70.35	78.62	80.54	84.79	95.26	25.24	16.97	15.05	10.80	0.33
(CH ₃) ₂ SiH ₂ → CH ₃ + (CH ₃)SiH ₂	87.51	62.73	71.05	71.97	75.47	84.57	24.78	16.46	15.54	12.04	2.94
(SiH ₃)SiH ₂ CH ₃ → SiH ₃ + (CH ₃)SiH ₂	73.17	30.33	63.64	67.92	65.65	70.61	42.84	9.53	5.25	7.52	2.56
(HO)SiH ₃ → SiH ₃ + OH	120.69	89.28	107.80	104.91	111.23	126.56	31.41	12.89	15.78	9.46	-5.87
SiH ₃ OCH ₃ → SiH ₃ + CH ₃ O	105.85	76.33	94.24	92.30	101.40	119.71	29.52	11.61	13.55	4.45	-13.86
(CH ₃)Si(OH)H ₂ → (CH ₃)SiH ₂ + OH	122.91	88.40	105.92	105.47	108.98	128.36	34.52	16.99	17.44	13.93	-5.45
(CH ₃)SiH ₂ OCH ₃ → (CH ₃)SiH ₂ + CH ₃ O	108.43	74.77	91.07	91.49	98.90	121.06	33.66	17.36	16.94	9.53	-12.63
(NH ₂)SiH ₃ → SiH ₃ + NH ₂	100.81	79.99	82.70	87.15	87.89	90.76	20.83	18.12	13.66	12.92	10.05
(CH ₃)SiH ₂ (NH ₂) → (CH ₃)SiH ₂ + NH ₂	102.27	79.05	81.13	86.73	85.09	93.21	23.22	21.14	15.54	17.18	9.06
SiH ₃ F → SiH ₃ + F	148.23	129.18	138.41	138.82	154.54	153.84	19.05	9.82	9.41	-6.31	-5.61
(F ₃ Si)SiH ₃ → SiH ₃ + SiF ₃	77.3	14.65	53.23	58.17	50.62	65.06	62.65	24.07	19.13	26.68	12.24
(CH ₃)SiH ₂ F → (CH ₃)SiH ₂ + F	150.94	127.94	136.79	138.50	151.76	155.29	23.00	14.15	12.44	-0.82	-4.35
(CF ₃)SiH ₃ → CF ₃ + SiH ₃	81.08	35.10	58.53	60.47	57.10	91.00	45.98	22.55	20.61	23.98	-9.92
(CH ₃)SiH ₂ (CF ₃) → CF ₃ + (CH ₃)SiH ₂	83.32	33.54	56.28	59.58	55.29	92.74	49.78	27.04	23.74	28.02	-9.42
(CH ₃)SiH ₂ (SiF ₃) → (CH ₃)SiH ₂ + SiF ₃	79.73	11.32	50.41	55.81	50.86	61.67	68.41	29.32	23.92	28.86	18.06
SiH ₃ Cl → SiH ₃ + Cl	105.49	91.15	98.73	101.28	104.30	105.31	14.34	6.76	4.21	1.19	0.18
(CH ₃)SiH ₂ Cl → (CH ₃)SiH ₂ + Cl	108.21	90.33	97.04	100.47	103.05	109.81	17.88	11.17	7.74	5.16	-1.60
SiH ₃ ⁻ → SiH ₃ + HS	84.31	62.13	77.03	80.61	91.15	94.68	22.18	7.28	3.70	-6.84	-10.37
(CH ₃)SiH ₂ (SH) → (CH ₃)SiH ₂ + HS	86.07	60.98	75.25	79.69	89.17	96.87	25.09	10.82	6.38	-3.10	-10.80
(CH ₃ S)SiH ₃ → SiH ₃ + CH ₃ S	79.51	53.86	71.58	73.12	88.20	90.76	25.65	7.93	6.39	-8.69	-11.25
(CH ₃)SiH ₂ (SCH ₃) → (CH ₃)SiH ₂ + CH ₃ S	80.92	52.25	68.69	71.16	86.69	93.04	28.67	12.23	9.77	-5.77	-12.12

energies where, errors of 2.6, 10.7, 12.2 and 18.0 kcal mol $^{-1}$ contribute to the errors in the heats of formation of the di-silanes and trisilanes. Oxygen–silicon bonds are predicted well with errors of 5 kcal mol $^{-1}$ when the for

Si–OH bonds, and 13 kcal mol $^{-1}$ for Si–OCH₃. The errors in sulfur–silicon bond energies do not show this dependence on the leaving group. Bond-heterolysis errors are again dominated by the errors in the ionization

Table 5 (Contd.)

$\text{SiH}_3(\text{PH}_2) \rightarrow \text{SiH}_3 + \text{PH}_2$	68.33	43.48	64.61	72.12	67.95	75.11	24.85	3.72	-3.79	0.38	-6.78
$(\text{CH}_3)\text{SiH}_2(\text{PH}_2) \rightarrow (\text{CH}_3)\text{SiH}_2 + \text{PH}_2$	69.05	42.74	61.13	70.53	66.86	73.59	26.31	7.92	-1.48	2.19	-4.54
$(\text{AlH}_2)\text{SiH}_3 \rightarrow \text{AlH}_2 + \text{SiH}_3$	66.89	48.92	-42.28	76.94	67.04	72.24	17.97	109.17	-10.05	-0.15	-5.35
$(\text{AlH}_2)\text{SiF}_3 \rightarrow \text{AlH}_2 + \text{SiF}_3$	72.64	31.98	-75.23	62.10	60.06	48.63	40.66	147.87	10.54	12.58	24.01
$\text{H}_3\text{TiSiH}_3 \rightarrow \text{SiH}_3 + \text{TiH}_3$	40.35	-123.09	-9.23	-109.64		44.98	163.44	49.58	149.99		-4.63
$(\text{TiH}_3)\text{SiF}_3 \rightarrow \text{SiF}_3 + \text{TiH}_3$	45.49	-219.48	-32.33	-107.86		29.80	264.97	77.82	153.35		15.69
$(\text{ZrH}_3)\text{SiH}_3 \rightarrow \text{SiH}_3 + \text{ZrH}_3$	52.32	178.26	213.76	127.74		62.80	-125.94	-161.44	-75.42		-10.48
Ionization potential Si	187.11	154.30	172.33	164.03	165.14	216.78	32.82	14.78	23.08	21.97	-29.67
Adiabatic IP $\text{SiH}_2 (^1\text{A}_1)$	208.34	173.69	178.96	176.34	188.02	208.68	34.65	29.38	32.00	20.32	-0.34
Adiabatic IP SiH_3	188.05	198.41	181.18	171.18	179.47	169.52	-10.36	6.87	16.87	8.58	18.53
Adiabatic IP SiH_4	263.39	227.81	207.82	220.94	271.32	245.08	35.58	55.57	42.45	-7.93	18.31
Adiabatic IP Si_2H_2	205.7	198.29	204.25	179.76	174.07	193.00	7.41	1.45	25.94	31.63	12.70
Adiabatic IP Si_2H_4	181.84	193.20	185.76	202.94	182.40	175.46	-11.36	-3.92	-21.10	-0.56	6.38
Adiabatic IP Si_2H_5	176.61	198.27	162.32	158.69	183.86	156.95	-21.66	14.29	17.92	-7.24	19.66
Adiabatic IP Si_2H_6	220.8	224.78	208.56	203.36	232.68	176.86	-3.98	12.24	17.44	-11.88	43.94
Statistics, Heats of Reaction (N=68, N=61 for MNDO/d)											
Mean Signed error							23.10	16.68	18.39	5.83	6.88
Mean Unsigned Error							42.76	32.99	28.36	16.64	18.74

potentials of monoatomic groups. Once again, MNDO/d gives results comparable to those obtained with AM1*.

Tables S1 and S2 of the supplementary material also show geometrical details for the silicon compounds. The errors in the AM1* bond lengths for silicon-containing compounds are smaller than those for aluminum, partly reflecting their increased weight in the error function because of their number. Silicon–nitrogen bonds are too long by about 0.22 Å, and Si–Si bonds are typically too short by 0.28 Å. The H–Si bonds have an MUE of 0.12 and the C–Si bonds a MUE of 0.04 Å, and, contrary to the aluminum case, F–Si bonds are only in error by 0.11 Å, and Si–Cl bond lengths are extremely well predicted with an MUE of 0.02 Å.

Titanium

The results for the experimental parameterization dataset for titanium are shown in Table 6.

The overall error in the heats of formation for titanium compounds is dominated by three compounds, TiH_4 (115.3), $\text{Ti}(\text{Cp})_2(\text{O}(\text{CO})\text{CCl}_3)_2$ (156.9) and $(\text{Me}_3\text{Si})_4\text{Ti}$ (174.4), which are all predicted to be significantly more stable than the experimental data indicates. TiH_4 is a particularly challenging task, and despite introduction of a distance-dependent core–core term (see above) remains significantly in error. While this term was unable to limit the error in this compound, it was able to increase the accuracy of reactions involving the breaking of other H–Ti bonds. The error in $(\text{Me}_3\text{Si})_4\text{Ti}$ reflects an overall trend in underestimating the steric repulsion of large substituent groups, with tetrakis(neopentyl)titanium having an error of 61.8 and tetrabenzyl titanium also to stable by 63.1 kcal mol⁻¹. To a lesser degree, this underestimation of steric repulsion is reflected in the series of tetra-*n*-alkoxy compounds, where the entire series is in error by about 28 kcal mol⁻¹, $\text{Ti}(\text{O-Et})_4$

(25.6), $\text{Ti}(\text{O-}n\text{-Pr})_4$ (28.3), $\text{Ti}(\text{O-}n\text{-Bu})_4$ (27.8), and $\text{Ti}(\text{O-}n\text{-Pe})_4$ (33.7). While the errors in these compounds are somewhat larger than desired, their systematic nature allows the model to be used for chemical reactions. Another error to note is that of titanocene where the error is –66.5 kcal mol⁻¹, however the DFT calculations also give a similar error.

The results for the heats of reaction for titanium compounds are shown in Table 7.

The adiabatic ionization potentials for titanium compounds are significantly underestimated with a MUE of 81.8 kcal mol⁻¹ (approximately 3.5 eV), much higher than desired. The atomic ionization potential is only 1.5 eV in error, which is comparable to the other elements. The MUE in bond-homolysis energies, 17.8 kcal mol⁻¹, is higher than for Al and Si. The largest error is for the breaking of the Cp–Ti bond (37.9 kcal mol⁻¹), about five times the C–Ti bond homolysis error of 8 kcal mol⁻¹. In contrast to titanium hydride, the H–Ti bond-homolysis energies are only in error by 15 kcal mol⁻¹. The bond-heterolysis energies have an MUE of 62.0 kcal mol⁻¹. When the positive charge resides on the Ti fragment, the energy is underestimated by 90 kcal mol⁻¹, which is directly comparable to the error to the ionization potential.

In contrast to previous semiempirical parameterizations, the geometrical data for titanium is depends largely on calculated data.

Tables S1 and S2 show geometrical parameters for the titanium compounds. The overall MUE in bond-lengths for AM1* is 0.12 Å, and bond angles, 11.4°. The errors in bond lengths compare favorably with those for Al and Si but those for bond angles are twice as large. However, they are dominated by errors in H–Ti–H and Ti–O–Ti angles. The bond length for titanium hydride is significantly in error (0.37 Å) and skews the error for H–Ti bonds. Without this compound, the error is generally 0.2 Å, more in line with the other elements. Carbon–titanium bonds comprise a

Table 6 Experimental and calculated heats of Formation, dipole moments and vertical ionization potentials for the titanium training set. Calculated ionization potentials are those given by Koopmans' theorem. The errors are color coded as for Table 2

Compound	Heat of Formation (kcal mol ⁻¹)					Error (kcal mol ⁻¹)			
	Exper.	AMI	PM3	PM5	AMI*	AMI	PM3	PM5	AMI*
TiH	116.40	37.35	38.02	28.47	1.10	79.05	78.38	87.93	115.30
Ti(C ₂)	174.50	177.30	175.63	162.69	169.92	-2.80	-1.13	11.81	4.58
Ti(Cp) ₂	-2.70	59.52	78.83	79.37	64.14	-62.22	-81.53	-82.07	-66.84
Ti(Cp) ₂ (CH ₃) ₂	12.60	12.18	15.23	6.63	33.04	0.42	-2.63	5.97	-20.44
(<i>neo</i> -C ₅ H ₁₁) ₄ Ti	-45.50	-120.81	-129.74	-153.37	-106.86	75.31	84.24	107.87	61.36
Ti(Cp) ₂ (C ₆ H ₅) ₂	83.70	71.64	94.05	80.83	84.86	12.06	-10.35	2.87	-1.16
Ti(Cp) ₂ (<i>m</i> -Tol) ₂	62.70	57.40	76.25	65.33	69.77	5.30	-13.55	-2.63	-7.07
Ti(Cp) ₂ (<i>p</i> -Tol) ₂	63.30	56.59	75.44	64.96	69.92	6.71	-12.14	-1.66	-6.62
Ti(Cp) ₂ (CH ₂ C ₆ H ₅) ₂	66.70	61.32	82.51	60.45	70.74	5.38	-15.81	6.25	-4.04
Ti(CH ₂ C ₆ H ₅) ₄	111.70	31.85	34.21	15.37	49.07	79.85	77.49	96.33	62.63
TiO	13.70	-7.93	0.62	-28.95	68.07	21.63	13.08	42.65	-54.37
TiO ₂	-71.00	-46.69	-42.11	-74.19	-15.05	-24.31	-28.89	3.19	-55.95
Ti ₂ O ₃	-136.00	-175.16	-218.89	-225.59	-107.75	39.16	82.89	89.59	-28.25
Ti ₂ O ₄	-242.00	-264.39	-321.91	-295.76	-200.39	22.39	79.91	53.76	-41.61
Ti(Cp) ₂ (OC ₆ H ₅) ₂	-71.10	-50.53	-41.02	-49.31	-57.89	-20.57	-30.08	-21.79	-13.21
Ti(Cp) ₂ (2-MeC ₆ H ₄ O) ₂	-82.50	-62.47	-53.74	-64.17	-70.88	-20.03	-28.76	-18.33	-11.62
Ti(Cp) ₂ (3-MeC ₆ H ₄ O) ₂	-72.80	-65.64	-59.47	-65.20	-72.78	-7.16	-13.33	-7.60	-0.02
Ti(Cp) ₂ (4-MeC ₆ H ₄ O) ₂	-82.40	-65.65	-59.58	-65.10	-72.75	-16.75	-22.82	-17.30	-9.65
Ti(Cp) ₂ (4-MeOC ₆ H ₄) ₂	2.90	-4.72	17.38	6.54	9.10	7.62	-14.48	-3.64	-6.20
Ti(OC ₂ H ₅) ₄	-325.20	-340.28	-337.45	-326.78	-349.16	15.08	12.25	1.58	23.96
Ti(O- <i>i</i> -C ₃ H ₇) ₄	-360.40	-358.01	-355.80	-358.07	-369.65	-2.39	-4.60	-2.33	9.25
Ti(O- <i>n</i> -C ₃ H ₇) ₄	-355.70	-363.86	-360.48	-345.50	-382.41	8.16	4.78	-10.20	26.71
Ti(O- <i>i</i> -C ₄ H ₉) ₄	-381.50	-382.17	-372.27	-384.19	-393.12	0.67	-9.23	2.69	11.62
Ti(O- <i>n</i> -C ₄ H ₉) ₄	-377.60	-387.48	-376.78	-366.85	-403.84	9.88	-0.82	-10.75	26.24
Ti(O- <i>s</i> -C ₄ H ₉) ₄	-382.50	384.40	-375.10	-381.00	-393.49	1.90	-7.40	-1.50	10.99
Ti(O- <i>t</i> -C ₄ H ₉) ₄	-395.70	-365.21	-375.80	-348.70	-380.81	-30.49	-19.90	-47.00	-14.89
Ti(O- <i>n</i> -C ₅ H ₁₁) ₄	-397.30	-412.93	-390.76	-395.39	-429.35	15.63	-6.54	-1.91	32.05
Ti(O- <i>neo</i> -C ₅ H ₁₁) ₄	-436.00	-395.22	-385.54	-403.61	-406.04	-40.78	-50.46	-32.39	-29.96
Ti(Cp) ₂ (O(CO)C ₆ H ₅) ₂	-162.20	-153.59	-159.38	-151.26	-155.89	-8.61	-2.82	-10.94	-6.31
TiN	112.10	110.47	118.78	123.29	124.94	1.63	-6.68	-11.19	-12.84
Ti(Cp) ₂ (NC ₈ H ₆) ₂	69.20	143.17	133.11	119.50	140.75	-73.97	-63.91	-50.30	-71.55
((C ₂ H ₅) ₂ N) ₄ Ti	-50.20	-54.92	-60.84	-48.17	-82.52	4.72	10.64	-2.03	32.32
((CH ₃) ₂ N) ₄ Ti	-96.40	-93.17	-91.13	-94.05	-126.34	-3.23	-5.27	-2.35	29.94
Ti(Cp) ₂ (N ₃) ₂	120.90	134.98	144.42	148.22	130.25	-14.08	-23.52	-27.32	-9.35
TiF	-4.00	-34.24	-6.56	-63.85	-11.12	30.24	2.56	59.85	7.12
TiF ₂	-164.50	-166.47	-146.90	-165.33	-127.91	1.97	-17.60	0.83	-36.59
TiF ₃ [•]	-284.10	-283.02	-266.16	-269.01	-265.61	-1.08	-17.94	-15.09	-18.49
TiF ₄	-370.80	-388.93	-380.62	-371.08	-413.88	18.13	9.82	0.28	43.08
TiF ₄ [•]	-426.30	-399.83	-402.96	-415.71	-356.55	-26.47	-23.34	-10.59	-69.75
TiF ₅ ⁻	-515.00	-505.22	-516.77	-511.93	-502.18	-9.78	1.77	-3.07	-12.82
Ti(Cp) ₂ (4-CF ₃ C ₆ H ₄) ₂	-246.90	-242.05	-223.43	-247.12	-231.02	-4.85	-23.47	0.22	-15.88
TiOF	-103.50	-111.02	-77.74	-125.52	-75.26	7.52	-25.76	-22.02	-28.24
TiOF ₂	-221.10	-221.16	-217.50	-221.12	-229.64	0.06	-3.60	0.02	8.54
Ti(Cp) ₂ (O(CO)CF ₃) ₂	-512.60	-509.15	-515.54	-506.48	-516.76	-3.45	2.94	-6.12	4.16
TiCl	24.20	10.96	21.76	-12.98	9.53	13.24	2.44	37.18	14.67
TiCl ₂	-57.00	-78.00	-77.34	-70.66	-44.24	21.00	20.34	13.66	-12.76
TiCl ₃	-128.90	-135.70	-136.62	-132.33	-103.00	6.80	7.72	3.43	-25.90
TiCl ₄	-182.40	-182.23	-180.69	-177.37	-176.76	-0.17	-1.71	-5.03	-5.64
Ti(Cp) ₂ (Cl)(Me)	-29.90	-24.15	-12.68	-20.84	-21.15	-5.75	-17.22	-9.06	-8.75
Ti(Cp) ₂ (Cl)(C ₆ H ₅)	9.70	4.31	25.32	16.71	2.32	5.39	-15.62	-7.01	7.38
Ti(Cp) ₂ Cl ₂	-63.20	-59.37	38.58	-45.04	-71.61	-3.83	-24.62	-18.16	8.41
Ti(Cp)Cl ₃	-124.50	-125.24	-115.37	-115.86	-133.75	0.74	-9.13	-8.64	9.25
TiOCl	-58.40	-69.51	-70.59	-82.01	-35.31	11.11	12.19	23.61	-23.09
TiOCl ₂	-130.40	-132.80	-138.28	-137.88	-123.68	2.40	7.88	7.48	-6.72
Ti(Cp) ₂ (2-ClC ₆ H ₄ O) ₂	-83.70	-61.90	-50.83	-68.34	-123.53	-21.80	-32.87	-15.36	39.83

large portion of the data and are well predicted, although there is a difference in the MUEs of π and σ bonds, with 0.06 and 0.15 Å, respectively. The results of the parameterization for the experimental heats of formation and DFT heats of reaction are shown in Tables 8 and 9, respectively.

Zirconium

As for titanium, the errors in the heats of formation for zirconium compounds are dominated by ZrH₄ (95.3 kcal mol⁻¹) and (Me₃Si)₄Zr (146.9 kcal mol⁻¹). The systematic underestimation of steric repulsion in

Table 6 (Contd.)

Ti(Cp) ₂ (O(CO)CCl ₃) ₂	-230.70	-227.56	-232.93	-233.39	-377.11	-3.14	2.23	2.69	146.41
TiS	76.20	23.24	30.79	-23.96	49.67	52.96	45.41	100.16	26.53
Ti(Cp) ₂ (SC ₂ H ₅) ₂	-25.30	-27.49	-19.01	-35.47	-13.74	2.19	-6.29	10.17	-11.56
Ti(Cp) ₂ (S- <i>n</i> -C ₃ H ₇) ₂	-38.20	-37.77	-27.81	-41.78	-25.37	-0.43	-10.39	3.58	-12.83
Ti(Cp) ₂ (S ₂ C ₆ H ₃ Me)	19.00	25.78	25.83	25.49	42.37	-6.78	-6.83	-6.49	-23.37
Ti(Cp) ₂ (SC ₆ H ₅) ₂	35.10	43.91	54.60	37.04	70.13	-8.81	-19.50	-1.94	-35.03
((CH ₃) ₃ SiCH ₂) ₄ Ti	-163.60	348.19	-115.32	331.07	-337.57	-511.79	-48.28	-494.67	173.97
Statistics, Heats of Formation (N=62)									
Mean Signed Error						-5.63	-3.58	-3.43	1.89
Mean Unsigned Error						24.55	21.61	28.45	28.32
DIPOLE MOMENT (Debye)									
TiO	2.96	3.96	4.36	4.57	7.34	-1.00	-1.40	-1.61	-4.38
IONIZATION POTENTIALS (eV)									
H ₃ TiCH ₃	11.67	11.35	11.96	11.29	7.76	0.32	-0.29	0.38	3.91
H ₃ TiOH	12.00	13.15	13.33	12.81	7.83	-1.15	-1.33	-0.81	4.17
Statistics, ionisation potential (N=2)									
Mean Signed Error						-0.42	-0.81	-0.22	4.04
Mean Unsigned Error						0.74	0.81	0.60	4.04

AM1 is reflected in the error for tetrakis(2,2-dimethylpropyl)zirconium (44.6 kcal mol⁻¹) and tetrabenzyl zirconium (20.7 kcal mol⁻¹). The results for ZrH are also analogous to the titanium situation where the error in this one compound is large while the results for the series of hydrogen–zirconium reactions are predicted with useful accuracy.

The error in the ionization potentials is lower for zirconium than for titanium, 36 kcal mol⁻¹. The atomic ionization potential is overestimated by 10 kcal mol⁻¹, increasing by 20 kcal mol⁻¹ with each additional hydrogen substitution. The bond-homolysis energies have an MUE of 13.7 kcal mol⁻¹. When examining ligand-exchange reactions, the MUE is 12.5 kcal mol⁻¹, approximately equal to the error in the homolysis energy. The bond heterolysis MUE is 75.5 kcal mol⁻¹, comparable to the titanium results. This error can also be traced to that in the ionization potential of ZrH₃.

Tables S1 and S2 show that the errors in geometrical parameters for zirconium are slightly larger than for titanium, but are still reasonable with a MUEs of 0.15 Å, and 6.7°. The largest errors in bond lengths again come from H–Zr bonds, where the MUE is 0.36 Å. There is again a difference in the MUEs of π and σ carbon–zirconium bonds, although they are both within a reasonable range. Most of the second-row bonds are consistently too long, and S–Zr and Al–Zr bonds and Si–Zr bonds being overestimated by 0.05, 0.18 and 0.15 Å. The exceptions to this are Zr–Cl, which has an MSE of 0.34 Å and Zr–P with is too short by nearly 0.5 Å.

Discussion

A complete summary of the errors in calculated energies obtained with AM1, PM3, PM5, MNDO/d and AM1* is given in Table 10.

AM1* gives mean unsigned errors for the entire dataset and for most elements 30–40% larger than those

obtained with the other parameterizations, of which PM5 is slightly better than AM1 or PM3 for this dataset. As found for P, S and Cl [1], the MNDO/d parameterization is particularly reliable, both for heats of formation and heats of reaction. However, AM1* results for heats of reaction are typically 50–100% better than for the other methods, of which AM1 generally performs best. The exception is MNDO/d. This situation is partly the result of the fact that the heats of formation are weighted less heavily in the AM1* parameterization because of the additional heats of reaction. However, we believe that the reason for this behavior also lies in the nature of the parameterization process and the data used to parameterize.

Consider the dimerization energy of AlF₃. The calculated heats of formation for the monomer all show moderate errors (–3.2, 2.5, –8.6 and 6.7 kcal mol⁻¹ for AM1, PM3, PM5 and AM1*, respectively). The errors for the dimer are generally larger (16.5, 1.9, 19.4 and 7.3) but significantly AM1*, which gives the second largest error for the monomer and the third largest for the dimer, gives the best result (error=0.8 kcal mol⁻¹) for the dimerization energy. If the experimental heats of formation were used to determine the dimerization energy, the value obtained (–51.5 kcal mol⁻¹) would be “in error” by 5.3 kcal mol⁻¹. PM3 gives a very good dimerization energy (error=2.2 kcal mol⁻¹) because it is very accurate for both monomer and dimer, whereas AM1 and PM5 give errors in reverse directions for monomer and dimer, resulting in a very large error for the dimerization energy. This is only one of many examples to be found in the tables, but illustrates the fundamental difficulty of using only heats of formation to parameterize. Rogue data [36, 37], which certainly is present in the parameterization dataset, can cause different systematic deviations according to the circumstances and the nature of the systems. The three Ti(Cp)₂(MeC₆H₄O)₂ isomers, for instance, show an inconsistency for the 3-isomer that has little effect on the parameterization. All four methods give an error about

Table 7 DFT and semiempirical calculated energies for the reactions used in the titanium training set. The errors are color coded as for Table 2

Reaction	ΔE_R (kcal mol ⁻¹)					Error (kcal mol ⁻¹)			
	DFT	AMI	PM3	PM5	AMI*	AMI	PM3	PM5	AMI*
H ₃ TiSiH ₃ → SiH ₃ ⁻ + TiH ₃ ⁻	-12.95	-159.98	-68.36	-171.06	36.84	147.03	55.41	158.11	-49.78
TiH ₄ → H ⁻ + TiH ₃ ⁺	277.64	347.72	358.08	364.43	178.10	-70.08	-80.44	-86.79	99.54
TiH ₄ → H ⁺ + TiH ₃ ⁻	340.87	326.53	359.43	304.74	323.52	14.34	-18.56	36.13	17.35
CH ₃ TiH ₃ → CH ₃ ⁻ + TiH ₃ ⁺	262.25	317.69	318.24	342.11	166.21	-55.44	-55.99	-79.86	96.04
CH ₃ TiH ₃ → CH ₃ ⁺ + TiH ₃ ⁻	256.05	261.80	262.84	255.13	276.92	-5.75	-6.79	0.92	-20.87
Ti(Cp) ₂ H ₂ → Cp ⁻ + Ti(Cp)H ₂ ⁺	217.31	217.59	194.35	219.90	132.77	-0.28	22.97	-2.59	84.55
Ti(OH)H ₃ → OH ⁻ + TiH ₃ ⁺	292.51	302.30	308.91	302.67	173.57	-9.79	-16.39	-10.16	118.94
Ti(OH)H ₃ → OH ⁺ + TiH ₃ ⁻	457.38	405.51	398.77	396.87	443.39	51.87	58.61	60.51	13.99
(NH ₂)TiH ₃ → NH ₂ ⁻ + TiH ₃ ⁺	288.65	314.75	305.70	320.40	170.83	-26.10	-17.05	-31.75	117.82
(NH ₂)TiH ₃ → NH ₂ ⁺ + TiH ₃ ⁻	352.17	321.34	292.53	319.14	344.03	30.83	59.64	33.03	8.14
TiH ₃ F → F ⁻ + TiH ₃ ⁺	276.98	358.86	315.95	324.44	214.90	-81.88	-38.97	-47.46	62.08
TiH ₃ F → F ⁺ + TiH ₃ ⁻	516.09	462.30	483.65	502.02	484.96	53.79	32.44	14.07	31.14
TiH ₃ Cl → Cl ⁻ + TiH ₃ ⁺	221.21	246.91	235.79	250.72	136.17	-25.70	-14.58	-29.51	85.05
TiH ₃ Cl → Cl ⁺ + TiH ₃ ⁻	373.17	344.25	308.63	307.93	336.24	28.92	64.55	65.24	36.93
(HS)TiH ₃ → TiH ₃ ⁺ + HS ⁻	219.75	253.58	259.34	277.29	105.12	-33.83	-39.59	-57.54	114.63
(HS)TiH ₃ → TiH ₃ ⁻ + HS ⁺	280.43	257.59	263.72	281.30	297.13	22.84	16.71	-0.87	-16.70
(PH ₂)TiH ₃ → PH ₂ ⁻ + TiH ₃ ⁺	218.83	207.98	243.67	286.62	180.50	10.85	-24.84	-67.79	38.33
(PH ₂)TiH ₃ → PH ₂ ⁺ + TiH ₃ ⁻	241.46	221.80	215.31	260.58	324.62	19.66	26.15	-19.12	-83.16
H ₃ TiSiH ₃ → SiH ₃ ⁻ + TiH ₃ ⁺	415.42	315.26	418.17	312.10	315.12	100.16	-2.75	103.32	100.30
(AlH ₂)TiH ₃ → AlH ₂ ⁻ + TiH ₃ ⁺	194.78	450.61	236.73	573.04	149.93	-255.83	-41.95	-378.26	44.85
(AlH ₂)TiH ₃ → AlH ₂ ⁺ + TiH ₃ ⁻	161.25	392.64	313.55	451.84	214.18	-231.39	-152.30	-290.59	-52.93
CH ₄ + CH ₃ TiH ₃ → CH ₄ + TiH ₄	0.17	-5.77	0.81	-11.33	12.37	5.94	-0.64	11.50	-12.20
CH ₄ + CH ₃ TiH ₃ → C ₂ H ₆ + TiH ₄	21.20	-10.81	-4.69	2.15	7.32	32.01	25.89	19.05	13.88
H ₂ + Ti(Cp) ₂ → Ti(Cp) ₂ H	-16.58	-62.95	-64.85	-101.19	-2.11	46.37	48.27	84.61	-14.47
CH ₄ + Ti(Cp) ₂ → Ti(Cp) ₂ H(CH ₃)	0.45	-49.70	-58.41	-74.24	-11.06	50.15	58.86	74.69	11.51
CH ₄ + Ti(Cp) ₂ H ₂ → H ₂ + Ti(Cp) ₂ H(CH ₃)	17.03	13.25	6.43	26.95	-8.95	3.78	10.60	-9.92	25.98
C ₂ H ₆ + Ti(Cp) ₂ → Ti(Cp) ₂ (CH ₃) ₂	-3.00	-29.89	-45.44	-57.52	-13.73	26.89	42.44	54.52	10.73
C ₂ H ₆ + Ti(Cp) ₂ H ₂ → H ₂ + Ti(Cp) ₂ (CH ₃) ₂	13.58	33.06	19.41	43.67	-11.62	-19.48	-5.83	-30.09	25.20
H ₂ + Ti(OH)H ₃ → H ₂ O + TiH ₄	52.09	0.21	20.08	-0.71	41.10	51.88	32.01	52.80	10.99
CH ₄ + Ti(OH)H ₃ → CH ₃ OH + TiH ₄	77.39	6.01	21.25	24.15	46.91	71.38	56.14	53.25	30.48
H ₂ O + Ti(Cp) ₂ → Ti(Cp) ₂ (OH)H	-44.94	-63.84	-86.48	-90.86	-40.18	18.90	41.54	45.92	-4.76
H ₂ O + Ti(Cp) ₂ H ₂ → H ₂ + Ti(Cp) ₂ (OH)H	-28.36	-0.89	-21.63	10.33	-38.07	-27.47	-6.73	-38.69	9.71
CH ₃ OH + Ti(Cp) ₂ → Ti(Cp) ₂ (OH)H	-49.34	-53.23	-77.84	-85.28	-53.08	3.89	28.50	35.94	3.74
HOOH + Ti(Cp) ₂ → Ti(Cp) ₂ (OH) ₂	132.13	-132.86	-150.88	-144.70	-153.45	0.73	18.75	12.57	21.31
HOOH + Ti(Cp) ₂ H ₂ → H ₂ + Ti(Cp)(OH) ₂	115.55	-69.91	-86.03	-43.51	-151.33	-45.64	-29.52	-72.04	35.78
HOOH + Ti(Cp) ₂ H ₂ → H ₂ O + Ti(Cp) ₂ (OH)H	101.75	-78.85	-74.31	-64.23	-116.06	-22.90	-27.44	-37.52	14.31
H ₂ + (NH ₂)TiH ₃ → NH ₃ + TiH ₄	35.33	-1.97	11.45	-9.41	23.73	37.30	23.88	44.74	11.60
CH ₄ + (NH ₂)TiH ₃ → CH ₃ (NH ₂) + TiH ₄	59.33	1.53	8.95	13.56	27.22	57.80	50.38	45.77	32.11
H ₂ + TiH ₃ F → HF + TiH ₄	62.34	24.17	31.53	8.71	49.84	38.17	30.81	53.63	12.51
CH ₄ + TiH ₃ F → CH ₃ F + TiH ₄	83.69	41.02	40.10	38.08	66.69	42.67	43.59	45.61	17.00
HF + Ti(Cp) ₂ → Ti(Cp) ₂ HF	-62.11	-84.06	-94.03	-102.05	-46.30	21.95	31.92	39.94	-15.81
HF + Ti(Cp) ₂ H ₂ → H ₂ + Ti(Cp) ₂ HF	-45.53	-21.10	-29.19	-0.86	-44.19	-24.43	-16.34	-44.67	-1.34
CH ₃ F + Ti(Cp) ₂ → Ti(Cp) ₂ H(CH ₃)	-63.2	-84.94	-94.29	-101.11	-69.95	21.74	31.09	37.91	6.75
F ₂ + Ti(Cp) ₂ → Ti(Cp) ₂ F ₂	210.33	-215.25	-207.62	-240.33	-208.15	4.91	-2.71	30.00	-2.18
F ₂ + Ti(Cp) ₂ H ₂ → H ₂ + Ti(Cp) ₂ F ₂	193.75	-152.29	-142.78	-139.14	-206.04	-41.46	-50.97	-54.61	12.29
F ₂ + Ti(Cp) ₂ H ₂ → HF + Ti(Cp) ₂ HF	159.95	-142.00	-119.59	-147.15	-165.10	-17.95	-40.36	-12.80	5.15
H ₂ + TiH ₃ Cl → HCl + TiH ₄	51.97	2.99	13.65	-15.71	50.20	48.98	38.32	67.68	1.77
CH ₄ + TiH ₃ Cl → CH ₃ Cl + TiH ₄	72.49	12.25	19.06	16.01	52.42	60.24	53.43	56.48	20.07
Ti(Cp) ₂ + HCl → Ti(Cp) ₂ HCl	-56.01	-69.00	-78.10	-80.19	-56.90	12.99	22.09	24.18	0.89
HCl + Ti(Cp) ₂ H ₂ → H ₂ + Ti(Cp) ₂ HCl	-39.43	-6.05	-13.25	21.00	-54.79	-33.38	-26.18	-60.43	15.36
Ti(Cp) ₂ + CH ₃ Cl → Ti(Cp) ₂ (CH ₃)Cl	-55.24	-64.71	-76.82	-82.79	-69.90	9.46	21.57	27.55	14.66

10 kcal mol⁻¹ larger for this compound than for the other isomers. More significant are errors in heats of formation that may skew the parameterization for a given type of bond can occur if only one member of a class of compounds is in error.

We have used DFT calculations extensively to check experimental data and to provide training data that would otherwise not be available. This procedure brings the danger that systematic errors in the DFT results will be introduced into the parameterization but we see little

Table 7 (Contd.)

$\text{Ti}(\text{Cp})_2 + \text{Cl}_2 \rightarrow \text{Ti}(\text{Cp})_2\text{Cl}_2$	126.90	-104.72	-105.83	-116.52	-155.61	-22.18	-21.07	-10.38	28.71
$\text{Ti}(\text{Cp})_2\text{H}_2 + \text{Cl}_2 \rightarrow \text{H}_2 + \text{Ti}(\text{Cp})_2\text{Cl}_2$	110.32	-41.77	-40.98	-15.33	-153.50	-68.55	-69.34	-94.99	43.18
$\text{Ti}(\text{Cp})_2\text{H}_2 + \text{CH}_3\text{Cl} \rightarrow \text{Ti}(\text{Cp})_2\text{HCl} + \text{HCl}$	-85.22	-35.92	-29.21	-40.68	-97.55	-49.30	-56.01	-44.54	12.33
$\text{H}_2 + (\text{HS})\text{TiH}_3 \rightarrow \text{H}_2\text{S} + \text{TiH}_4$	32.51	9.69	21.38	19.31	52.68	22.82	11.13	13.20	-20.16
$\text{CH}_4 + (\text{HS})\text{TiH}_3 \rightarrow \text{CH}_3\text{SH} + \text{TiH}_4$	52.60	7.74	16.39	36.74	45.84	44.86	36.21	15.86	6.76
$\text{Ti}(\text{Cp})_2 + \text{H}_2\text{S} \rightarrow \text{Ti}(\text{Cp})_2(\text{SH})\text{H}$	-42.09	-72.56	-85.95	-104.93	-40.39	30.47	43.86	62.84	-1.70
$\text{H}_2\text{S} + \text{Ti}(\text{Cp})_2\text{H}_2 \rightarrow \text{H}_2 + \text{Ti}(\text{Cp})_2(\text{SH})\text{H}$	-25.51	-9.61	-21.11	-3.74	-38.28	-15.90	-4.41	-21.77	12.77
$\text{Ti}(\text{Cp})_2 + \text{CH}_3\text{SH} \rightarrow \text{Ti}(\text{Cp})_2(\text{CH}_3)(\text{SH})$	-40.16	-55.40	-73.65	-90.14	-40.26	15.24	33.49	49.98	0.10
$\text{HSSH} + \text{Ti}(\text{Cp})_2 \rightarrow \text{Ti}(\text{Cp})_2(\text{SH})_2$	-72.19	-81.79	-103.33	-112.53	-70.25	9.60	31.14	40.34	-1.94
$\text{HSSH} + \text{Ti}(\text{Cp})_2\text{H}_2 \rightarrow \text{H}_2 + \text{Ti}(\text{Cp})_2(\text{SH})_2$	-55.62	-18.83	-38.48	-11.34	-68.14	-36.79	-17.14	-44.28	12.52
$\text{HSSH} + \text{Ti}(\text{Cp})_2\text{H}_2 \rightarrow \text{Ti}(\text{Cp})_2(\text{SH})\text{H} + \text{H}_2\text{S}$	-43.51	-10.57	-18.20	-18.07	-36.87	-32.94	-25.31	-25.44	-6.64
$\text{TiH}_4 \rightarrow \text{H} + \text{TiH}_3$	59.80	74.31	72.17	84.17	44.02	-14.51	-12.37	-24.37	15.78
$\text{CH}_3\text{TiH}_3 \rightarrow \text{CH}_3 + \text{TiH}_3$	61.26	49.99	48.47	66.62	37.83	11.27	12.79	-5.36	23.43
$\text{Ti}(\text{Cp})_2\text{H}_2 \rightarrow \text{Cp} + \text{Ti}(\text{Cp})\text{H}_2$	84.40	46.66	19.89	46.51	46.36	37.74	64.51	37.89	38.04
$\text{Ti}(\text{Cp})_2\text{H}_2 \rightarrow \text{H} + \text{Ti}(\text{Cp})_2\text{H}$	54.78	57.24	54.10	72.96	39.95	-2.45	0.68	-18.18	14.83
$\text{Ti}(\text{Cp})_2\text{H}(\text{CH}_3) \rightarrow \text{CH}_3 + \text{Ti}(\text{Cp})_2\text{H}$	39.04	25.44	23.15	39.78	30.35	13.60	15.89	-0.74	8.69
$\text{Ti}(\text{OH})\text{H}_3 \rightarrow \text{OH} + \text{TiH}_3$	119.10	77.12	83.03	98.85	87.71	41.98	36.07	20.25	31.39
$\text{Ti}(\text{Cp})_2(\text{OH})\text{H} \rightarrow \text{OH} + \text{Ti}(\text{Cp})_2\text{H}$	90.35	60.72	66.51	78.03	80.62	29.63	23.84	12.32	9.73
$(\text{NH}_2)\text{TiH}_3 \rightarrow \text{NH}_2 + \text{TiH}_3$	93.41	60.08	56.40	78.05	55.48	33.33	37.01	15.36	37.93
$\text{TiH}_3\text{F} \rightarrow \text{F} + \text{TiH}_3$	141.47	134.37	119.85	135.54	129.73	7.10	21.62	5.93	11.74
$\text{Ti}(\text{Cp})_2\text{HF} \rightarrow \text{F} + \text{Ti}(\text{Cp})_2\text{H}$	119.64	114.23	99.43	116.47	120.02	5.41	20.21	3.17	-0.38
$(\text{CF}_3)\text{TiH}_3 \rightarrow \text{CF}_3 + \text{TiH}_3$	125.06	97.40	57.28	73.98	131.52	27.66	67.78	51.08	-6.45
$\text{TiH}_3\text{Cl} \rightarrow \text{Cl} + \text{TiH}_3$	101.23	73.62	69.79	84.49	78.04	27.61	31.45	16.74	23.19
$\text{Ti}(\text{Cp})_2\text{HCl} \rightarrow \text{Cl} + \text{Ti}(\text{Cp})_2\text{H}$	83.67	59.61	51.32	67.98	78.56	24.07	32.36	15.69	5.11
$(\text{HS})\text{TiH}_3 \rightarrow \text{TiH}_3 + \text{HS}$	72.16	64.95	66.53	96.62	75.23	7.21	5.63	-24.46	-3.07
$\text{Ti}(\text{Cp})_2(\text{SH})\text{H} \rightarrow \text{Ti}(\text{Cp})_2\text{H} + \text{HS}$	60.15	47.79	48.19	69.84	56.77	12.36	11.96	-9.69	3.38
$(\text{PH}_2)\text{TiH}_3 \rightarrow \text{PH}_2 + \text{TiH}_3$	44.32	11.61	41.03	79.94	96.34	32.71	3.29	-35.62	-52.02
$\text{H}_3\text{TiSiH}_3 \rightarrow \text{SiH}_3 + \text{TiH}_3$	40.35	-123.09	-9.23	-109.64	44.98	163.44	49.58	149.99	-4.63

Table 8 Experimental and calculated heats of Formation, dipole moments and vertical ionization potentials for the zirconium training set. The errors are color coded as for Table 2

Compound	Heat of Formation (kcal mol^{-1})					Error (kcal mol^{-1})			
	Exper.	AMI	PM3	PM5	AMI*	AMI	PM3	PM5	AMI*
ZrH	123.40	83.07	83.48	92.76	28.12	40.33	39.92	30.64	95.28
$\text{Zr}(\text{Cp})_2(\text{Me})_2$	8.89	16.02	15.27	22.42	38.99	-7.13	-6.38	-13.53	-30.10
tetrakis-(2,2-dimethylpropyl)-zirconium	-61.50	-61.43	-79.26	-72.60	-105.69	-0.07	17.76	11.10	44.19
$\text{Zr}(\text{Cp})_2(\text{C}_6\text{H}_5)_2$	87.90	70.74	81.78	74.26	91.73	17.16	6.12	13.64	-3.83
$\text{Zr}(\text{CH}_2\text{C}_6\text{H}_5)_4$	85.40	64.02	61.27	60.22	65.11	21.38	24.13	25.18	20.29
ZrO	14.00	20.49	25.06	29.62	32.10	-6.49	-11.06	-15.62	-18.10
ZrO ₂	-68.40	-69.31	-67.44	-72.52	-66.06	0.91	-0.96	4.12	-2.34
$\text{Zr}(\text{O}-i\text{-C}_3\text{H}_7)_4$	-409.30	-408.67	-408.12	-408.75	-417.43	-0.63	-1.18	-0.55	8.13
ZrN	170.50	98.72	68.47	79.93	147.26	71.78	102.03	90.57	23.24
$((\text{CH}_3)_2\text{N})_4\text{Zr}$	-69.80	-72.82	-72.93	-69.56	-76.57	3.02	3.13	-0.24	6.77
$((\text{C}_2\text{H}_5)_2\text{N})_4\text{Zr}$	-114.60	-96.05	-99.71	-105.30	-120.54	-18.55	-14.89	-9.30	5.94
ZrF	19.80	2.63	7.34	4.57	37.23	17.17	12.46	15.23	-17.43
ZrF ₂	-133.40	-139.23	-130.85	-134.01	-118.82	5.83	-2.55	0.61	-14.58
ZrF ₃ *	-264.20	-268.51	-264.13	-272.20	-258.31	4.31	0.06	8.00	-5.89
ZrF ₄	-400.00	-392.18	-400.36	-395.65	-416.74	-7.82	0.36	-4.35	16.74
ZrCl	49.10	51.67	48.91	51.93	51.15	-2.57	0.19	-2.83	-2.05
ZrCl ₂	-44.50	-44.81	-48.05	-44.49	-30.73	0.31	3.55	-0.01	-13.77
ZrCl ₃ *	-125.30	-125.72	-128.94	-60.12	-109.28	-0.42	-3.64	65.18	-16.02
ZrCl ₄	-207.93	-209.36	-207.94	-207.98	-213.67	1.43	0.01	0.05	5.74
$\text{Zr}(\text{Cp})_2\text{Cl}_2$	-103.60	-77.85	-63.86	-74.09	-91.56	-25.75	-39.74	-29.51	-12.04
$((\text{CH}_3)_3\text{SiCH}_2)_4\text{Zr}$	-185.30	-185.73	-185.10	-185.35	-331.88	0.43	-0.20	0.05	146.58
Statistics, Heats of Formation (N=22)									
Mean Signed Error						5.46	6.15	8.97	11.27
Mean Unsigned Error						12.07	13.82	16.21	24.24

Table 9 DFT and semiempirical calculated energies for the reactions used in the zirconium training set. The errors are color coded as for Table 2

Reaction	ΔE_R (kcal mol ⁻¹)					Error (kcal mol ⁻¹)			
	DFT	AMI	PM3	PM5	AMI*	AMI	PM3	PM5	AMI*
ZrH ₄ → H ⁻ + ZrH ₃ ⁺	284.95	409.29	427.68	392.42	197.05	-124.34	-142.73	-107.47	87.90
ZrH ₄ → H ⁺ + ZrH ₃ ⁻	378.33	285.23	313.49	277.46	284.42	93.10	64.84	100.87	93.91
(CH ₃)ZrH ₃ → CH ₃ ⁻ + ZrH ₃ ⁺	267.31	375.93	390.30	360.64	172.78	-108.62	-122.99	-93.33	94.53
(CH ₃)ZrH ₃ → CH ₃ ⁺ + ZrH ₃ ⁻	291.26	217.17	219.35	218.41	225.45	74.09	71.91	72.85	65.81
(HO)ZrH ₃ → OH ⁻ + ZrH ₃ ⁺	297.87	397.29	409.44	364.70	197.09	-99.42	-111.57	-66.83	100.78
(HO)ZrH ₃ → OH ⁺ + ZrH ₃ ⁻	492.88	397.64	383.75	403.64	408.86	95.24	109.13	89.24	84.02
(NH ₂)ZrH ₃ → NH ₂ ⁻ + ZrH ₃ ⁺	293.62	402.79	409.67	373.30	179.60	-109.17	-116.05	-79.68	114.02
(NH ₂)ZrH ₃ → NH ₂ ⁺ + ZrH ₃ ⁻	387.29	306.52	280.94	316.77	294.75	80.78	106.35	70.52	92.54
ZrH ₃ F → F ⁻ + ZrH ₃ ⁺	281.95	418.69	402.06	366.34	227.28	-136.74	-120.11	-84.39	54.67
ZrH ₃ F → F ⁺ + ZrH ₃ ⁻	551.20	419.28	454.20	488.66	439.29	131.92	97.00	62.54	111.91
ZrH ₃ Cl → Cl ⁻ + ZrH ₃ ⁺	229.24	310.99	323.51	298.90	156.44	-81.75	-94.27	-69.65	72.80
ZrH ₃ Cl → Cl ⁺ + ZrH ₃ ⁻	411.34	305.47	280.79	300.83	298.46	105.87	130.55	110.51	112.88
(HS)ZrH ₃ → ZrH ₃ ⁺ + HS ⁻	226.90	245.06	248.05	632.90	132.66	-18.16	-21.15	-406.00	94.24
(HS)ZrH ₃ → ZrH ₃ ⁻ + HS ⁺	317.73	146.21	136.89	581.65	266.62	171.52	180.84	-263.91	51.11
(PH ₂)ZrH ₃ → ZrH ₃ ⁺ + PH ₂ ⁻	224.55	261.54	310.30	443.08	185.99	-36.99	-85.75	-218.53	38.56
(PH ₂)ZrH ₃ → ZrH ₃ ⁻ + PH ₂ ⁺	277.32	172.50	166.39	361.77	272.06	104.82	110.93	-84.45	5.26
(ZrH ₃)SiH ₃ → SiH ₃ ⁻ + ZrH ₃ ⁺	421.30	650.66	688.37	565.76	336.26	-229.36	-267.07	-144.46	85.04
(ZrH ₃)SiH ₃ → SiH ₃ ⁺ + ZrH ₃ ⁻	23.08	72.56	86.28	27.34	-0.07	-49.48	-63.20	-4.26	23.15
(AlH ₂)ZrH ₃ → ZrH ₃ ⁺ + AlH ₂ ⁻	205.71	426.65	273.78	802.83	137.35	-220.94	-68.07	-597.12	68.36
(AlH ₂)ZrH ₃ → ZrH ₃ ⁻ + AlH ₂ ⁺	202.33	265.83	235.05	626.35	143.56	-63.49	-32.71	-424.02	58.77
Zr(Cp) ₂ + H ₂ → Zr(Cp) ₂ (H) ₂	-40.68	-95.56	-66.15	-64.64	-38.46	54.88	25.47	23.96	-2.22
Zr(Cp) ₂ + CH ₄ → Zr(Cp) ₂ HMe	-27.84	-59.55	-45.17	-25.55	-35.72	31.71	17.33	-2.29	7.88
Zr(Cp) ₂ H ₂ + CH ₄ → Zr(Cp) ₂ HMe + H ₂	12.85	36.00	20.99	39.09	2.74	-23.15	-8.14	-26.24	10.11
Zr(Cp) ₂ + C ₂ H ₆ → Zr(Cp) ₂ (Me) ₂	-34.59	-17.49	-17.59	3.19	-27.20	-17.10	-17.01	-37.78	-7.39
Zr(Cp) ₂ H ₂ + C ₂ H ₆ → Zr(Cp) ₂ (Me) ₂ + H ₂	6.09	78.07	48.57	67.83	11.26	-71.98	-42.48	-61.74	-5.17
Zr(Cp) ₂ + H ₂ O → Zr(Cp) ₂ (OH)H	-73.92	-106.32	-96.12	-75.68	-82.64	32.39	22.20	1.76	8.72
Zr(Cp) ₂ H ₂ + HOH → Zr(Cp) ₂ (OH)H + H ₂	-33.24	-10.76	-29.97	-11.04	-44.18	-22.48	-3.27	-22.20	10.94
Zr(Cp) ₂ + CH ₃ OH → Zr(Cp) ₂ (OH)Me	-82.74	-71.24	-71.76	-58.37	-84.18	-11.50	-10.98	-24.37	1.44
Zr(Cp) ₂ + HOOH → Zr(Cp) ₂ (OH) ₂	170.30	-190.13	-172.43	-155.45	-200.17	19.83	2.13	-14.85	29.87
Zr(Cp) ₂ H ₂ + HOOH → Zr(Cp) ₂ (OH) ₂ + H ₂	129.62	-94.57	-106.28	-90.81	-161.71	-35.05	-23.34	-38.81	32.09
Zr(Cp) ₂ H ₂ + HOOH → Zr(Cp) ₂ (OH)H + H ₂ O	106.63	-88.72	-82.65	-85.59	-122.17	-17.91	-23.98	-21.04	15.54
Zr(Cp) ₂ + HF → Zr(Cp) ₂ HF	-91.76	-96.17	-95.59	-76.14	-78.18	4.41	3.83	-15.62	-13.58
Zr(Cp) ₂ H ₂ + HF → Zr(Cp) ₂ HF + H ₂	-51.08	-0.61	-29.43	-11.50	-39.72	-50.47	-21.65	-39.58	-11.36
Zr(Cp) ₂ + CH ₃ F → Zr(Cp) ₂ FMe	-97.63	-75.10	-81.59	-63.97	-90.72	-22.53	-16.04	-33.66	-6.91
Zr(Cp) ₂ + F ₂ → Zr(Cp) ₂ F ₂	249.85	-208.23	-209.25	-224.06	-236.12	-41.62	-40.60	-25.79	-13.73
Zr(Cp) ₂ H ₂ + F ₂ → Zr(Cp) ₂ F ₂ + H ₂	209.17	-112.67	-143.10	-159.42	-197.65	-96.50	-66.07	-49.75	-11.52
Zr(Cp) ₂ H ₂ + F ₂ → Zr(Cp) ₂ HF + HF	165.50	-121.50	-119.84	-157.80	-160.63	-44.00	-45.66	-7.70	-4.87
Zr(Cp) ₂ + HCl → Zr(Cp) ₂ HCl	-87.40	-89.20	-76.56	-53.22	-95.19	1.80	-10.84	-34.18	7.79
Zr(Cp) ₂ H ₂ + HCl → Zr(Cp) ₂ HCl + H ₂	-46.72	6.35	-10.41	11.42	-56.73	-53.07	-36.31	-58.14	10.01
Zr(Cp) ₂ + CH ₃ Cl → Zr(Cp) ₂ ClMe	-91.67	-62.79	-60.68	-44.27	-95.78	-28.89	-30.99	-47.40	4.11
Zr(Cp) ₂ + Cl ₂ → Zr(Cp) ₂ Cl ₂	169.73	-114.63	-103.29	-100.67	-194.99	-55.10	-66.44	-69.06	25.26
Zr(Cp) ₂ H ₂ + Cl ₂ → Zr(Cp) ₂ Cl ₂ + H ₂	129.05	-19.08	-37.14	-36.03	-156.52	-109.98	-91.91	-93.02	27.47
Zr(Cp) ₂ H ₂ + Cl ₂ → Zr(Cp) ₂ HCl + HCl	-92.51	-23.52	-26.37	-50.26	-99.49	-68.99	-66.14	-42.25	6.98
Zr(Cp) ₂ + H ₂ S → Zr(Cp) ₂ (SH)H	-70.81	-20.68	0.40	-353.56	-88.71	-50.13	-71.21	282.75	17.90
Zr(Cp) ₂ H ₂ + HSH → Zr(Cp) ₂ (SH)H + H ₂	-30.13	74.87	66.55	-288.92	-50.24	-105.00	-96.68	258.79	20.11
Zr(Cp) ₂ + CH ₃ SH → Zr(Cp) ₂ (SH)Me	-74.17	17.98	26.84	-319.63	-77.03	-92.15	-101.00	245.46	2.86
Zr(Cp) ₂ + HSSH → Zr(Cp) ₂ (SH) ₂	109.62	54.23	70.36	-550.80	-133.32	-163.85	-179.98	441.18	23.70
Zr(Cp) ₂ H ₂ + HSSH → Zr(Cp) ₂ (SH) ₂ + H ₂	-68.93	149.79	136.51	-486.17	-94.86	-218.72	-205.44	417.24	25.93
Zr(Cp) ₂ H ₂ + HSSH → Zr(Cp) ₂ (SH)H + HSH	-48.12	73.91	69.46	-303.25	-48.84	-122.03	-117.58	255.13	0.72
ZrH ₄ → H + ZrH ₃	70.13	93.33	86.80	82.81	66.03	-23.20	-16.67	-12.68	4.10

alternative at the moment. The dichotomy between the results for (experimental) heats of formation and (DFT) bond-dissociation energies illustrates that there are insufficient accurate experimental data for a truly robust parameterization for elements like the ones treated here.

There is, however, a more fundamental reason than missing or inaccurate experimental data for using heats of reaction rather than relying only on heats of formation. Semiempirical molecular-orbital techniques are almost never used to calculate heats of formation (i.e.

Table 9 (Contd.)

$(\text{CH}_3)\text{ZrH}_3 \rightarrow \text{CH}_3 + \text{ZrH}_3$	58.58	38.77	41.30	37.50	44.73	19.81	17.28	21.08	13.85
$(\text{OH})\text{ZrH}_3 \rightarrow \text{OH} + \text{ZrH}_3$	110.58	106.68	107.55	109.25	112.80	3.90	3.03	1.33	-2.22
$(\text{NH}_2)\text{ZrH}_3 \rightarrow \text{NH}_2 + \text{ZrH}_3$	104.47	114.06	113.15	114.66	60.92	-9.59	-8.68	-10.19	43.55
$\text{ZrH}_3\text{F} \rightarrow \text{F} + \text{ZrH}_3$	140.54	129.82	132.38	136.98	141.63	10.72	8.16	3.56	-1.09
$\text{ZrH}_3\text{Cl} \rightarrow \text{Cl} + \text{ZrH}_3$	106.31	83.29	81.17	87.43	106.58	23.02	25.14	18.88	-0.27
$(\text{HS})\text{ZrH}_3 \rightarrow \text{ZrH}_3 + \text{HS}$	80.11	-0.60	-6.77	364.88	94.81	80.71	86.88	-284.77	-14.70
$(\text{PH}_2)\text{ZrH}_3 \rightarrow \text{ZrH}_3 + \text{PH}_2$	56.12	31.12	60.45	220.11	98.49	25.00	-4.33	-163.99	-42.37
$(\text{ZrH}_3)\text{SiH}_3 \rightarrow \text{SiH}_3 + {}_{4748}$	52.32	178.26	213.76	127.74	62.80	-125.94	-161.44	-75.42	-10.48
$(\text{AlH}_2)\text{ZrH}_3 \rightarrow \text{AlH}_2 + \text{ZrH}_3$	44.58	180.81	56.35	545.21	46.94	-136.23	-11.77	-500.63	-2.36
$\text{TiZr} \rightarrow \text{Ti} + \text{Zr}$	102.66	66.59	273.31	22.99	93.33	36.07	-170.65	79.67	9.33
Cyclic Zr-O-Ti $\rightarrow \text{Zr} + \text{TiO}$	124.57	65.13	236.96	46.53	146.16	59.44	-112.39	78.04	-21.59
Ionization potential Zr [Zr \rightarrow Zr +]	124.71	141.28	142.07	138.48	137.23	-16.57	-17.36	-13.77	-12.52
Adiabatic IP ZrH	153.48	242.63	254.21	246.15	143.20	-89.15	-100.73	-92.67	10.28
Adiabatic IP ZrH ₂	152.71	241.75	248.49	248.98	112.89	-89.04	-95.78	-96.27	39.82
Adiabatic IP ZrH ₃	177.27	273.99	293.43	266.84	103.95	-96.72	-116.16	-89.57	73.33
Adiabatic IP ZrH ₄	190.08	255.11	244.06	245.54	102.37	-65.03	-53.98	-55.46	87.71
Adiabatic IP ZrO	128.32	220.73	217.52	215.35	114.82	-92.41	-89.20	-87.03	13.50
Adiabatic IP ZrN	154.89	248.25	239.82	228.91	175.25	-93.36	-84.93	-74.02	-20.36
Adiabatic IP ZrS	173.00	219.86	220.67	130.73	143.28	-46.86	-47.67	42.27	29.72
Statistics, Heats of Reaction (N=69)									
Mean Signed Error						-35.13	-38.38	-33.16	27.83
Mean Unsigned error						71.68	69.77	110.78	33.76

the heat of formation is not the quantity of interest). They are used to compare energies between isomers, calculate bond energies, heats of reaction, complexation and binding energies and a host of other applications that all depend on the difference between one or more calculated energies. Thus, the heats of formation initially provided the basis for parameterizations of methods like MINDO/3 and MNDO because there were few alternatives. We do not usually care if, as in the case of the AlF_3 dimerization, if the calculated heat of formation is off by 6–7 kcal mol⁻¹, as for AM1*, or even more. What we care about is the energy difference between the sum of two monomers and the dimer. Moreover, in the case of sequential parameterizations (first fitting H, C, N, O compounds, fixing the parameters and then fitting F, etc. As in MNDO, AM1, and AM1*), then known limitations in the previous parameters can significantly skew the results of a computational study in which reaction energetics are calculated.

For the above reasons, we have made extensive use of calculated heats of reaction for the parameterization of AM1* for Al, Si, Ti and Zr. We will continue this practice for further transition-metal parameterizations. Detailed comparisons between AM1* and the methods like PM5 that rely more heavily on heats of formation will show whether the former really is more robust for applications.

References

1. Winget P, Horn AHC, Selçuki C, Martin B, Clark T (2003) *J Mol Model* 9:408–414
2. Dewar MJS, Zoebisch EG, Healy EF, Stewart JJP (1985) *J Am Chem Soc* 107:3902–3909
3. Voityuk AA, Rösch N (2000) *J Phys Chem A* 104:4089–4094
4. Dewar MJS, Thiel W (1977) *J Am Chem Soc* 99:4899–4907
5. Thiel W (1998) In: Schleyer PvR, Allinger NL, Clark T, Gasteiger J, Kollman PA, Schaefer III HF, Schreiner PR (eds) *Encyclopedia of computational chemistry*. Wiley, Chichester, p 1599
6. Stewart JJP (1989) *J Comp Chem* 10:209–220
7. Stewart JJP (1989) *J Comp Chem* 10:221–264
8. Stewart JJP (1998) In: Schleyer PvR, Allinger NL, Clark T, Gasteiger J, Kollman PA, Schaefer III HF, Schreiner PR (eds) *Encyclopedia of computational chemistry*. Wiley, Chichester, p 2080
9. (1999) Weitkamp J, Puppe L (eds) *Catalysis and zeolites: fundamentals and applications*. Springer, Berlin
10. (2001) Blom R, Follestad A, Rytter E, Tilset M, Ystenes M (eds) *Organometallic catalysts and olefin polymerization: catalysts for a new millennium*. Springer, Berlin
11. Thiel W, Voityuk AA (1994) *J Mol Struct (Theochem)* 119:141–154
12. Thiel W, Voityuk AA (1996) *J Phys Chem* 100:616–626
13. Dewar MJS, Holder AJ (1990) *Organometallics* 9:508–511
14. Dewar MJS, Jie C (1987) *Organometallics* 6:1486–1490
15. Bredow T, Geudtner G, Jug K (2001) *J Comp Chem* 22:861–887
16. Linstrom P, Mallard W (2003) *NIST Chemistry WebBook*, NIST Standard Reference Database Number 69, (<http://webbook.nist.gov/>). National Institute of Standards and Technology, Gaithersburg MD, p 20899
17. Winget P, Clark T (2004) *J Comp Chem* 25:725–733
18. Becke AD (1988) *Phys Rev A* 38:3098–3100
19. Lee C, Yang W, Parr RG (1988) *Phys Rev B* 37:785–789
20. Becke AD (1993) *J Chem Phys* 98:5648–5652
21. Frisch MJ, Trucks GW, Schlegel HB, Scuseria GE, Robb MA, Cheeseman JR, Zakrzewski VG, Montgomery JA, Stratman RE, Burant JC, Dapprich S, Millam JM, Daniels AD, Kudin KN, Strain MC, Farkas O, Tomasi J, Barone V, Cossi M, Cammi R, Mennucci B, Pomelli C, Adamo C, Clifford S, Ochterski J, Petersson GA, Ayala PY, Cui Q, Morokuma K, Malick DK, Rabuck AD, Raghavachari K, Foresman JB, Cioslowski J, Ortiz JV, Baboul AG, Stefanov BB, Liu C, Liashenko A, Piskorz P, Komaromi I, Gomperts R, Martin RL, Fox DJ, Keith T, Al-Laham MA, Peng CY, Nanayakkara

Table 10 Summary of the errors obtained with AM1, PM3, PM5 and AM1* classified by compound and reaction type. The highest errors for each type are highlighted in **Bold**, the lowest in *Italics*

	<i>N</i>	AM1	PM3	PM5	AM1*
All compounds	234	15.39	15.52	14.91	21.05
By Element:					
H	140	16.23	14.55	15.33	21.02
C	107	16.56	14.31	15.38	22.83
O	66	14.67	18.27	15.38	21.86
N	14	16.07	21.52	14.72	26.07
F	40	12.35	11.20	11.84	20.21
Cl	49	8.89	10.17	9.23	18.25
S	6	11.86	19.08	21.67	19.34
P	1	13.27	4.79	2.31	13.28
Si	100	16.04	9.38	12.33	22.94
Al	53	13.88	20.98	12.20	12.99
Ti	62	24.55	21.61	28.45	28.32
Zr	21	12.07	13.83	16.21	24.24
Reactions by type:					
Homolytic BDE	73	34.20	43.30	35.71	11.43
Adiabatic IP	38	37.17	37.05	33.26	46.20
Ligand Exchange	82	37.39	36.69	55.06	12.90
Heterolytic BDE	76	59.38	68.15	71.49	48.14
All	284	41.76	46.70	50.34	26.75
Reactions by Element:					
H	251	43.31	47.52	53.34	24.35
C	124	34.20	36.02	43.98	15.06
O	42	33.36	39.69	30.96	31.27
N	19	34.80	50.25	29.25	38.25
F	47	46.05	43.06	29.17	25.62
Cl	38	31.33	40.79	36.02	25.62
S	35	47.63	53.19	97.86	20.18
P	13	30.73	39.31	52.53	23.37
Si	68	42.76	32.99	28.36	18.74
Al	68	32.53	66.85	50.46	17.77
Ti	98	42.58	34.86	48.62	35.62
Zr	69	71.68	69.77	110.78	33.76
Reactions by Reactant and Product:					
H ₂	34	43.04	36.89	57.42	15.25
CH ₄	18	29.89	25.90	23.66	14.68
AlH ₂	18	28.95	100.92	52.99	9.55
AlH ₃	17	15.59	50.40	16.97	11.36
AlH ₂ ⁺	11	45.82	38.51	78.32	27.86
AlH ₂ ⁻	11	75.30	144.81	105.43	30.02
SiH ₃ ⁺	13	43.15	48.65	38.99	32.19
SiH ₃ [•]	28	44.39	30.39	24.60	15.72
CH ₃ SiH ₂ [•]	13	32.57	16.24	13.17	7.22
TiH ₃ [•]	12	70.25	32.86	67.22	21.72
TiH ₄	15	40.87	34.25	41.79	21.48
Ti(Cp) ₂	15	19.70	31.82	42.09	9.28
Ti(Cp) ₂ H ₂	18	29.27	29.03	40.84	21.36
ZrH ₃ ⁺	11	114.75	115.08	177.91	80.38
Zr(Cp) ₂	15	41.86	41.07	86.68	11.56
Zr(Cp) ₂ H ₂	16	69.84	55.67	89.27	12.45

- A, Gonzalez C, Challacombe M, Gill PMW, Johnson BG, Chen W, Wong MW, Andres JL, Gonzales C, Head-Gordon M, Replogle ES, Pople JA (1998) Gaussian 98. Gaussian Inc., Pittsburgh, PA
22. Hay PJ, Wadt WR (1985) *J Chem Phys* 82:270–283
23. Hay PJ, Wadt WR (1985) *J Chem Phys* 82:284–298
24. Hay PJ, Wadt WR (1985) *J Chem Phys* 82:299–310
25. Hehre WJ, Ditchfield R, Pople JA (1972) *J Chem Phys* 56:2257–2261
26. Hariharan PC, Pople JA (1973) *Theor Chim Acta* 28:213–222
27. Francel MM, Pietro WJ, Hehre WJ, Binkley JS, Gordon MS, DeFrees DJ, Pople JA (1982) *J Chem Phys* 77:3654–3665
28. Frisch MJ, Pople JA, Binkley JS (1984) *J Chem Phys* 80:3265–3269
29. Clark T, Chandrasekhar J, Spitznagel GW, Schleyer PvR (1983) *J Comp Chem* 4:294–301
30. Krishnan R, Binkley JS, Seeger R, Pople JA (1980) *J Chem Phys* 72:650–654
31. McLean AD, Chandler GS (1980) *J Chem Phys* 72:5639–5648
32. Sanchez RS, Winget P, Horn AHC, Selçuki C, Martin B, Clark T (to be submitted) *J Mol Model*
33. Sanchez RS, Winget P, Horn AHC, Selçuki C, Martin B, Clark T (2004) Database (<http://www.chemie.uni-erlangen.de/ccc/parabase.html>), Erlangen
34. Clark T, Alex A, Beck B, Chandrasekhar J, Gedeck P, Horn AHC, Hutter M, Martin B, Rauhut G, Sauer W, Schindler T, Steinke T (2003) Computer-Chemie-Centrum, Universitaet Erlangen-Nürnberg, Erlangen
35. Stewart JJP (2002) FQS Poland, Krakow
36. Stewart JJP (2003) 226th National ACS meeting (COMP)
37. Stewart JJP (2004) Beyond Michael Dewar's legacy: modern semiempirical MO theory (Michael Dewar memorial symposium), 227th National ACS meeting (COMP). Anaheim, CA, March 29, 2004