Thermochemistry of the Boranes

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A compilation is presented of published experimental and computational reports (191 references) on the structures, vibrational frequencies, molar enthalpies of formation and standard entropies for 26 gas phase boranes for the temperature range from 0 to 1500 K. The thermochemical properties have been collated via standard programs and are listed in a convenient tabular format. Levels of uncertainties in the thermodynamic functions have not been assessed, because of the limited experimental and computational data. The tabulated values were fitted to standard seven-parameter (NASA) polynomials to facilitate the computation of enthalpies of formation, entropies, and heat capacities for modeling purposes. Within the context of intrinsic uncertainties, the equilibrium compositions of the gas phase were calculated, constrained to constant temperature and volume, for several boron–hydrogen (B/H) ratios, at various temperatures and pressures. The (unexpected) results indicate that in none of the reported gas-phase kinetics studies was thermodynamic equilibrium attained, even though the measured concentration profiles appear to extrapolate to steady state product distributions. © *1998 American Institute of Physics and American Chemical Society.* [S0047-2689(98)00104-4]

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List of Symbols

T	temperature (K)
R	universal gas constant $(J \cdot K^{-1} \cdot mol^{-1})$
C_P°	standard heat capacity at constant pressure $(J \cdot K^{-1} \cdot mol^{-1})$
S°	standard entropy $(J \cdot K^{-1} \cdot mol^{-1})$
$\Delta_f H^\circ$	standard enthalpy of formation $(kJ \cdot mol^{-1})$
H°	standard enthalpy $(J \cdot mol^{-1})$
$\Delta_f G^\circ$	standard Gibbs free energy of formation $(kJ \cdot mol^{-1})$
G°	standard Gibbs free energy $(J \cdot mol^{-1})$
K_f	equilibrium constant of formation for the reaction of forming the given compound from its elements
a_i	coefficients of the NASA polynomial, $= 1,2,...,7$

1. Introduction

The boranes have attracted much attention due to their unique chemical properties. They play crucial roles in sev-

TABLE 1. Thermal data of boranes at 298.15 K and 1 bar

Species	Name	CAS number	$\Delta_f H^\circ$ (kJ·mol^{-1})	S° (J·K^{-1}·mol^{-1})	C_P° (J·K^{-1}·mol^{-1})
BH	borane (1)	13766-26-2	442.7	171.85	29.18
BH$_2$	borane (2)	14452-64-3	318.0	193.67	34.98
BH$_3$	borane (3)	13283-31-3	89.2	188.23	36.02
BH$_4$	borane (4)	37365-60-9	236.4	211.61	44.28
BH$_5$	borane (5)	35325-82-7	79.9	230.55	54.12
B$_2$H	diborane (1)		737.6	214.29	42.33
B$_2$H$_2$	diborane (2)	56125-74-7	396.5	213.24	46.89
single-bridge B$_2$H$_3$	diborane (3)		306.7	236.07	52.53
double-bridge B$_2$H$_3$	diborane (3)		315.9	233.22	52.48
single-bridge B$_2$H$_4$	diborane (4)	18099-45-1	211.0	236.15	57.12
double-bridge B$_2$H$_4$	diborane (4)	18099-45-1	209.7	227.83	51.52
single-bridge B$_2$H$_5$	diborane (5)	124521-90-0	254.7	243.47	58.27
double-bridge B$_2$H$_5$	diborane (5)	124521-90-0	275.1	245.55	53.16
B$_2$H$_6$	diborane (6)	19287-45-7	36.4	232.05	56.65
C$_s$-B$_3$H$_7$	triborane (7)	12429-70-8	128.4	267.99	76.71
C$_{2v}$-B$_3$H$_7$	triborane (7)	12429-70-8	146.4	265.96	81.62
B$_3$H$_9$	triborane (9)	36350-66-0	138.9	278.33	91.70
B$_4$H$_4$	tetraborane (7)	158511-74-1	326.2	277.61	80.38
B$_4$H$_{10}$	tetraborane (10)	18283-93-7	66.1	280.27	93.17
B$_4$H$_{12}$	tetraborane (12)	60349-62-4	188.3	315.89	128.25
B$_5$H$_9$	pentaborane (9)	19624-22-7	73.2	280.62	99.59
B$_5$H$_{11}$	pentaborane (11)	18433-84-6	103.3	320.96	130.31
B$_6$H$_{10}$	hexaborane (10)	23777-80-2	94.6	296.84	125.74
B$_8$H$_{12}$	octaborane (12)	19469-16-0	147.3	337.65	157.03
B$_9$H$_{15}$	nonaborane (15)	19465-30-6	158.4	364.91	187.02
B$_{10}$H$_{14}$	decaborane (14)	17702-41-9	47.0	350.74	186.10

TABLE 2. Molecular constants used in the calculation of thermochemical parameters

Species	Point group	Symmetry number	Rotational constants (cm^{-1})	Ground state degeneracy	Vibrational frequencies (cm^{-1})
BH	C$_{\infty v}$	1	12.04	1	2368
BH$_2$	C$_{2v}$	2	41.7, 7.24, 6.0	2	2658, 973, 2507
BH$_3$	D$_{3h}$	6	7.87, 7.87, 3.88	1	1147, 2602, 2602, 1197, 1197,2495
BH$_4$	C$_{2v}$	2	2.94, 3.84, 7.24	2	2390, 1967, 1333, 939, 1850, 598, 2505, 993, 837
BH$_5$	C$_s$	1	2.83, 3.07, 3.65	1	3306, 2544, 2475, 2260, 1481, 1087, 1134, 1070, 912, 832, 605, 108
B$_2$H	C$_{\infty v}$	1	0.848, 0.848	2	2689, 865, 475, 475
B$_2$H$_2$	D$_{\infty h}$	2	0.853, 0.853	3	570, 570, 640, 640, 1278, 2745, 2783
single-bridge B$_2$H$_3$	C$_{2v}$	2	0.705, 0.775, 7.85	2	2707, 2591, 2513, 1174, 958, 889, 852, 424, 409
double-bridge B$_2$H$_3$	C$_{2v}$	2	0.810, 0.871, 11.63	2	2770, 2719, 1884, 1297, 1147, 793, 651, 598, 359
single-bridge B$_2$H$_4$	D$_{2d}$	2	0.662, 0.662, 4.06	1	2554, 1252, 821, 455, 2529, 1197, 2594, 2594, 1011, 1011, 473, 473
double-bridge B$_2$H$_4$	C$_{2v}$	2	0.841, 0.846, 6.96	1	2794, 2062, 1357, 1206, 753, 1212, 535, 2059, 814, 2756, 1338, 541
single-bridge B$_2$H$_5$	C$_{2v}$	2	0.589, 0.627, 3.12	2	2716, 2701, 2607, 2590, 1865, 1687, 1188, 1152, 1084, 936, 897, 788, 682, 463, 457
double-bridge B$_2$H$_5$	C$_s$	1	0.628, 0.697, 3.46	2	2671, 2660, 2580, 2194, 2010, 1724, 1654, 1216, 1042, 968, 935, 888, 832, 799, 389
B$_2$H$_6$	D$_{2h}$	4	2.656, 0.606, 0.557	1	2530, 2088, 1183, 790, 833, 1760, 860, 2609, 949, 369, 2596, 915, 1924, 973, 1020, 2520, 1603, 1172
C$_s$-B$_3$H$_7$	C$_s$	1	0.307, 0.445, 0.652	1	299, 406, 627, 705, 706, 730, 790, 839, 897, 959, 963, 1071, 1094, 1183, 1219, 1312, 1434, 2060, 2118, 2543, 2556, 2643, 2655, 2658
C$_{2v}$-B$_3$H$_7$	C$_{2v}$	2	0.307, 0.529, 0.531	1	303, 422, 449, 581, 584, 620, 783, 881, 895, 937, 937, 1024, 1063, 1172, 1172, 1214, 1753, 2001, 2503, 2522, 2573, 2583, 2594, 2656
B$_3$H$_9$	C$_{3v}$	3	0.248, 0.414, 0.414	1	2677, 2662, 2549, 2537, 2537, 2163, 2123, 2123, 1716, 1716, 1675, 1163, 1139, 1139, 1084, 1084, 1016, 932, 907, 907, 819, 819, 800, 538, 538, 490, 353, 211, 211, 2662
B$_4$H$_4$	C$_s$	1	0.745, 0.304, 0.216	1	221, 434, 522, 571, 670, 691, 723, 726, 772, 828, 881, 1046, 1233, 1397, 2199, 2638, 2687, 2688
B$_4$H$_{10}$	C$_{2v}$	2	0.187, 0.207, 0.367	1	2570, 2570, 2475, 2095, 1444, 1255, 1145, 965, 908, 827, 785, 559, 2150, 1308, 1117, 1023, 868, 737, 662, 2570, 2150, 1324, 1196, 966, 846, 779, 525, 2570, 2475, 2150, 1388, 1140, 1064, 898, 472, 236
B$_4$H$_{12}$	C$_{2v}$	2	0.193, 0.288, 0.335	1	2715, 2677, 2562, 2540, 2238, 1512, 1179, 1133, 1047, 776, 596, 380, 323, 141, 2047, 1535, 1125, 925, 715, 683, 314, 237, 2679, 2541, 2199, 1508, 1156, 1074, 876, 791, 604, 323, 2700, 2558, 2254, 1539, 1160, 1057, 902, 744, 599, 251
B$_5$H$_9$	C$_{4v}$	4	0.166, 0.238, 0.238	1	2628, 2610, 1844, 1126, 985, 799, 702, 1358, 732, 1813, 1079, 741, 241, 2610, 1684, 1036, 785, 599, 2610, 1800, 1634, 1410, 1035, 890, 711, 618, 569, 2610, 1800, 1634, 1410, 1035, 890, 711, 618, 569
B$_5$H$_{11}$	C$_1$	1	0.124, 0.160, 0.280	1	160, 246, 329, 362, 388, 503, 536, 552, 615, 640, 669, 690, 707, 772, 800, 825, 844, 887, 914, 936, 961, 990, 1055, 1070, 1115, 1130, 1158, 1191, 1260, 1321, 1597, 1805, 2062, 2175, 2231, 2466, 2478, 2532, 2558, 2563, 2564, 2572
B$_6$H$_{10}$	C$_s$	1	0.105, 0.170, 0.172	1	335, 349, 502, 539, 548, 551, 594, 623, 651, 664, 678, 688, 706, 710, 772, 797, 808, 853, 860, 873, 910, 924, 949, 1029, 1039, 1060, 1073, 1130, 1382, 1486, 1517, 1580, 1791, 1794, 1902, 1903, 2536, 2547, 2555, 2570, 2578, 2585

TABLE 2. Molecular constants used in the calculation of thermochemical parameters—Continued

Species	Point group	Symmetry number	Rotational constants (cm^{-1})	Ground state degeneracy	Vibrational frequencies (cm^{-1})
B_8H_{12}	C_s	1	0.066, 0.084, 0.118	1	2715, 2708, 2677, 2669, 2658, 1946, 1901, 1848 1525, 1166, 1133, 1102, 1065, 1008, 984, 961, 907, 875, 830, 782, 750, 733, 711, 687, 653, 620, 571, 543, 432, 265, 2705, 2697, 2670, 1915, 1585, 1488, 1414, 1096, 1001, 974, 953, 904, 881, 854, 749, 723, 715, 687, 653, 575, 515, 428, 339, 303
B_9H_{15}	C_s	1	0.0485, 0.0533, 0.0870	1	2711, 2692, 2677, 2675, 2666, 2659, 2544, 2251, 1970, 1897, 1636, 1284, 1199, 1184, 1140, 1056, 1012, 1001, 989, 904, 890, 857, 820, 803, 736, 726, 696, 687, 649, 633, 623, 565, 522, 456, 364, 294, 207, 2702, 2688, 2663, 2265, 1956, 1705, 1527, 1348, 1163, 1113, 1051, 996, 984, 952, 919, 906, 891, 856, 779, 723, 711, 697, 655, 571, 536, 472, 436, 367, 196
$B_{10}H_{14}$	C_{2v}	2	0.0489, 0.0573, 0.0746	1	2707, 2691, 2674, 2660, 1943, 1733, 1215, 1001, 994, 965, 852, 847, 758, 736, 679, 643, 627, 544, 416, 336, 2685, 1864, 1563, 1124, 997, 943, 934, 856, 758, 718, 668, 571, 503, 230, 2690, 2657, 1890, 1629, 1166, 1044, 966, 927, 795, 742, 720, 696, 605, 597, 338, 2703, 2684, 2672, 1920, 1628, 1144, 1054, 992, 924, 902, 822, 769, 707, 672, 624,524, 444

eral industrial processes such as electronics and the synthesis of high-temperature materials. To optimize their practical applications, fundamental data for their thermal properties (enthalpies of formation, entropies, and heat capacities) are required. Although numerous studies of the thermochemistry of the boranes have been reported, as of this date only the JANAF Thermochemical Tables[1] and Gurvich et al.[2] provide comprehensive literature surveys and critical thermal data for a few boranes. The objective of the present study is to compile a survey of the boranes, particularly of those whose thermal properties that have not been reviewed, thus to complement the JANAF table[1] and Gurvich et al.[2] In several cases, their databases need to be updated since more accurate experimental measurements have become available. Also, we evaluated the seven polynomial coefficients (based on the NASA format)[3] for the boranes to facilitate thermal equilibrium calculations and kinetic modeling.

Finally, we present the first attempt of gas-phase borane thermal equilibrium calculations over a wide range of temperatures (from 300 to 1000 K) for various boron–hydrogen ratios. The resulting equilibrated borane concentrations provide contrast with the published steady state borane concentrations as reported in several pyrolysis kinetic studies.

1.1. Borane Species Considered

Table 1 lists 26 borane species that are covered in the present study. Also cited in the table are their Chemical Abstract Service (CAS) numbers along with their enthalpies of formation, molar entropies, and heat capacities at 298.15 K and 1 bar. The molecular constants used in the statistical

mechanics calculations for the thermochemical properties are summarized in Table 2. Reviews of the literature that cover their physical and thermal properties are presented in Sec. 2.

We note that 13 additional species have been identified, but one or more essential parameters (enthalpy of formation, vibrational frequencies, or molecular geometry) are unavailable for statistical mechanics calculations. They are: B_4H_6, B_4H_8, $(B_5H_8)_2$, B_6H_{12}, B_8H_8, B_8H_{14}, B_8H_{18}, B_9H_9, B_9H_{13}, $B_{10}H_{10}$, $B_{12}H_{16}$, $B_{18}H_{22}$, and $B_{19}H_{19}$. A still longer list of the borane species generated by electron impact ionization was published by Rozett and co-workers.[4,5] Additional thermodynamic investigations of these species are clearly needed.

1.2. Comments on Thermal Parameter Evaluations and Calculations

The present literature survey covers about a half century. The recommended values for the structures, vibrational frequencies, and enthalpies of formation are based on experimental determinations, theoretical calculations, reviews, and empirical estimations, but the heaviest weight was given to experimental determinations. Consistency among the published values was a criterion for selection of final magnitudes. For 14 of the 26 species, there are partial or extended experimental data, and for 12 only the computed or empirically estimated values are available for minimum energy structures, enthalpies of formation, and vibrational frequencies. The assigned values upon which the calculated thermal parameters are based are subject to varying levels of uncer-

TABLE 3. Ideal gas thermodynamic parameters of BH at 1 bar

T (K)	C°_P	S°	$-[G^{\circ}-H^{\circ}(298.15\ \text{K})]/T$	$H^{\circ}-H^{\circ}(298.15\ \text{K})$	$\Delta_f H^{\circ}$	$\Delta_f G^{\circ}$	$\log_{10} K_f$
		$(\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1})$			$(\text{kJ}\cdot\text{mol}^{-1})$		
0	0.000	0.000	∞	−8.639	439.476	439.476	−∞
100	29.126	140.014	197.766	−5.775	440.816	431.882	−225.592
200	29.143	160.207	174.516	−2.862	442.050	422.433	−110.328
298.15	29.181	171.849	171.849	0.000	442.667	412.651	−72.295
300	29.182	172.029	171.849	0.054	442.673	412.465	−71.816
400	29.347	180.442	172.995	2.979	442.783	402.367	−52.544
500	29.741	187.029	175.166	5.931	442.543	392.285	−40.982
600	30.340	192.502	177.612	8.934	442.100	382.272	−33.280
700	31.052	197.231	180.084	12.003	441.545	372.344	−27.785
800	31.792	201.426	182.495	15.145	440.928	362.500	−23.669
900	32.503	205.212	184.812	18.360	440.274	352.735	−20.472
1000	33.160	208.671	187.027	21.644	439.594	343.045	−17.919
1100	33.752	211.860	189.142	24.990	438.890	333.424	15.833
1200	34.280	214.820	191.160	28.392	438.164	323.868	−14.098
1300	34.748	217.583	193.087	31.844	437.414	314.373	−12.632
1400	35.162	220.173	194.930	35.340	436.639	304.938	−11.377
1500	35.530	222.612	196.695	38.875	435.835	295.558	−10.292

tainties. Thus, we provide a preliminary view of current estimates of equilibrium partitions of borane species for a practical range of temperatures.

The thermal properties are calculated using conventional statistical mechanics relations under the ideal gas, rigid rotor, and harmonic oscillator approximation.[1] The selected theoretical vibrational frequencies are scaled by 0.943 for high-level (Moller–Plesset) ab initio calculations and by 0.90 for Hartree–Fock level calculations.[6] The electronic state contributions are calculated by directly summing over the energy levels.[1] Although little or no such information is available for most of the boranes, note that for the present application the electronic state contributions have little impact on the calculated thermal properties. In all calculations the atomic mass of boron was set to be 10.811 $\text{g}\cdot\text{mol}^{-1}$, which is an average of ^{10}B and ^{11}B weight by their natural abundance. The fundamental constants in the statistical mechanics calculations are those of Cohen and Taylor.[7] Systeme International (SI) units are used throughout.

To maintain internal consistency, it is essential to select enthalpies of formation for gas-phase boron and hydrogen, since these quantities are required to derive enthalpies of formation of the boranes from experimentally determined atomization energies. The enthalpy of formation of atomic hydrogen is well-established and reported in JANAF:[1] 217.999 ±0.006 $\text{kJ}\cdot\text{mol}^{-1}$ at 298.15 K. However, for gas-phase boron, there are significant discrepancies in the literature. The JANAF editors accepted the value recommended by an earlier CODATA analysis of experiments reported prior to 1976. Subsequently, there were four experimental determinations.[8–11] Three were in close agreement with JANAF tables[1] and with Cox et al.[8(b)] The exception is that

of Storms and Mueller,[9] which is higher than others by about 12 $\text{kJ}\cdot\text{mol}^{-1}$ but has the smallest assigned experimental error. Nordine and co-workers[10,11] suggested that reaction between gaseous boron and the container used by Storms and Mueller[9] may have led to a significant error. We followed JANAF[1] by adopting $\Delta_f H^{\circ}(\text{B, g, 298.15 K})=560\pm12$ $\text{kJ}\cdot\text{mol}^{-1}$.

1.3. A Brief Historical Account of Borane Research

The first recorded unsuccessful attempt to prepare boranes was made by Wohler in 1858.[12] During the following half century several skillful investigators explored a variety of techniques for synthesizing and identifying gaseous species that incorporated boron and hydrogen. None proved definitive until, in a concrete effort, Stock (beginning about 1908) developed techniques for manipulating the synthetic and characterizing operations in the absence of air and water.[13] In the United States, intensive studies of hydrides of boron were undertaken by Schlesinger in 1929,[14] while in Germany Stock's program was carried forward by Wiberg. In the United States, Schlesinger's investigations were extended by Burg and Brown. A second spurt in synthetic activity occurred in 1958 under the direction of Schaeffer,[15] and thereafter many syntheses, characterizations, and theoretical analyses were published. An abbreviated list of reviews and treatises that have been presented during five decades is given in several reviews.[16–19]

That the boranes may serve as exceptionally high energy (exotic) fuels for propulsion was discussed informally on the Caltech campus during 1936, and seriously proposed by the British in 1947. The U. S. Department of Defense (DoD)

TABLE 4. Ideal gas thermodynamic parameters of BH_2 at 1 bar

T (K)	C_P°	S°	$-[G^\circ - H^\circ(298.15\text{ K})]/T$	$H^\circ - H^\circ(298.15\text{ K})$	$\Delta_f H^\circ$	$\Delta_f G^\circ$	
	(J·K^{-1}·mol^{-1})			(kJ·mol^{-1})			$\log_{10} K_f$
0	0.000	0.000	∞	-10.024	317.641	317.641	$-\infty$
100	33.259	156.902	223.880	-6.698	317.944	312.357	-163.156
200	33.631	180.015	196.822	-3.361	318.254	306.617	-80.079
298.15	34.975	193.671	193.671	0.000	317.984	300.943	-52.723
300	35.006	193.888	193.672	0.065	317.975	300.837	-52.379
400	36.665	204.191	195.065	3.650	317.291	295.219	-38.551
500	38.305	212.577	197.753	7.412	316.399	289.801	-30.275
600	39.961	219.775	200.837	11.363	315.440	284.572	-24.774
700	41.634	226.182	204.008	15.522	314.506	279.502	-20.856
800	43.268	232.021	207.150	19.897	313.645	274.560	-17.927
900	44.807	237.421	210.217	24.484	312.877	269.723	-15.654
1000	46.217	242.459	213.192	29.267	312.193	264.964	-13.840
1100	47.482	247.184	216.069	34.226	311.583	260.271	-12.359
1200	48.603	251.631	218.849	39.338	311.029	255.632	-11.127
1300	49.589	255.827	221.534	44.581	310.509	251.038	-10.087
1400	50.454	259.793	224.126	49.933	310.007	246.482	-9.196
1500	51.210	263.549	226.630	55.377	309.509	241.962	-8.426

initiated an extensive project[20] in 1952 to develop a fuel with properties similar to JP-4, but one that burned with a much higher flame speed and generated a high specific impulse. Different branches of DoD supported research and development of combinations of boron, carbon, and hydrogen (designated: carboranes) that underwent extensive testing.[21,22] Research and development waxed and waned because the ideal high energy fuel (relative to cost, combustion product tolerance, etc.) proved elusive. However, interest in the boranes has not subsided, and is now directed at exploring their many unconventional structures via high level *ab initio* quantum computations. The boranes present particularly challenging aspects that test the reliability of current *ab initio* programs to account for the experimental data and for predicting the possible existence of the boron–hydrogen combinations not yet identified or fully characterized.

2. Thermodynamic Properties of the Boranes

2.1. BH

The listed ideal gas thermodynamic parameters (Table 3) for BH are identical to those of JANAF.[1] The molecular constants and vibrational frequency cited by Herzberg[23,24] were used in the JANAF tables and were confirmed by Bauer *et al.*[25] and Johns *et al.*[26] The value 439.48 ± 8.4 kJ·mol^{-1} for $\Delta_f H^\circ$(BH, 0 K) was adopted by JANAF and compares favorably with the recommended value ($442.94 \pm$ kJ·mol^{-1}) by Gurvich *et al.*[2] That value was derived from the dissociation energy (D_0) estimated by Hurley[27] (327.2 kJ·mol^{-1}) and agreed well with that recommended by Huber and

Herzberg[28] (330.1 kJ·mol^{-1}). Recent *ab initio* calculations,[29-37] however, favor slightly higher D_0 values, ranging from 338.5 to 350.2 kJ·mol^{-1}.

2.2. BH$_2$

The ultraviolet spectrum and molecular structure of BH_2 were reported by Herzberg and Johns.[38] In the ground state ($X\ ^2A_1$) it is bent (C_{2v} symmetry), whereas in the first excited state ($A\ ^2B_1$), it is linear. Several recent high-level *ab initio* calculations[33,39-41] led to structures in good agreement with those measured. In this study, we select the rotational constants of Herzberg and Johns,[38,42] and the vibrational frequencies and the energy difference calculated by Kolbuszewski *et al.*[41]

For $\Delta_f H^\circ$(BH$_2$, 298 K), the JANAF tables proposed a low value (200.83 kJ·mol^{-1}) based on an early appearance potential measurement by Fehlner and Koski.[43] However, recent *ab initio* calculations by Pople *et al.*,[32] Curtiss and Pople,[36] Martin *et al.*,[29] Martin *et al.*,[37] and Allendorf and Melius[34] gave much higher values, in the range 312.96–321.33 kJ·mol^{-1}. We select 317.98 kJ·mol^{-1}, which is an average of the *ab initio* results. This value is also in good agreement with that recommended by Gurvich *et al.*[2] (318.29 kJ·mol^{-1}). The ideal gas thermodynamic parameters for BH$_2$ are listed in Table 4. Compared with those of Gurvich *et al.*[2] the maximum differences for the values of C_P° and S° are 3.0 and 0.4 J·K^{-1}·mol^{-1}, respectively, which are due to differences in the assigned vibrational frequencies.

TABLE 5. Ideal gas thermodynamic parameters of BH_3 at 1 bar

T (K)	C_P°	S°	$-[G^\circ - H^\circ(298.15\ K)]/T$	$H^\circ - H^\circ(298.15\ K)$	$\Delta_f H^\circ$	$\Delta_f G^\circ$	$\log_{10} K_f$
	$(J \cdot K^{-1} \cdot mol^{-1})$			$(kJ \cdot mol^{-1})$			
0	0.000	0.000	∞	−10.060	93.051	93.051	$-\infty$
100	33.258	151.334	218.672	−6.734	91.854	91.860	−47.982
200	33.630	174.436	191.432	−3.399	90.815	92.235	−24.089
298.15	36.017	188.232	188.232	0.000	89.196	93.257	−16.338
300	36.082	188.455	188.233	0.067	89.162	93.283	−16.242
400	40.103	199.367	189.694	3.870	87.243	94.943	−12.398
500	44.427	208.781	192.589	8.096	85.354	97.088	−10.143
600	48.594	217.253	196.004	12.749	83.633	99.601	−8.671
700	52.470	225.039	199.603	17.805	82.127	102.384	−7.640
800	55.993	232.280	203.240	23.232	80.840	105.368	−6.880
900	59.135	239.060	206.848	28.991	79.758	108.502	−6.297
1000	61.898	245.437	210.391	35.046	78.844	111.745	−5.837
1100	64.306	251.452	213.853	41.359	78.068	115.073	−5.464
1200	66.393	257.139	217.225	47.896	77.401	118.468	−5.157
1300	68.198	262.526	220.505	54.628	76.809	121.916	−4.899
1400	69.759	267.639	223.690	61.528	76.273	125.407	−4.679
1500	71.111	272.499	226.783	68.573	75.772	128.934	−4.490

2.3. BH_3

The structure and vibrational frequencies were measured by Kawaguchi and co-workers, using Fourier transform-infrared (FT-IR) and diode laser spectroscopy.[44–46] In the ground state ($X\ ^1A_1$), this species is planar (D_{3h}).[47–49] Kawaguchi[46] also called attention to an earlier mis-assignment of frequencies derived from the matrix-isolation spectra by Kaldor and Porter.[50] The measured vibrational frequencies are in close agreement with ab initio values by Stanton et al.,[51] Martin and Lee,[52] and Galbraith et al.[53] In the present calculations, the rotational constants and the vi-

TABLE 6. Ideal gas thermodynamic parameters of BH_4 at 1 bar

T (K)	C_P°	S°	$-[G^\circ - H^\circ(298.15\ K)]/T$	$H^\circ - H^\circ(298.15\ K)$	$\Delta_f H^\circ$	$\Delta_f G^\circ$	$\log_{10} K_f$
	$(J \cdot K^{-1} \cdot mol^{-1})$			$(kJ \cdot mol^{-1})$			
0	0.000	0.000	∞	−10.771	243.773	243.773	$-\infty$
100	33.381	171.627	246.069	−7.444	241.078	244.091	−127.498
200	36.972	195.547	215.414	−3.973	238.828	247.967	−64.761
298.15	44.282	211.613	211.613	0.000	236.396	252.967	−44.318
300	44.431	211.888	211.614	0.082	236.351	253.071	−44.063
400	52.367	225.766	213.453	4.925	234.019	259.003	−33.822
500	59.687	238.251	217.183	10.534	232.051	265.484	−27.734
600	66.214	249.723	221.663	16.836	230.514	272.323	−23.707
700	71.918	260.369	226.441	23.749	229.396	279.386	−20.848
800	76.820	270.301	231.310	31.193	228.651	286.581	−18.711
900	80.984	279.596	236.164	39.089	228.218	293.852	−17.054
1000	84.499	288.316	240.948	47.368	228.026	301.156	−15.731
1100	87.458	296.512	245.630	55.970	228.020	308.471	−14.648
1200	89.953	304.232	250.195	64.844	228.150	315.780	−13.745
1300	92.061	311.517	254.635	73.948	228.370	323.075	−12.981
1400	93.849	318.407	258.946	83.246	228.650	330.351	−12.325
1500	95.374	324.935	263.130	92.709	228.963	337.604	−11.756

TABLE 7. Ideal gas thermodynamic parameters of BH_5 at 1 bar

T (K)	C_P°	S°	$-[G^\circ - H^\circ(298.15\ \text{K})]/T$	$H^\circ - H^\circ(298.15\ \text{K})$	$\Delta_f H^\circ$	$\Delta_f G^\circ$	$\log_{10} K_f$
	$(\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1})$			$(\text{kJ}\cdot\text{mol}^{-1})$			
0	0.000	0.000	∞	−12.751	89.535	89.535	−∞
100	40.200	181.824	272.600	−9.078	85.687	92.717	−48.429
200	45.121	210.945	235.192	−4.849	82.847	100.848	−26.338
298.15	54.123	230.552	230.552	0.000	79.904	110.310	−19.326
300	54.310	230.888	230.553	0.100	79.851	110.500	−19.239
400	64.242	247.888	232.804	6.034	77.156	121.135	−15.818
500	73.061	263.195	237.376	12.910	74.994	132.390	−13.830
600	80.612	277.201	242.862	20.603	73.384	144.030	−12.539
700	87.091	290.127	248.703	28.997	72.277	155.898	−11.633
800	92.672	302.129	254.640	37.992	71.607	167.893	−10.962
900	97.481	313.329	260.546	47.505	71.305	179.952	−10.444
1000	101.622	323.820	266.354	57.465	71.292	192.026	−10.030
1100	105.186	333.677	272.031	67.810	71.509	204.090	−9.691
1200	108.254	342.964	277.559	78.486	71.902	216.128	−9.408
1300	110.899	351.736	282.930	89.447	72.418	228.127	−9.166
1400	113.183	360.040	288.144	100.654	73.025	240.084	−8.957
1500	115.163	367.918	293.202	112.074	73.691	251.993	−8.775

brational frequencies are those of Kawaguchi[46] supplemented with (2495 cm^{-1}), calculated by Martin and Lee.[52]

The spread in the literature values cited for the enthalpy of formation of BH_3 is about 27 kJ·mol^{-1} (from 79.50 to 106.69 kJ·mol^{-1}).[1,2,32–34,37,54–64] From the recent measured atomization energy reported by Ruscic et al.,[62] $\Delta_f H^\circ$ (BH_3, 0 K) was calculated to be 93.05 kJ·mol^{-1}, which is also in close agreement with that of Gurvich et al.,[2] Saxon,[61] Martin,[37] and Allendorf and Melius.[34] The ideal gas

thermodynamic parameters for BH_3 are given in Table 5. The maximum differences in the values of C_P° and S° between Table 5 and those of Gurvich et al.[2] and the JANAF tables[1] are 2.5 and 5.4 J·K^{-1}·mol^{-1}, respectively. The deviations are due mainly to the difference in the assigned vibrational frequencies.

TABLE 8. Ideal gas thermodynamic parameters of B_2H at 1 bar

T (K)	C_P°	S°	$-[G^\circ - H^\circ(298.15\ \text{K})]/T$	$H^\circ - H^\circ(298.15\ \text{K})$	$\Delta_f H^\circ$	$\Delta_f G^\circ$	$\log_{10} K_f$
	$(\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1})$			$(\text{kJ}\cdot\text{mol}^{-1})$			
0	0.000	0.000	∞	−10.116	734.185	734.185	−∞
100	29.944	175.908	247.845	−7.194	735.559	723.067	−377.685
200	36.555	198.541	217.989	−3.890	736.851	710.051	−185.443
298.15	42.331	214.287	214.287	0.000	737.639	696.709	−122.058
300	42.419	214.549	214.288	0.078	737.649	696.455	−121.262
400	46.192	227.310	216.002	4.523	737.915	682.669	−89.146
500	48.669	237.901	219.353	9.274	737.742	668.870	−69.875
600	50.474	246.941	223.216	14.235	737.277	655.136	−57.034
700	51.923	254.834	227.181	19.357	736.620	641.496	−47.868
800	53.149	261.849	231.084	24.612	735.832	627.959	−41.001
900	54.209	268.172	234.859	29.981	734.953	614.529	−35.666
1000	55.132	273.932	238.483	35.449	733.993	601.196	−31.403
1100	55.933	279.225	241.949	41.004	732.967	587.966	−27.920
1200	56.629	284.123	245.262	46.633	731.881	574.833	−25.021
1300	57.233	288.680	248.429	52.326	730.731	561.793	−22.573
1400	57.757	292.941	251.458	58.076	729.519	548.843	−20.477
1500	58.212	296.942	254.358	63.876	728.246	535.981	−18.664

TABLE 9. Ideal gas thermodynamic parameters of B_2H_2 at 1 bar

T (K)	C_P°	S°	$-[G^\circ - H^\circ(298.15\ K)]/T$	$H^\circ - H^\circ(298.15\ K)$	$\Delta_f H^\circ$	$\Delta_f G^\circ$	$\log_{10} K_f$
	$(J \cdot K^{-1} \cdot mol^{-1})$			$(kJ \cdot mol^{-1})$			
0	0.000	0.000	∞	−10.371	397.061	397.061	$-\infty$
100	29.550	173.929	248.489	−7.456	396.930	389.671	−203.540
200	37.566	196.420	217.243	−4.165	396.861	382.427	−99.878
298.15	46.885	213.238	213.238	0.000	396.538	375.402	−65.768
300	47.034	213.528	213.239	0.087	396.530	375.271	−65.339
400	53.730	228.036	215.171	5.146	395.957	368.264	−48.089
500	58.452	240.560	219.026	10.767	395.193	361.425	−37.757
600	62.066	251.550	223.549	16.800	394.335	354.753	−30.883
700	65.044	261.349	228.262	23.161	393.448	348.226	−25.984
800	67.601	270.211	232.960	29.801	392.569	341.825	−22.319
900	69.828	278.317	237.556	36.686	391.717	335.535	−19.474
1000	71.775	285.800	242.011	43.789	390.891	329.335	−17.202
1100	73.474	292.757	246.311	51.090	390.092	323.218	−15.348
1200	74.953	299.263	250.456	58.568	389.317	317.174	−13.806
1300	76.240	305.377	254.448	66.207	388.551	311.195	−12.504
1400	77.360	311.145	258.293	73.992	387.792	305.273	−11.390
1500	78.336	316.606	262.001	81.909	387.032	299.405	−10.426

2.4. BH_4

Although BH_4 was identified by electron spin resonance (ESR) spectra by Claxton et al.[65] and Symons et al.,[66] there are no experimental determinations of its vibrational frequencies, structure, or enthalpy of formation. That the configuration of BH_4 has C_{2v} symmetry was confirmed recently by Van Zee et al.[67] The theoretical calculations by Paddon-Row and Wong,[68] Boldyrev and Simon,[69] and Saxon[61] are in close agreement. In the present calculations, the rotational constants, $\Delta_f H^\circ(BH_4, 298.15\ K)$, and vibrational frequencies are those of Saxon.[61] The ideal gas thermodynamic parameters for BH_4, 298.15 K are listed in Table 6.

2.5. BH_5

The existence of BH_5 has long been surmised, but the first experimental observation of this species was only reported recently by Tague and Andrews.[70] Theoretical analyses suggested that it is a complex of $H_2 - BH_3$ with C_s symmetry.[71–73] The rotational constants are calculated from the structure reported by Schreiner et al.[72] The vibrational frequencies are those measured by Tague and Andrews (2544, 2475, and 1134 cm^{-1}) supplemented with the calculations by Schreiner et al. (scaling factor=0.943).[72]

There is no experimental determination of its enthalpy of formation. Watts and Bartlett[73] and Schreiner et al.[72] predicted a low enthalpy for complexation (i.e., $H_2 + BH_3 \rightarrow BH_5$) at 0 K (−3.56 and −5.86 $kJ \cdot mol^{-1}$, respectively). Using 93.05 $kJ \cdot mol^{-1}$ for $\Delta_f H^\circ(BH_3, 0\ K)$, values for $\Delta_f H^\circ(BH_5, 0\ K)$ and $\Delta_f H^\circ(BH_5, 298.15\ K)$ are derived, 89.54 $kJ \cdot mol^{-1}$ and 79.90 $kJ \cdot mol^{-1}$, respectively. The ideal gas thermodynamic parameters for BH_5 are given in Table 7.

2.6. B_2H

All the values for B_2H are based on theoretical calculations reported by Adams and Page.[74] They predicted a linear structure (B−B−H), with $C_{\infty v}$ symmetry. The scaling factor for their computed frequencies was 0.943. No other experimental or theoretical data are available. Table 8 lists the ideal gas thermodynamic parameters for this species.

2.7. B_2H_2

Ab initio calculations by Adams and Page,[74] Curtiss and Pople,[75] and Treboux and Barthelat[76] indicated a linear structure, $D_{\infty h}$ symmetry, for the ground state ($^3\Sigma_g$). The first excited state ($^1\Delta_g$) was predicted to be 5140 cm^{-1} above the ground state. The rotational constants were derived from the structure reported by Curtiss and Pople.[75] The vibrational frequencies reported in these three studies are in close agreement; those of Curtiss and Pople[75] (scaled by 0.943) are used in the present calculations. $\Delta_f H^\circ(B_2H_2, g, 298.15\ K)$ is estimated from the computed energy of dissociation ($B_2H_6 \rightarrow B_2H_2 + 2H_2$) by Curtiss and Pople[75] to be 402.50 $kJ \cdot mol^{-1}$. On taking account of the zero-point-energy differences, $\Delta_f H^\circ(B_2H_2, 0\ K) = 397.06\ kJ \cdot mol^{-1}$ and $\Delta_f H^\circ(B_2H_2, g, 298.15\ K) = 396.54\ kJ \cdot mol^{-1}$ were derived. The ideal gas thermodynamic parameters for B_2H_2 are listed in Table 9.

2.8. B_2H_3

The single-bridge and the double-bridge structures of neutral B_2H_3 were investigated theoretically by Adams and Page,[74] which is the only study available. Adams and Page[74]

TABLE 10. Ideal gas thermodynamic parameters of B_2H_3 (single bridge: B–B) at 1 bar

T (K)	C_P°	S°	$-[G^\circ - H^\circ(298.15\ K)]/T$	$H^\circ - H^\circ(298.15\ K)$	$\Delta_f H^\circ$	$\Delta_f G^\circ$	$\log_{10} K_f$
	(J·K⁻¹·mol⁻¹)			(kJ·mol⁻¹)			
0	0.000	0.000	∞	−11.939	309.876	309.876	−∞
100	34.773	190.487	276.372	−8.588	308.681	304.803	−159.210
200	43.312	217.041	240.582	−4.708	307.854	301.237	−78.674
298.15	52.528	236.071	236.071	0.000	306.687	298.225	−52.247
300	52.693	236.397	236.072	0.097	306.663	298.172	−51.916
400	60.677	252.693	238.240	5.781	305.262	295.550	−38.594
500	66.980	266.936	242.584	12.176	303.810	293.289	−30.639
600	72.115	279.616	247.719	19.138	302.417	291.318	−25.361
700	76.478	291.068	253.106	26.573	301.135	289.571	−21.608
800	80.258	301.533	258.515	34.415	299.981	287.999	−18.804
900	83.548	311.181	263.838	42.609	298.952	286.566	−16.632
1000	86.403	320.135	269.025	51.110	298.021	285.238	−14.899
1100	88.872	328.488	274.055	59.876	297.169	284.002	−13.486
1200	91.005	336.315	278.921	68.873	296.373	282.841	−12.312
1300	92.846	343.674	283.622	78.068	295.602	281.747	−11.321
1400	94.436	350.614	288.161	87.434	294.842	280.710	−10.473
1500	95.813	357.178	292.546	96.948	294.076	279.726	−9.741

concluded that both structures have C_{2v} symmetry. We adopted the rotational constants, vibrational frequencies, and $\Delta_f H^\circ$ they reported.[74] For the vibrational frequencies, 0.943 is the scaling factor. The ideal gas thermodynamic parameters for the single-bridge B_2H_3 and double-bridge B_2H_3 are listed in Tables 10 and 11, respectively.

2.9. B_2H_4

The isomers of B_2H_4 have either a single-bridge (B–B) or a double-bridge (B–H–B; B–H–B). For neutral B_2H_4, there are as yet no experimental spectra or structure determinations. Several *ab initio* studies suggested that the single-

TABLE 11. Ideal gas thermodynamic parameters of B_2H_3 (double bridges: B–B and B–H–B) at 1 bar

T (K)	C_P°	S°	$-[G^\circ - H^\circ(298.15\ K)]/T$	$H^\circ - H^\circ(298.15\ K)$	$\Delta_f H^\circ$	$\Delta_f G^\circ$	$\log_{10} K_f$
	(J·K⁻¹·mol⁻¹)			(kJ·mol⁻¹)			
0	0.000	0.000	∞	−11.912	319.108	319.108	−∞
100	34.728	187.816	273.411	−8.559	317.915	314.304	−164.172
200	43.148	214.221	237.729	−4.701	317.066	311.012	−81.227
298.15	52.479	233.223	233.223	0.000	315.892	308.279	−54.008
300	52.642	233.548	233.224	0.097	315.868	308.232	−53.667
400	60.629	249.825	235.389	5.775	314.460	305.895	−39.945
500	67.137	264.077	239.730	12.174	313.013	303.921	−31.750
600	72.538	276.810	244.868	19.165	311.649	302.233	−26.311
700	77.107	288.344	250.267	26.654	310.420	300.764	−22.443
800	81.009	298.902	255.696	34.564	309.335	299.459	−19.552
900	84.348	308.641	261.045	42.837	308.385	298.284	−17.312
1000	87.205	317.680	266.262	51.418	307.534	297.206	−15.524
1100	89.649	326.109	271.323	60.264	306.762	296.211	−14.066
1200	91.740	334.001	276.221	69.336	306.041	295.286	−12.853
1300	93.533	341.417	280.954	78.602	305.341	294.420	−11.830
1400	95.073	348.406	285.525	88.034	304.647	293.605	−10.954
1500	96.401	355.012	289.939	97.610	303.943	292.841	−10.197

TABLE 12. Ideal gas thermodynamic parameters of B_2H_4 (single bridge: B–B) at 1 bar

T (K)	C_P°	S°	$-[G^\circ - H^\circ(298.15\ \text{K})]/T$	$H^\circ - H^\circ(298.15\ \text{K})$	$\Delta_f H^\circ$	$\Delta_f G^\circ$	$\log_{10} K_f$
	(J·K⁻¹·mol⁻¹)			(kJ·mol⁻¹)			
0	0.000	0.000	∞	−12.341	217.985	217.985	−∞
100	34.638	188.819	278.765	−8.995	215.285	216.610	−113.144
200	45.367	215.820	241.004	−5.037	213.189	218.757	−57.133
298.15	57.124	236.154	236.154	0.000	210.964	221.958	−38.885
300	57.335	236.508	236.155	0.106	210.922	222.026	−38.658
400	67.733	254.473	238.534	6.376	208.653	226.072	−29.521
500	76.276	270.536	243.356	13.590	206.560	230.673	−24.098
600	83.423	285.092	249.118	21.585	204.734	235.673	−20.517
700	89.559	298.424	255.222	30.241	203.205	240.955	−17.980
800	94.880	310.738	261.402	39.469	201.961	246.434	16.090
900	99.493	322.187	267.527	49.194	200.975	252.057	−14.629
1000	103.477	332.881	273.534	59.347	200.195	257.774	−13.465
1100	106.906	342.908	279.389	69.870	199.580	263.563	−12.515
1200	109.854	352.340	285.079	80.712	199.090	269.403	−11.727
1300	112.388	361.235	290.599	91.827	198.679	275.281	−11.061
1400	114.570	369.646	295.947	103.178	198.322	281.188	−10.491
1500	116.453	377.616	301.129	114.732	197.991	287.118	−9.998

bridge (D_{2d}) and the double-bridge (C_{2v}) are the most stable.[77–80] These calculations indicate that the two isomers differ only by 0.42 kJ·mol⁻¹, with the single-bridge higher. $\Delta_f H^\circ$(double-bridge B_2H_4, 0 K) was determined experimentally to be 217.57 kJ·mol⁻¹ by Ruscic et al.,[81] which we accepted, although Dill et al.[79] and Curtiss and Pople[77] favored slightly higher values (242.67 and 231.79 kJ·mol⁻¹)

for $\Delta_f H^\circ$(double-bridge B_2H_4, 0 K). The vibrational frequencies are also taken from Curtiss and Pople[77] and scaled by 0.943. Tables 12 and 13 give the ideal gas thermodynamic parameters for the single-bridge B_2H_4 and double-bridge B_2H_4, respectively.

TABLE 13. deal gas thermodynamic parameters of B_2H_4 (double B–H–B bridges) at 1 bar

T (K)	C_P°	S°	$-[G^\circ - H^\circ(298.15\ \text{K})]/T$	$H^\circ - H^\circ(298.15\ \text{K})$	$\Delta_f H^\circ$	$\Delta_f G^\circ$	$\log_{10} K_f$
	(J·K⁻¹·mol⁻¹)			(kJ·mol⁻¹)			
0	0.000	0.000	∞	−11.529	217.567	217.566	−∞
100	33.721	184.395	266.373	−8.198	214.852	216.620	−113.148
200	40.903	209.544	232.186	−4.528	212.467	219.291	−57.272
298.15	51.517	227.825	227.825	0.000	209.734	223.211	−39.105
300	51.721	228.144	227.826	0.095	209.681	223.295	−38.878
400	62.392	244.505	229.984	5.808	206.856	228.262	−29.807
500	71.939	259.477	234.406	12.536	204.275	233.918	−24.437
600	80.214	273.343	239.754	20.154	202.073	240.061	−20.899
700	87.303	286.255	245.485	28.539	200.273	246.541	−18.397
800	93.339	298.318	251.344	37.579	198.841	253.251	−16.535
900	98.459	309.615	257.197	47.176	197.728	260.124	−15.097
1000	102.792	320.220	262.975	57.245	196.862	267.103	−13.952
1100	106.461	330.194	268.637	67.712	196.192	274.161	−13.019
1200	109.572	339.594	274.162	78.518	195.666	281.274	−12.243
1300	112.218	348.472	279.540	89.611	195.233	288.428	−11.589
1400	114.477	356.873	284.766	100.949	194.863	295.611	−11.029
1500	116.412	364.839	289.841	112.496	194.526	302.819	−10.545

TABLE 14. Ideal gas thermodynamic parameters of B_2H_5 (single B–H–B bridge) at 1 bar

T (K)	C_P°	S°	$-[G^\circ - H^\circ(298.15\,K)]/T$	$H^\circ - H^\circ(298.15\,K)$	$\Delta_f H^\circ$	$\Delta_f G^\circ$	$\log_{10} K_f$
	(J·K^{-1}·mol^{-1})			(kJ·mol^{-1})			
0	0.000	0.000	∞	−12.234	266.100	266.100	−∞
100	34.298	196.811	285.740	−8.893	261.896	267.458	−139.703
200	44.341	223.195	248.340	−5.029	258.359	274.393	−71.663
298.15	58.273	243.468	243.468	0.000	254.739	283.033	−49.585
300	58.536	243.829	243.469	0.108	254.672	283.209	−49.310
400	71.942	262.549	245.931	6.647	251.220	293.252	−38.294
500	83.386	279.867	251.008	14.430	248.233	304.115	−31.770
600	93.100	295.952	257.174	23.267	245.786	315.531	−27.469
700	101.420	310.945	263.797	33.003	243.868	327.315	−24.424
800	108.569	324.966	270.576	43.512	242.428	339.338	−22.156
900	114.703	338.117	277.358	54.683	241.402	351.519	−20.401
1000	119.954	350.482	284.058	66.423	240.706	363.792	−19.002
1100	124.442	362.130	290.631	78.649	240.274	376.123	−17.860
1200	128.278	373.127	297.052	91.290	240.044	388.486	−16.910
1300	131.561	383.528	303.308	104.286	239.954	400.863	−16.107
1400	134.379	393.383	309.393	117.586	239.964	413.241	−15.418
1500	136.805	402.739	315.307	131.149	240.038	425.615	−14.821

2.10. B_2H_5

There are two possible isomers of B_2H_5, with one or two (B–H–B) bridges. No experimental data are available for neutral B_2H_5. It has been suggested by *ab initio* calculations[82,83] that the single-bridge (C_{2v}) is the more stable form while the double-bridge (C_s) structure is higher by 20.92 kJ·mol^{-1}. Ruscic *et al.*[84] determined an upper limit

of the B–H bond breaking energy in B_2H_6 (i.e., the reaction $B_2H_6 \rightarrow B_2H_5 + H$) to be 429.70 kJ·mol^{-1}. This value is consistent with those of Curtiss and Pople[82] and Trachtman *et al.*[85] $\Delta_f H^\circ$(single-bridge B_2H_5, 0 K) was thus estimated to be 266.10 kJ·mol^{-1}; $\Delta_f H^\circ$(double-bridge B_2H_5, 0 K) =287.02 kJ·mol^{-1}. The vibrational frequencies computed by Trachtman *et al.*[85] were scaled by 0.943. The ideal gas

TABLE 15. Ideal gas thermodynamic parameters of B_2H_5 (double B–H–B bridges) at 1 bar

T (K)	C_P°	S°	$-[G^\circ - H^\circ(298.15\,K)/T]$	$H^\circ - H^\circ(298.15)$	$\Delta_f H^\circ$	$\Delta_f G^\circ$	$\log_{10} K_f$
	(J·K^{-1}·mol^{-1})			(kJ·mol^{-1})			
0	0.000	0.000	∞	−11.667	287.020	287.020	−∞
100	34.259	201.472	284.704	−8.323	282.818	287.914	−150.388
200	41.176	226.974	250.001	−4.605	279.135	294.414	−76.892
298.15	53.161	245.549	245.549	0.000	275.091	302.765	−53.042
300	53.406	245.879	245.550	0.099	275.015	302.937	−52.745
400	66.468	263.049	247.803	6.098	271.024	312.856	−40.854
500	78.353	279.184	252.481	13.351	267.507	323.731	−33.819
600	88.815	294.415	258.213	21.721	264.593	335.260	−29.187
700	97.918	308.807	264.423	31.069	262.286	347.229	−25.910
800	105.761	322.407	270.829	41.263	260.531	359.488	−23.472
900	112.466	335.262	277.280	52.183	259.254	371.941	−21.587
1000	118.168	347.414	283.692	63.723	258.358	384.511	−20.084
1100	123.007	358.910	290.012	75.788	257.766	397.157	−18.859
1200	127.116	369.794	296.211	88.300	257.406	409.848	−17.840
1300	130.611	380.111	302.272	101.191	257.211	422.562	−16.978
1400	133.594	389.902	308.184	114.405	257.135	435.286	−16.240
1500	136.149	399.208	313.945	127.895	257.138	448.010	−15.601

TABLE 16. Ideal gas thermodynamic parameters of B_2H_6 at 1 bar

T (K)	C_P°	S°	$-[G^\circ - H^\circ(298.15\ K)]/T$	$H^\circ - H^\circ(298.15\ K)$	$\Delta_f H^\circ$	$\Delta_f G^\circ$	$\log_{10} K_f$
	$(J \cdot K^{-1} \cdot mol^{-1})$			$(kJ \cdot mol^{-1})$			
0	0.000	0.000	∞	-11.933	52.297	52.297	$-\infty$
100	34.462	186.824	272.677	-8.585	46.600	58.197	-30.399
200	42.210	212.647	236.732	-4.817	41.621	71.706	-18.727
298.15	56.654	232.050	232.050	0.000	36.401	87.581	-15.344
300	56.956	232.402	232.051	0.105	36.305	87.900	-15.304
400	73.122	251.019	234.480	6.615	31.372	105.859	-13.823
500	87.841	268.951	239.593	14.679	27.204	124.978	-13.056
600	100.703	286.131	245.929	24.121	23.898	144.859	-12.611
700	111.798	302.509	252.851	34.760	21.413	165.227	-12.329
800	121.285	318.074	260.040	46.427	19.655	185.898	-12.138
900	129.342	332.837	267.315	58.970	18.513	206.755	-12.000
1000	136.159	346.828	274.573	72.254	17.860	227.708	-11.894
1100	141.919	360.083	281.750	86.166	17.595	248.708	-11.810
1200	146.792	372.646	288.806	100.609	17.627	269.720	-11.740
1300	150.925	384.564	295.717	115.500	17.872	290.721	-11.681
1400	154.444	395.881	302.471	130.773	18.273	311.696	-11.629
1500	157.452	406.641	309.060	146.372	18.779	332.637	-11.583

thermodynamic parameters for the single-bridge B_2H_5 and double-bridge B_2H_5 are listed in Tables 14 and 15, respectively.

2.11. B_2H_6

The structure[86-94] and vibrational frequencies[94-103] of B_2H_6 have been investigated extensively. It has D_{2h} symmetry. Duncan and co-workers[99-101] presented a comprehensive analysis and literature review of its structure and vibrational frequencies. Their results were adopted for the present calculations. The published values for $\Delta_f H^\circ(B_2H_6$, g, 298.15 K) range from 23.43 to 41.59 kJ·mol^{-1}.[1,2,62,63,104-108] We accepted 36.40 kJ·mol^{-1} for $\Delta_f H^\circ(B_2H_6$, g, 298.15 K), which was derived from $\Delta_f H^\circ(B_2H_6$, g, 0 K)=52.30 kJ·mol^{-1}, suggested by Ruscic et al.[62] This value is in close agreement with those determined by Gunn (35.98 kJ·mol^{-1}),[107] recommended by Gurvich et al. (36.82 kJ·mol^{-1}),[2] and Wagman et al. (35.56 kJ·mol^{-1}).[63] The ideal gas thermodynamic parameters for B_2H_6 are listed in Table 16.

2.12. B_3H_7

B_3H_7 may exist in two stable configurations with C_s and C_{2v} symmetries.[109] Experimental spectra, structures, and enthalpies of formation are not available, but there are numerous theoretical proposals for their structures and relative stability.[109-120] Apparently, the C_s structure, with double-bridge hydrogens, locates a global minimum. The second lowest-energy structure, with C_{2v} symmetry, is 17.99 kJ·mol^{-1} higher. McKee[110] reported a value of 128.45 kJ·mol^{-1} for $\Delta_f H^\circ(C_s$-B_3H_7, g, 298.15 K), which we

adopted; it is in agreement with that of Stanton et al.[111] $\Delta_f H^\circ(C_{2v}$-B_3H_7, g, 298.15 K) is calculated to be 146.44 kJ·mol^{-1}. The computed frequencies of Stanton et al.[111] are scaled by 0.943 for the present calculations. Tables 17 and 18 give the ideal gas thermodynamic parameters for C_s-B_3H_7 and C_{2v}-B_3H_7, respectively.

2.13. B_3H_9

Ab initio calculations[111,115,119-125] of B_3H_9 indicate that its C_{3v} structure is the most stable. The rotational constants used in this study are derived from the calculated structure proposed by Stanton et al.[124] The vibrational frequencies are those of Duke et al.;[125] a scaling factor of 0.943 was used. McKee[110] derived a value of 138.91 kJ·mol^{-1} for $\Delta_f H^\circ$ (B_3H_9, g, 298.15 K), which we accepted. The ideal gas thermodynamic parameters for B_3H_9 are listed in Table 19.

2.14. B_4H_4

Early ab initio calculations indicated that the T_d configuration was the most stable.[126-129] However, a later analysis by Mach et al.[130] showed that a structure with C_s symmetry locates a global minimum that is approximately 25.1 kJ·mol^{-1} lower than that of T_d. The rotational constants were derived from the structure of Mach et al.[130] The vibrational frequencies (scaled by 0.943) were computed by Carpenter,[131] who also concluded that C_s has the lower energy. The ideal gas thermodynamic parameters for B_4H_4 are listed in Table 20.

TABLE 17. Ideal gas thermodynamic parameters of B_3H_7 (C_s) at 1 bar

T (K)	C_P°	S°	$-[G^\circ-H^\circ(298.15\ \mathrm{K})]/T$	$H^\circ-H^\circ(298.15\ \mathrm{K})$	$\Delta_f H^\circ$	$\Delta_f G^\circ$	$\log_{10} K_f$
	(J·K⁻¹·mol⁻¹)			(kJ·mol⁻¹)			
0	0.000	0.000	∞	−14.085	147.640	147.640	−∞
100	36.431	212.970	319.912	−10.694	140.463	154.512	−80.708
200	52.815	242.538	274.217	−6.336	134.393	170.925	−44.640
298.15	76.709	267.994	267.994	0.000	128.449	190.132	−33.310
300	77.169	268.470	267.995	0.142	128.343	190.516	−33.171
400	100.457	293.942	271.311	9.053	122.993	212.071	−27.693
500	119.923	318.521	278.314	20.103	118.620	234.866	−24.536
600	135.967	341.849	286.977	32.923	115.245	258.449	−22.500
700	149.326	363.842	296.403	47.208	112.782	282.524	−21.082
800	160.534	384.535	306.139	62.717	111.107	306.894	−20.038
900	169.965	404.004	315.942	79.255	110.093	331.437	−19.236
1000	177.915	422.335	325.674	96.660	109.595	356.059	−18.598
1100	184.625	439.615	335.255	114.797	109.505	380.712	−18.078
1200	190.305	455.930	344.638	133.551	109.722	405.361	−17.645
1300	195.127	471.358	353.797	152.829	110.151	429.984	−17.277
1400	199.237	485.973	362.721	172.553	110.731	454.567	−16.960
1500	202.757	499.842	371.404	192.657	111.405	479.102	−16.684

2.15. B₄H₁₀

The structure of B_4H_{10} was confirmed to have C_{2v} symmetry by x-ray diffraction,[132] electron diffraction,[133–135] and microwave spectroscopy.[134,136] The published geometric parameters are in good agreement; the rotational constants are those of Dain et al.[134] Its infrared and Raman spectra were also investigated.[137,138] The experimental frequency assign-

ments of Dahl and Taylor[137] along with two calculated vibrational frequencies by McKee[110] (779 and 525 cm⁻¹) were used. Its enthalpy of formation was estimated empirically[139,140] and confirmed by ab initio calculations.[110] The spread in the published values of $\Delta_f H^\circ$ (B_4H_{10}, g, 298.15 K) covers the range from 57.74 to 72.38

TABLE 18. Ideal gas thermodynamic parameters of B_3H_7 (C_{2v}) at 1 bar

T (K)	C_P°	S°	$-[G^\circ-H^\circ(298.15\ \mathrm{K})]/T$	$H^\circ-H^\circ(298.15\ \mathrm{K})$	$\Delta_f H^\circ$	$\Delta_f G^\circ$	$\log_{10} K_f$
	(J·K⁻¹·mol⁻¹)			(kJ·mol⁻¹)			
0	0.000	0.000	∞	−14.821	164.896	164.896	−∞
100	36.972	207.408	321.641	−11.423	157.725	172.331	−90.015
200	57.119	238.578	272.632	−6.811	151.909	189.233	−49.422
298.15	81.622	265.958	265.958	0.000	146.440	208.731	−36.568
300	82.071	266.465	265.960	0.151	146.343	209.118	−36.410
400	104.337	293.223	269.457	9.506	141.438	230.804	−30.139
500	122.591	318.534	276.768	20.883	137.391	253.630	−26.496
600	137.665	342.259	285.728	33.919	134.232	277.190	−24.131
700	150.344	364.459	295.407	48.337	131.902	301.212	−22.476
800	161.102	385.257	305.352	63.924	130.305	325.515	−21.254
900	170.245	404.774	315.326	80.503	129.332	349.983	−20.312
1000	178.012	423.124	325.198	97.927	128.853	374.526	−19.563
1100	184.610	440.409	334.893	116.067	128.766	399.100	−18.951
1200	190.220	456.719	344.372	134.816	128.978	423.671	−18.442
1300	195.002	472.138	353.613	154.083	129.396	448.215	−18.009
1400	199.090	486.743	362.605	173.793	129.962	472.720	−17.637
1500	202.598	500.602	371.347	193.882	130.621	497.179	−17.313

TABLE 19. Ideal gas thermodynamic parameters of B_3H_9 at 1 bar

T (K)	C_P°	S°	$-[G^\circ - H^\circ(298.15 \text{ K})]/T$	$H^\circ - H^\circ(298.15 \text{ K})$	$\Delta_f H^\circ$	$\Delta_f G^\circ$	$\log_{10} K_f$
	(J·K⁻¹·mol⁻¹)			(kJ·mol⁻¹)			
0	0.000	0.000		−16.763	163.889	163.889	−∞
100	43.570	210.550	341.998	−13.145	153.940	178.305	−93.135
200	65.835	247.277	285.875	−7.720	146.243	205.710	−53.725
298.15	91.697	278.337	278.337	0.000	138.909	236.471	−41.428
300	92.187	278.905	278.339	0.170	138.777	237.078	−41.278
400	117.368	308.945	282.264	10.672	132.114	270.877	−35.372
500	139.343	337.555	290.486	23.535	126.629	306.226	−31.991
600	158.322	364.680	300.612	38.441	122.412	342.564	−29.822
700	174.703	390.347	311.614	55.113	119.398	379.511	−28.319
800	188.778	414.618	322.987	73.305	117.453	416.812	−27.215
900	200.803	437.566	334.455	92.800	116.422	454.305	−26.367
1000	211.033	459.267	345.861	113.405	116.120	491.867	−25.692
1100	219.721	479.799	357.113	134.955	116.404	529.432	−25.140
1200	227.102	499.242	368.154	157.306	117.140	566.953	−24.678
1300	233.384	517.675	378.953	180.339	118.203	604.399	−24.285
1400	238.749	535.172	389.492	203.952	119.508	641.752	−23.944
1500	243.347	551.805	399.763	228.063	120.981	679.004	−23.645

kJ·mol⁻¹.[63,110,139,140] We adopted 66.11 kJ·mol⁻¹, suggested by Wagman et al.[63] The ideal gas thermodynamic parameters for B_4H_{10} are listed in Table 21.

2.16. B_4H_{12}

Theoretical studies[115,141] indicated that the C_{2v} structure was the most stable; it is about 46.0 kJ·mol⁻¹ lower than the

D_3 isomer.[142] The rotational constants were calculated from the structure of Shen et al.[141] $\Delta_f H^\circ$ (B_4H_{12}, 0 K) was determined to be 222.16 kJ·mol⁻¹ from the theoretical dimerization energy (i.e., for the reaction $2B_2H_6 = B_4H_{12}$) reported by Shen et al.[141] The vibrational frequencies also were selected from Shen et al. with a scaling factor of 0.943. Table 22 gives the ideal gas thermodynamic parameters for B_4H_{12}.

TABLE 20. Ideal gas thermodynamic parameters of B_4H_4 at 1 bar

T (K)	C_P°	S°	$-[G^\circ - H^\circ(298.15 \text{ K})]/T$	$H^\circ - H^\circ(298.15 \text{ K})$	$\Delta_f H^\circ$	$\Delta_f G^\circ$	$\log_{10} K_f$
	(J·K⁻¹·mol⁻¹)			(kJ·mol⁻¹)			
0	0.000	0.000	∞	−14.928	333.046	333.046	−∞
100	38.280	218.610	333.313	−11.470	330.410	328.817	−171.754
200	57.465	250.309	284.246	−6.787	328.373	328.011	−85.666
298.15	80.384	277.614	277.614	0.000	326.184	328.296	−57.515
300	80.779	278.113	277.616	0.149	326.143	328.309	−57.163
400	99.313	304.021	281.022	9.199	323.929	329.364	−43.010
500	113.086	327.735	288.030	19.852	321.812	330.970	−34.576
600	123.641	349.325	296.475	31.710	319.888	332.988	−28.989
700	132.067	369.039	305.453	44.510	318.192	335.309	−25.021
800	138.976	387.140	314.549	58.073	316.717	337.856	−22.059
900	144.723	403.851	323.555	72.267	315.439	340.580	−19.766
1000	149.542	419.356	332.369	86.987	314.299	343.431	−17.939
1100	153.601	433.804	340.941	102.150	313.264	346.396	−16.449
1200	157.035	447.321	349.249	117.686	312.292	349.453	−15.211
1300	159.952	460.008	357.286	133.539	311.336	352.592	−14.167
1400	162.441	471.956	365.054	149.662	310.370	355.801	−13.275
1500	164.575	483.238	372.560	166.016	309.372	359.080	−12.504

TABLE 21. Ideal gas thermodynamic parameters of B_4H_{10} at 1 bar

T (K)	C_P°	S°	$-[G^\circ - H^\circ(298.15 \text{ K})]/T$	$H^\circ - H^\circ(298.15 \text{ K})$	$\Delta_f H^\circ$	$\Delta_f G^\circ$	$\log_{10} K_f$
	(J·K^{-1}·mol^{-1})			(kJ·mol^{-1})			
0	0.000	0.000	∞	−15.488	97.810	97.810	−∞
100	37.691	219.203	339.717	−12.051	86.156	114.722	−59.924
200	58.674	250.627	287.628	−7.400	76.005	147.227	−38.451
298.15	93.172	280.272	280.272	0.000	66.107	184.313	−32.290
300	93.859	280.850	280.274	0.173	65.931	185.048	−32.219
400	129.516	312.826	284.392	11.374	57.150	226.122	−29.528
500	160.227	345.127	293.315	25.906	50.143	269.210	−28.124
600	185.804	376.673	304.594	43.247	44.915	313.545	−27.296
700	207.049	406.960	317.071	62.923	41.281	358.626	−26.761
800	224.715	435.797	330.125	84.538	38.999	404.128	−26.386
900	239.417	463.140	343.399	107.767	37.834	449.853	−26.108
1000	251.672	489.019	356.679	132.340	37.535	495.652	−25.890
1100	261.914	513.500	369.833	158.034	37.914	541.450	−25.711
1200	270.504	536.669	382.779	184.668	38.806	587.193	−25.559
1300	277.742	558.615	395.469	212.090	40.055	632.846	−25.428
1400	283.872	579.428	407.872	240.179	41.564	678.392	−25.311
1500	289.091	599.196	419.973	268.834	43.243	723.820	−25.205

2.17. B_5H_9

B_5H_9 has C_{4v} symmetry, determined experimentally (x-ray diffraction,[143] electron diffraction,[144,145] and microwave spectroscopy[146,147] and supported by ab initio calculations.[110,148]) The rotational constants were derived from the data compiled by Beaudet.[148] The vibrational fre-

quencies were measured by Kalasinsky,[149] and supplemented with five ab initio scaled values by McKee[110] (1358, 732, 1813, 1079, and 1684 cm^{-1}). The scaling factor is 0.94.[110]

$\Delta_f H^\circ(B_5H_9, \text{g}, 298.15 \text{ K})$ was determined experimentally by Gunn and Green[150] and Prosen et al.[151] The JANAF tables accepted an average value (73.22 kJ·mol^{-1}), which

TABLE 22. Ideal gas thermodynamic parameters of B_4H_{12} at 1 bar

T (K)	C_P°	S°	$-[G^\circ - H^\circ(298.15 \text{ K})]/T$	$H^\circ - H^\circ(298.15 \text{ K})$	$\Delta_f H^\circ$	$\Delta_f G^\circ$	$\log_{10} K_f$
	(J·K^{-1}·mol^{-1})			(kJ·mol^{-1})			
0	0.000	0.000	∞	−21.752	222.164	222.164	−∞
100	52.672	224.869	403.368	−17.850	207.977	246.049	−128.521
200	90.147	272.762	326.394	−10.726	197.604	288.282	−75.290
298.15	128.249	315.891	315.891	0.000	188.259	334.807	−58.656
300	128.947	316.686	315.893	0.238	188.095	335.718	−58.453
400	164.130	358.726	321.387	14.936	179.904	386.203	−50.432
500	194.016	398.655	332.885	32.885	173.392	438.563	−45.816
600	219.347	436.329	347.017	53.587	168.596	492.078	−42.838
700	240.955	471.808	362.336	76.631	165.391	546.267	−40.762
800	259.405	505.220	378.129	101.673	163.584	600.813	−39.228
900	275.124	536.706	394.017	128.421	162.963	655.519	−38.045
1000	288.484	566.404	409.785	156.619	163.286	710.234	−37.098
1100	299.832	594.446	425.309	186.050	164.363	764.882	−36.321
1200	309.476	620.960	440.519	216.529	166.022	819.407	−35.667
1300	317.691	646.064	455.374	247.898	168.097	873.778	−35.108
1400	324.711	669.871	469.852	280.027	170.482	927.975	−34.623
1500	330.733	692.485	483.947	312.807	173.078	981.991	−34.195

TABLE 23. Ideal gas thermodynamic parameters of B_5H_9 at 1 bar

T (K)	C_P°	S°	$-[G^\circ - H^\circ(298.15\ \text{K})]/T$	$H^\circ - H^\circ(298.15\ \text{K})$	$\Delta_f H^\circ$	$\Delta_f G^\circ$	$\log_{10} K_f$
	(J·K^{-1}·mol^{-1})			(kJ·mol^{-1})			
0	0.000	0.000		−16.056	101.336	101.336	−∞
100	37.366	217.140	343.421	−12.628	91.148	114.915	−60.024
200	61.695	249.018	288.477	−7.892	82.096	142.182	−37.134
298.15	99.589	280.617	280.617	0.000	73.220	173.581	−30.410
300	100.307	281.236	280.619	0.185	73.061	174.205	−30.331
400	136.791	315.213	285.005	12.083	65.068	209.159	−27.313
500	167.645	349.157	294.452	27.352	58.528	245.968	−25.696
600	193.144	382.052	306.329	45.433	53.524	283.954	−24.720
700	214.111	413.452	319.409	65.830	49.925	322.662	−24.077
800	231.345	443.205	333.041	88.131	47.522	361.799	−23.623
900	245.534	471.300	346.858	111.998	46.101	401.182	−23.284
1000	257.251	497.795	360.640	137.156	45.426	440.672	−23.018
1100	266.970	522.784	374.255	163.382	45.326	480.206	−22.803
1200	275.074	546.372	387.625	190.496	45.649	519.731	−22.623
1300	281.869	568.665	400.701	218.353	46.252	559.220	−22.469
1400	287.601	589.769	413.459	246.834	47.045	598.651	−22.336
1500	292.468	609.782	425.886	275.844	47.949	638.019	−22.217

accords with that of Wagman et al.[63] McKee[110] reported a theoretical value of 64.02 kJ·mol^{-1}. Here we adopted the value recommended in the JANAF tables[1]. The ideal gas thermodynamic parameters for B_5H_9 are given in Table 23. The maximum differences on the values of C°_p and S° between Table 23 and those of the JANAF tables[1] are 1.4 and 12.0 J·K^{-1}·mol^{-1}, respectively.

2.18. B_5H_{11}

The structure of B_5H_{11} was determined initially to have C_s symmetry by x-ray[152,153] and electron diffraction[145] and supported by early theoretical calculations.[154,155] However, recent electron[156] and x-ray diffraction[157] determinations and

TABLE 24. Ideal gas thermodynamic parameters of B_5H_{11} at 1 bar

T (K)	C_P°	S°	$-[G^\circ - H^\circ(298.15\ \text{K})]/T$	$H^\circ - H^\circ(298.15\ \text{K})$	$\Delta_f H^\circ$	$\Delta_f G^\circ$	$\log_{10} K_f$
	(J·K^{-1}·mol^{-1})			(kJ·mol^{-1})			
0	0.000	0.000	∞	−20.776	135.207	135.207	−∞
100	46.877	235.147	405.750	−17.060	122.309	154.348	−80.622
200	85.282	278.480	331.426	−10.589	112.297	190.374	−49.720
298.15	130.312	320.958	320.958	0.000	103.345	230.641	−40.407
300	131.131	321.766	320.960	0.242	103.190	231.432	−40.295
400	171.525	365.212	326.610	15.441	95.591	275.369	−35.959
500	204.234	407.132	338.556	34.288	89.706	321.027	−33.537
600	230.770	446.794	353.324	56.082	85.487	367.717	32.012
700	252.604	484.060	369.367	80.285	82.756	414.991	−30.967
800	270.722	519.011	385.912	106.480	81.293	462.564	−30.202
900	285.815	551.796	402.541	134.329	80.881	510.262	−29.614
1000	298.419	582.581	419.022	163.560	81.274	557.951	−29.144
1100	308.974	611.534	435.220	193.945	82.295	605.573	−28.756
1200	317.845	638.809	451.060	225.298	83.780	653.085	−28.428
1300	325.332	664.554	466.502	257.468	85.574	700.460	−28.144
1400	331.683	688.903	481.526	290.327	87.581	747.686	−27.896
1500	337.097	711.976	496.127	323.773	89.713	794.761	−27.676

TABLE 25. Ideal gas thermodynamic parameters of B_6H_{10} at 1 bar

T (K)	C_P°	S°	$-[G^\circ - H^\circ(298.15\text{ K})]/T$	$H^\circ - H^\circ(298.18\text{ K})$	$\Delta_f H^\circ$	$\Delta_f G^\circ$	$\log_{10} K_f$
	(J·K^{-1}·mol^{-1})			(kJ·mol^{-1})			
0	0.000	0.000	∞	−18.628	125.549	125.549	−∞
100	37.696	221.711	373.954	−15.224	113.814	142.191	−74.272
200	75.030	257.381	306.706	−9.865	103.705	174.544	−45.585
298.15	125.739	296.836	296.836	0.000	94.558	211.304	−37.019
300	126.653	297.617	296.839	0.233	94.401	212.030	−36.917
400	171.231	340.392	302.369	15.209	86.669	252.450	−32.966
500	206.570	382.552	314.215	34.169	80.627	294.626	−30.779
600	234.639	422.790	328.988	56.281	76.209	337.869	−29.414
700	257.233	460.718	345.125	80.915	73.222	381.735	−28.485
800	275.602	496.307	361.823	107.588	71.432	425.940	−27.811
900	290.643	529.666	378.639	135.924	70.613	470.316	−27.296
1000	303.030	560.950	395.322	165.628	70.518	514.732	−26.886
1100	313.291	590.328	411.729	196.460	70.975	559.135	−26.551
1200	321.839	617.966	427.775	228.229	71.826	603.482	−26.268
1300	329.005	644.018	443.417	260.782	72.922	647.748	−26.026
1400	335.050	668.627	458.633	293.993	74.173	691.920	−25.815
1500	340.180	691.923	473.416	327.761	75.498	735.997	−25.629

high-level *ab initio* calculations[110,158-160] indicated that the C_1 isomer is more stable than its C_s counterpart by about 4.2 kJ·mol^{-1} or less.[159,160] The rotational constants were derived from the data compiled by Beaudet[148] which are in good agreement with a recent experimental determination by Brain *et al.*[156] The vibrational frequencies are those calculated by McKee;[110] they were scaled by a factor of 0.90. The published values for $\Delta_f H^\circ$ (B_5H_{11}, g, 298.15 K) are in the range from 101.67 to 116.73 kJ·mol^{-1}.[63,110,139,140,161,162] Among them, *ab initio* calculations by McKee[110] gave a value of

101.67 kJ·mol^{-1}. The evaluation of Wagman *et al.*[63] (103.35 kJ·mol^{-1}) was accepted in the present calculations. Table 24 gives the ideal gas thermodynamic parameters for B_5H_{11}.

2.19. B_6H_{10}

The crystal structure of B_6H_{10} determined by x-ray diffraction[163] allocated C_s symmetry to this species, but solution nuclear magnetic resonance (NMR) spectra[164-167] in-
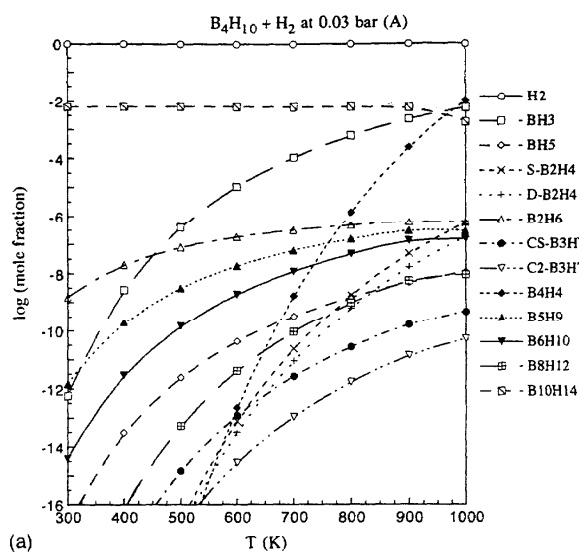
TABLE 26. Ideal gas thermodynamic parameters of B_8H_{12} at 1 bar

T (K)	C_P°	S°	$-[G^\circ - H^\circ(298.15\text{ K})]/T$	$H^\circ - H^\circ(298.15\text{ K})$	$\Delta_f H^\circ$	$\Delta_f G^\circ$	$\log_{10} K_f$
	(J·K^{-1}·mol^{-1})			(kJ·mol^{-1})			
0	0.000	0.000	∞	−22.156	185.635	185.635	−∞
100	42.250	246.283	432.723	−18.644	170.961	207.015	−108.132
200	92.007	288.755	349.920	−12.233	158.544	247.958	−64.759
298.15	157.032	337.652	337.652	0.000	147.277	294.295	−51.558
300	158.209	338.627	337.655	0.292	147.082	295.208	−51.399
400	215.453	392.292	344.584	19.083	137.534	346.076	−45.192
500	260.231	445.389	359.466	42.962	130.027	399.119	−41.695
600	295.276	496.058	378.048	70.806	124.449	453.496	−39.480
700	323.247	543.753	398.350	101.782	120.557	508.667	−37.957
800	345.951	588.450	419.349	135.280	118.073	564.292	−36.844
900	364.591	630.308	440.489	170.837	116.738	620.167	−35.993
1000	380.019	669.545	461.453	208.092	116.265	676.127	−35.317
1100	392.871	706.386	482.063	246.755	116.454	732.109	−34.764
1200	403.642	741.046	502.215	286.597	117.123	788.056	−34.303
1300	412.721	773.723	521.855	327.428	118.092	843.936	−33.909
1400	420.417	804.598	540.959	369.095	119.256	899.727	−33.569
1500	426.979	833.833	559.518	411.473	120.514	955.430	−33.270

TABLE 27. Ideal gas thermodynamic parameters of B_9H_{15} at 1 bar

T (K)	C_P°	S°	$-[G^\circ - H^\circ(298.15\ K)]/T$	$H^\circ - H^\circ(298.15\ K)$	$\Delta_f H^\circ$	$\Delta_f G^\circ$	$\log_{10} K_f$
	(J·K^{-1}·mol^{-1})			(kJ·mol^{-1})			
0	0.000	0.000	∞	−26.068	206.768	206.768	$-\infty$
100	49.467	255.494	478.725	−22.323	187.805	238.078	−124.357
200	110.660	306.422	379.555	−14.627	172.299	294.487	−76.911
298.15	187.019	364.906	364.906	0.000	158.408	357.483	−62.628
300	188.399	366.067	364.909	0.347	158.169	358.720	−62.458
400	255.626	429.831	373.147	22.674	146.433	427.407	−55.813
500	308.549	492.798	390.818	50.990	137.248	498.761	−52.104
600	350.366	552.892	412.869	84.014	130.476	571.742	−49.774
700	384.106	609.524	436.959	120.795	125.827	645.682	−48.181
800	411.765	662.679	461.887	160.633	122.970	720.158	−47.021
900	434.659	712.541	486.997	202.990	121.593	794.910	−46.135
1000	453.728	759.354	511.917	247.438	121.344	869.735	−45.430
1100	469.689	803.370	536.432	293.632	121.975	944.550	−44.852
1200	483.113	844.831	560.421	341.291	123.258	1019.282	−44.367
1300	494.458	883.961	583.818	390.185	124.966	1093.892	−43.952
1400	504.096	920.966	606.591	440.126	126.967	1168.351	−43.591
1500	512.327	956.034	628.728	490.958	129.133	1242.658	−43.272

dicated C_{5v} symmetry. Microwave spectra[168] and *ab initio* calculations[110,160] favor C_s. The higher symmetry that is consistent with the NMR spectra may be due to hydrogen migration.[148] The rotational constants were calculated from the structural data compiled by Beaudet.[148] The vibrational frequencies are those calculated by McKee[110] and were scaled by 0.90. Literature citations for $\Delta_f H^\circ$ (B_6H_{10}, g, 298.15 K) are in the range 82.01–94.56 kJ·mol^{-1}.[63,110,139,140,150] We adopted a value of 94.56

kJ·mol^{-1}, as recommended by Wagman *et al.*[63] The ideal gas thermodynamic parameters for B_6H_{10} are given in Table 25.

2.20. B$_8$H$_{12}$

The x-ray diffraction data[169] indicated that the structure of B_8H_{12} has C_s symmetry, which is supported by *ab initio* calculations.[110,170] However, the NMR spectra[171,172] favor C_{2v} symmetry. In this case also, the higher symmetry is most likely due to rapid bridge-hydrogen tautomerism. The rota-

TABLE 28. Ideal gas thermodynamic parameters of $B_{10}H_{14}$ at 1 bar

T (K)	C_P°	S°	$-[G^\circ - H^\circ(298.15\ K)]/T$	$H^\circ - H^\circ(298.15\ K)$	$\Delta_f H^\circ$	$\Delta_f G^\circ$	$\log_{10} K_f$
	(J·K^{-1}·mol^{-1})			(kJ·mol^{-1})			
0	0.000	0.000	∞	−24.709	93.979	93.979	$-\infty$
100	43.093	248.287	460.012	−21.173	76.283	122.271	−63.867
200	103.884	293.868	365.120	−14.251	61.017	174.258	−45.511
298.15	186.093	350.742	350.742	0.000	47.279	232.835	−40.791
300	187.572	351.898	350.746	0.346	47.044	233.988	−40.740
400	258.795	416.033	359.007	22.810	35.536	298.104	−38.928
500	313.617	479.941	376.836	51.552	26.507	364.836	−38.114
600	356.112	541.032	399.158	85.124	19.766	433.177	−37.711
700	389.879	598.557	423.579	122.485	15.011	502.480	−37.495
800	417.247	652.467	448.857	162.887	11.913	572.344	−37.370
900	439.714	702.951	474.316	205.772	10.169	642.523	−37.290
1000	458.319	750.272	499.570	250.702	9.441	712.821	−37.233
1100	473.828	794.704	524.402	297.332	9.499	783.161	−37.189
1200	486.834	836.507	548.687	345.384	10.124	853.476	−37.150
1300	497.803	875.920	572.357	394.631	11.105	923.726	−37.115
1400	507.107	913.160	595.382	444.889	12.315	993.883	−37.082
1500	515.043	948.425	617.753	496.007	13.637	1063.947	−37.049

TABLE 29. The thermodynamic (NASA) polynomials for hydrides of boron[a]

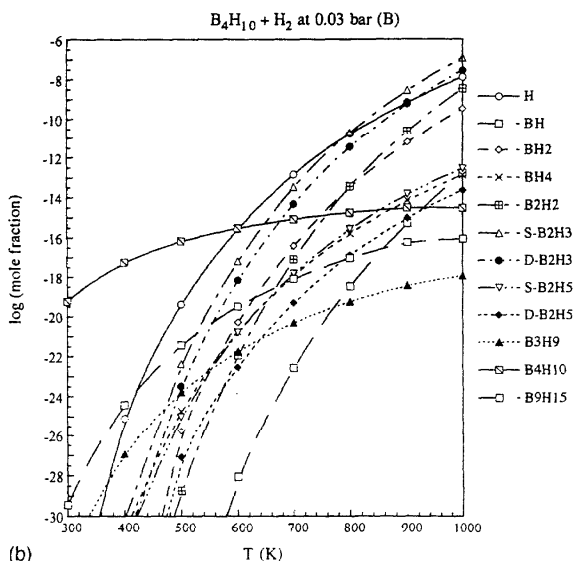| Species	a_1	a_2	a_3	a_4	a_5	a_6	a_7
BH[b]	$3.686\,220\,6\times10^{+0}$	$-1.305\,543\,5\times10^{-3}$	$2.674\,210\,5\times10^{-6}$	$-9.107\,373\,8\times10^{-10}$	$-1.559\,113\,6\times10^{-13}$	$5.217\,633\,0\times10^{+4}$	$-5.524\,540\,1\times10^{-2}$
	$2.891\,907\,9\times10^{+0}$	$1.583\,294\,6\times10^{-3}$	$-5.826\,172\,9\times10^{-7}$	$1.024\,206\,8\times10^{-10}$	$-6.766\,956\,9\times10^{-15}$	$5.232\,871\,4\times10^{+4}$	$3.796\,243\,3\times10^{+0}$
BH$_2$	$3.329\,424\,0\times10^{+0}$	$4.000\,397\,4\times10^{-3}$	$-4.950\,936\,5\times10^{-6}$	$5.480\,506\,5\times10^{-10}$	$-2.300\,100\,6\times10^{-12}$	$3.711\,091\,6\times10^{+4}$	$3.321\,928\,5\times10^{+0}$
	$2.579\,118\,5\times10^{+0}$	$4.572\,175\,6\times10^{-3}$	$-1.859\,847\,6\times10^{-6}$	$3.394\,567\,4\times10^{-10}$	$-2.318\,742\,8\times10^{-14}$	$3.769\,052\,8\times10^{+4}$	$7.853\,256\,3\times10^{+0}$
BH$_3$	$3.588\,842\,9\times10^{+0}$	$-6.707\,100\,9\times10^{-4}$	$1.467\,026\,6\times10^{-6}$	$-1.515\,288\,8\times10^{-10}$	$5.011\,922\,4\times10^{-12}$	$9.585\,394\,2\times10^{+3}$	$1.862\,758\,5\times10^{+0}$
	$3.049\,575\,0\times10^{+0}$	$6.588\,030\,4\times10^{-3}$	$-2.575\,708\,4\times10^{-6}$	$4.625\,570\,4\times10^{-10}$	$-3.137\,104\,9\times10^{-14}$	$9.357\,702\,4\times10^{+3}$	$3.016\,739\,0\times10^{+0}$
BH$_4$	$2.266\,476\,4\times10^{+0}$	$1.008\,337\,9\times10^{-2}$	$-2.701\,129\,9\times10^{-6}$	$-8.011\,130\,2\times10^{-10}$	$3.124\,167\,7\times10^{-12}$	$2.729\,843\,4\times10^{+4}$	$9.475\,581\,9\times10^{+0}$
	$4.931\,710\,1\times10^{+0}$	$7.963\,875\,0\times10^{-3}$	$-3.202\,599\,6\times10^{-6}$	$5.866\,226\,8\times10^{-10}$	$-4.034\,351\,8\times10^{-14}$	$2.615\,350\,2\times10^{+4}$	$-5.929\,320\,6\times10^{+0}$
BH$^-$	$2.075\,790\,2\times10^{+0}$	$1.686\,150\,3\times10^{-2}$	$-6.114\,199\,8\times10^{-6}$	$-2.537\,095\,3\times10^{-10}$	$1.938\,960\,0\times10^{-12}$	$8.299\,910\,8\times10^{+3}$	$1.116\,424\,8\times10^{+1}$
	$5.802\,446\,1\times10^{+0}$	$9.622\,869\,6\times10^{-3}$	$-3.757\,856\,5\times10^{-6}$	$6.746\,275\,8\times10^{-10}$	$-4.573\,394\,8\times10^{-14}$	$7.010\,083\,8\times10^{+3}$	$-9.083\,339\,2\times10^{+0}$
B$_2$H	$2.001\,135\,1\times10^{+0}$	$1.688\,398\,3\times10^{-2}$	$-2.814\,880\,5\times10^{-6}$	$2.332\,082\,8\times10^{-10}$	$-7.429\,141\,6\times10^{-12}$	$8.757\,677\,3\times10^{+4}$	$1.039\,739\,0\times10^{+1}$
	$5.159\,842\,1\times10^{+0}$	$2.194\,678\,3\times10^{-2}$	$-8.491\,892\,0\times10^{-6}$	$1.516\,302\,0\times10^{-10}$	$-1.028\,625\,3\times10^{-14}$	$8.697\,982\,9\times10^{+4}$	$-4.505\,881\,5\times10^{+0}$
B$_2$H$_3$	$6.737\,336\,7\times10^{-1}$	$2.612\,590\,6\times10^{-2}$	$-4.059\,584\,8\times10^{-6}$	$3.272\,012\,0\times10^{-8}$	$-1.029\,477\,9\times10^{-11}$	$4.662\,942\,6\times10^{+4}$	$1.555\,530\,8\times10^{+1}$
	$5.113\,764\,8\times10^{+0}$	$5.273\,085\,0\times10^{-3}$	$-2.049\,956\,2\times10^{-6}$	$3.618\,395\,7\times10^{-10}$	$-2.416\,359\,4\times10^{-14}$	$4.595\,536\,6\times10^{+4}$	$-5.160\,978\,8\times10^{+0}$
single-bridge B$_2$H$_3$	$1.452\,693\,6\times10^{+0}$	$2.331\,767\,5\times10^{-2}$	$-2.924\,046\,6\times10^{-6}$	$2.120\,510\,7\times10^{-8}$	$-6.347\,547\,2\times10^{-12}$	$3.563\,613\,2\times10^{+4}$	$1.428\,872\,8\times10^{+1}$
	$5.908\,534\,6\times10^{+0}$	$6.724\,208\,3\times10^{-3}$	$-2.630\,824\,2\times10^{-6}$	$4.728\,053\,0\times10^{-10}$	$-3.208\,482\,8\times10^{-14}$	$3.453\,650\,5\times10^{+4}$	$-7.860\,658\,4\times10^{+0}$
double-bridge B$_2$H$_3$	$1.840\,491\,1\times10^{+0}$	$2.035\,634\,7\times10^{-2}$	$-2.181\,132\,7\times10^{-6}$	$1.404\,325\,6\times10^{-8}$	$-3.946\,779\,9\times10^{-12}$	$3.670\,648\,5\times10^{+4}$	$1.234\,770\,4\times10^{+1}$
	$6.100\,409\,3\times10^{+0}$	$6.608\,436\,9\times10^{-3}$	$-2.604\,565\,8\times10^{-6}$	$4.706\,189\,5\times10^{-10}$	$-3.206\,551\,2\times10^{-14}$	$3.553\,850\,8\times10^{+4}$	$-9.377\,834\,1\times10^{+0}$
single-bridge B$_2$H$_4$	$1.081\,417\,2\times10^{+0}$	$2.635\,528\,6\times10^{-2}$	$-2.841\,797\,2\times10^{-6}$	$1.887\,755\,4\times10^{-8}$	$-5.452\,189\,8\times10^{-12}$	$2.409\,562\,3\times10^{+4}$	$1.549\,047\,0\times10^{+1}$
	$6.250\,774\,1\times10^{+0}$	$9.319\,360\,9\times10^{-3}$	$-3.668\,304\,7\times10^{-6}$	$6.619\,342\,6\times10^{-10}$	$-4.502\,898\,1\times10^{-14}$	$2.267\,587\,8\times10^{+4}$	$-1.082\,775\,3\times10^{+1}$
double-bridge B$_2$H$_4$	$1.641\,450\,2\times10^{+0}$	$1.661\,483\,0\times10^{-2}$	$-3.031\,652\,6\times10^{-6}$	$-5.806\,323\,9\times10^{-10}$	$2.947\,275\,7\times10^{-12}$	$2.403\,418\,1\times10^{+4}$	$1.327\,476\,1\times10^{+1}$
	$5.849\,024\,5\times10^{+0}$	$9.867\,005\,2\times10^{-3}$	$-3.930\,371\,3\times10^{-6}$	$7.153\,196\,9\times10^{-10}$	$-4.896\,566\,2\times10^{-14}$	$2.247\,816\,3\times10^{+4}$	$-1.000\,850\,1\times10^{+1}$
single-bridge B$_2$H$_5$	$3.040\,132\,7\times10^{-1}$	$2.824\,347\,5\times10^{-2}$	$-2.219\,058\,9\times10^{-6}$	$1.030\,388\,8\times10^{-8}$	$-2.233\,136\,3\times10^{-12}$	$2.946\,866\,1\times10^{+4}$	$2.002\,884\,0\times10^{+1}$
	$6.392\,480\,2\times10^{+0}$	$1.212\,108\,3\times10^{-2}$	$-4.794\,558\,6\times10^{-6}$	$8.679\,464\,7\times10^{-10}$	$-5.913\,965\,2\times10^{-14}$	$2.757\,217\,0\times10^{+4}$	$-1.199\,730\,3\times10^{+1}$
double-bridge B$_2$H$_5$	$1.059\,574\,1\times10^{+0}$	$1.873\,091\,4\times10^{-2}$	$-4.889\,931\,1\times10^{-6}$	$-9.045\,219\,7\times10^{-10}$	$3.957\,938\,9\times10^{-12}$	$3.195\,776\,1\times10^{+4}$	$1.800\,440\,3\times10^{+1}$
	$5.609\,052\,0\times10^{+0}$	$1.303\,866\,7\times10^{-2}$	$-5.201\,667\,2\times10^{-6}$	$9.471\,914\,1\times10^{-10}$	$-6.480\,776\,7\times10^{-14}$	$3.013\,743\,7\times10^{+4}$	$-7.693\,251\,0\times10^{+0}$
B$_2$I$_6$	$2.848\,077\,8\times10^{-1}$	$2.246\,769\,3\times10^{-2}$	$1.811\,227\,2\times10^{-6}$	$-1.442\,581\,8\times10^{-8}$	$6.241\,982\,6\times10^{-12}$	$3.303\,862\,1\times10^{+4}$	$1.962\,133\,8\times10^{+1}$
	$6.171\,717\,4\times10^{+0}$	$1.549\,489\,3\times10^{-2}$	$-6.202\,242\,3\times10^{-6}$	$1.132\,188\,2\times10^{-9}$	$-7.762\,684\,0\times10^{-14}$	$9.591\,312\,8\times10^{+2}$	$-1.366\,039\,2\times10^{+1}$
C$_2$-B$_2$H$_7$	$-2.423\,006\,7\times10^{+0}$	$5.490\,261\,4\times10^{-2}$	$-5.563\,431\,3\times10^{-6}$	$3.339\,730\,8\times10^{-8}$	$-8.833\,467\,7\times10^{-12}$	$1.632\,449\,8\times10^{+4}$	$3.161\,834\,8\times10^{+1}$
	$9.659\,723\,9\times10^{+0}$	$1.777\,937\,3\times10^{-2}$	$-7.070\,895\,6\times10^{-6}$	$1.284\,929\,8\times10^{-9}$	$-8.780\,523\,5\times10^{-14}$	$1.290\,469\,1\times10^{+4}$	$-3.047\,667\,7\times10^{+1}$
C$_s$-B$_2$H$_7$	$-2.859\,243\,6\times10^{+0}$	$5.177\,413\,5\times10^{-2}$	$-4.308\,632\,8\times10^{-6}$	$1.899\,266\,4\times10^{-8}$	$-3.420\,406\,9\times10^{-12}$	$1.434\,469\,9\times10^{+4}$	$3.483\,955\,3\times10^{+1}$
	$9.515\,860\,8\times10^{+0}$	$1.802\,131\,8\times10^{-2}$	$-7.196\,377\,0\times10^{-6}$	$1.311\,509\,6\times10^{-9}$	$-8.982\,538\,6\times10^{-14}$	$1.064\,716\,0\times10^{+4}$	$-2.976\,530\,4\times10^{+1}$
B$_3$H$_9$	$-7.283\,849\,7\times10^{-1}$	$4.701\,612\,0\times10^{-2}$	$-2.749\,809\,5\times10^{-6}$	$7.014\,546\,6\times10^{-10}$	$-4.213\,820\,4\times10^{-13}$	$1.506\,347\,9\times10^{+4}$	$2.476\,886\,5\times10^{+1}$
	$9.925\,092\,6\times10^{+0}$	$2.341\,426\,1\times10^{-2}$	$-9.332\,886\,1\times10^{-6}$	$1.698\,447\,5\times10^{-9}$	$-1.161\,639\,7\times10^{-13}$	$1.143\,456\,0\times10^{+4}$	$-3.259\,691\,5\times10^{+1}$
B$_4$H$_3$	$-2.642\,754\,7\times10^{+0}$	$6.108\,274\,9\times10^{-2}$	$-8.252\,664\,4\times10^{-6}$	$5.931\,566\,6\times10^{-8}$	$-1.724\,708\,4\times10^{-11}$	$3.792\,394\,1\times10^{+3}$	$3.341\,294\,4\times10^{+1}$
	$1.080\,342\,4\times10^{+1}$	$1.088\,197\,2\times10^{-2}$	$-4.335\,554\,3\times10^{-6}$	$7.892\,095\,3\times10^{-10}$	$-5.402\,787\,0\times10^{-14}$	$3.471\,681\,4\times10^{+3}$	$-3.314\,451\,3\times10^{+1}$
B$_5$H$_{10}$	$-5.660\,709\,9\times10^{+0}$	$6.684\,744\,1\times10^{-2}$	$-3.446\,398\,0\times10^{-6}$	$-1.816\,087\,0\times10^{-8}$	$5.370\,994\,2\times10^{-12}$	$6.972\,443\,2\times10^{+3}$	$4.756\,566\,2\times10^{+1}$
B$_5$H$_{12}$	$1.232\,412\,1\times10^{+1}$	$2.735\,989\,3\times10^{-2}$	$-1.102\,843\,9\times10^{-5}$	$2.022\,767\,4\times10^{-9}$	$-1.391\,190\,0\times10^{-13}$	$1.073\,428\,6\times10^{+3}$	$-4.878\,948\,9\times10^{+1}$
	$-2.268\,296\,7\times10^{+0}$	$7.480\,823\,0\times10^{-2}$	$-5.970\,649\,4\times10^{-6}$	$2.809\,257\,1\times10^{-8}$	$-6.228\,944\,6\times10^{-12}$	$2.046\,848\,1\times10^{+3}$	$3.102\,999\,4\times10^{+1}$
B$_5$H$_9$	$1.450\,857\,7\times10^{+1}$	$3.056\,346\,1\times10^{-2}$	$-1.216\,823\,6\times10^{-5}$	$2.212\,565\,7\times10^{-9}$	$-1.512\,353\,5\times10^{-13}$	$1.523\,378\,0\times10^{+4}$	$-5.726\,663\,1\times10^{+1}$
	$-5.968\,600\,8\times10^{+0}$	$7.343\,313\,6\times10^{-2}$	$-4.719\,440\,9\times10^{-6}$	$8.600\,509\,0\times10^{-9}$	$2.074\,854\,4\times10^{-9}$	$7.720\,777\,2\times10^{+3}$	$4.787\,924\,1\times10^{+1}$
B$_5$H$_{11}$	$1.403\,926\,9\times10^{+1}$	$2.584\,017\,7\times10^{-2}$	$-1.046\,476\,9\times10^{-5}$	$1.925\,300\,5\times10^{-9}$	$-1.327\,771\,4\times10^{-13}$	$1.388\,141\,3\times10^{+3}$	$-5.831\,327\,7\times10^{+1}$
	$-6.830\,455\,0\times10^{+0}$	$1.012\,035\,4\times10^{-1}$	$-1.024\,392\,8\times10^{-4}$	$5.841\,754\,6\times10^{-8}$	$-1.445\,987\,0\times10^{-11}$	$1.076\,418\,1\times10^{+3}$	$5.141\,047\,4\times10^{+1}$
B$_6$H$_{10}$	$1.735\,610\,3\times10^{+1}$	$2.822\,682\,0\times10^{-2}$	$-1.135\,436\,8\times10^{-5}$	$2.079\,520\,9\times10^{-9}$	$-1.428\,868\,8\times10^{-13}$	$3.936\,796\,0\times10^{+3}$	$-7.301\,842\,8\times10^{+1}$
	$-1.060\,173\,7\times10^{+1}$	$1.177\,604\,2\times10^{-1}$	$-1.257\,864\,4\times10^{-4}$	$7.308\,527\,3\times10^{-8}$	$-1.801\,240\,9\times10^{-11}$	$1.027\,490\,5\times10^{+3}$	$6.597\,543\,4\times10^{+1}$
B$_8$H$_{12}$	$1.861\,825\,6\times10^{+1}$	$2.726\,169\,3\times10^{-2}$	$-1.104\,335\,7\times10^{-5}$	$2.032\,599\,0\times10^{-9}$	$-1.401\,673\,1\times10^{-13}$	$2.256\,999\,5\times10^{+3}$	$-8.351\,404\,0\times10^{+1}$
	$-1.519\,854\,2\times10^{+1}$	$1.587\,149\,2\times10^{-1}$	$-1.787\,751\,6\times10^{-4}$	$1.082\,513\,1\times10^{-7}$	$-2.728\,661\,6\times10^{-11}$	$1.656\,856\,2\times10^{+4}$	$8.692\,661\,0\times10^{+1}$
B$_9$H$_{15}$	$2.324\,979\,1\times10^{+1}$	$3.420\,112\,8\times10^{-2}$	$-1.375\,320\,5\times10^{-5}$	$2.518\,944\,0\times10^{-9}$	$-1.730\,801\,7\times10^{-13}$	$6.392\,478\,0\times10^{+3}$	$-1.081\,835\,6\times10^{+2}$
	$-1.722\,750\,7\times10^{+1}$	$1.845\,508\,8\times10^{-1}$	$-2.072\,243\,8\times10^{-4}$	$1.272\,976\,3\times10^{-7}$	$-3.282\,708\,6\times10^{-11}$	$1.758\,022\,7\times10^{+3}$	$9.516\,878\,3\times10^{+1}$
B$_{10}$H$_{14}$	$2.656\,000\,4\times10^{+1}$	$4.259\,469\,8\times10^{-2}$	$-1.708\,409\,7\times10^{-5}$	$3.123\,013\,5\times10^{-9}$	$-2.142\,674\,1\times10^{-13}$	$5.924\,869\,1\times10^{+3}$	$-1.271\,668\,5\times10^{+2}$
	$-2.150\,596\,6\times10^{+1}$	$2.085\,036\,2\times10^{-1}$	$-2.496\,640\,9\times10^{-4}$	$1.603\,576\,1\times10^{-7}$	$-4.257\,187\,9\times10^{-11}$	$4.739\,737\,9\times10^{+3}$	$1.123\,144\,8\times10^{+2}$
	$2.801\,084\,2\times10^{+1}$	$4.127\,483\,0\times10^{-2}$	$-1.658\,485\,0\times10^{-5}$	$3.035\,372\,7\times10^{-9}$	$-2.085\,062\,3\times10^{-13}$	$-7.984\,781\,3\times10^{-3}$	$-1.371[8]34\,2\times10^{+2}$

[a]For each borane species, the first row is for the temperature range 298.15–1000 K; the second row is for the temperature range 1000–5000 K.

[b]Coefficients were taken from A. Burcat and B. McBride, "Ideal Gas Thermodynamic Data for Combustion and Air-Polution Use" Technion-Israel Institute of Technology, Haifa, Israel (1995).
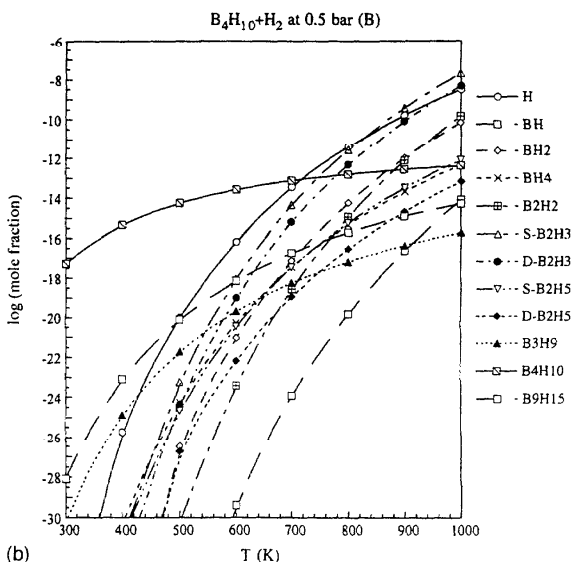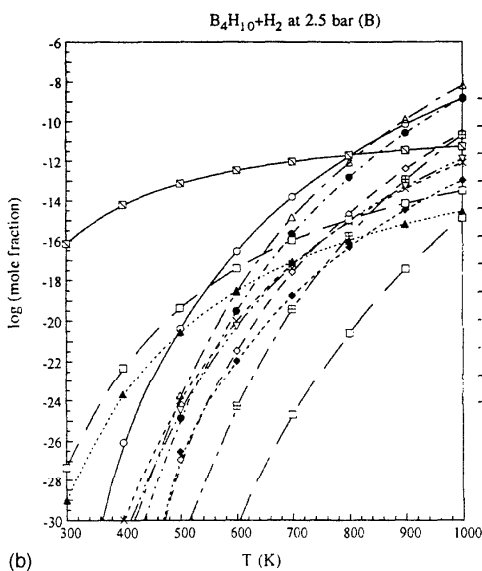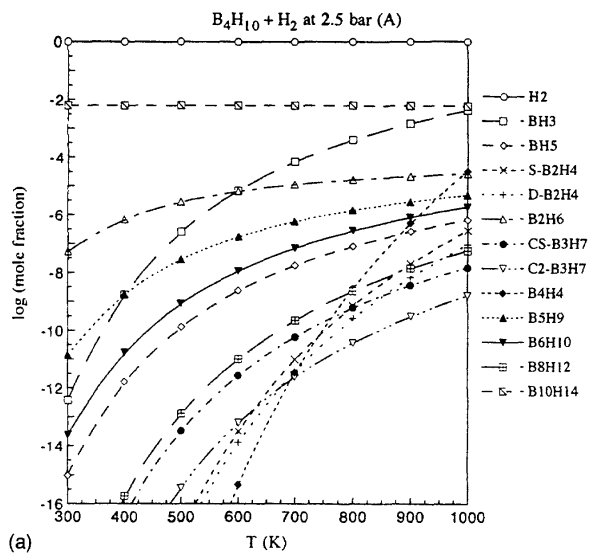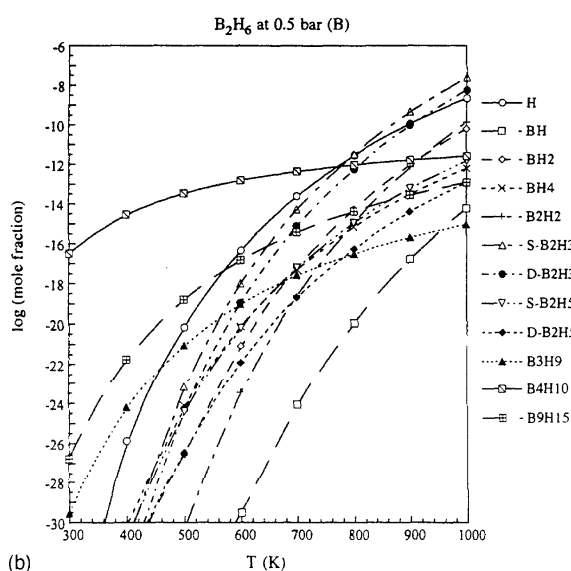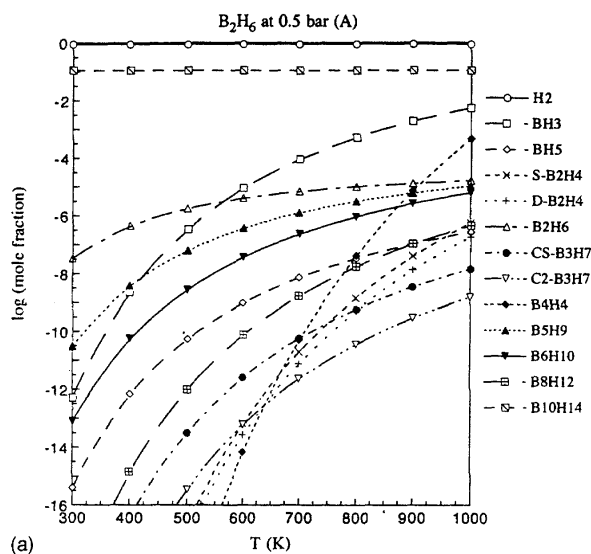
FIG. 1. (A) Computed equilibrium mole fractions for 13 species (excluding the formation of species in condensed phases) for a sample represented by the B/H ratio = 0.030, equivalent to a mixture of 98.4% H_2 and 1.6% B_4H_{10}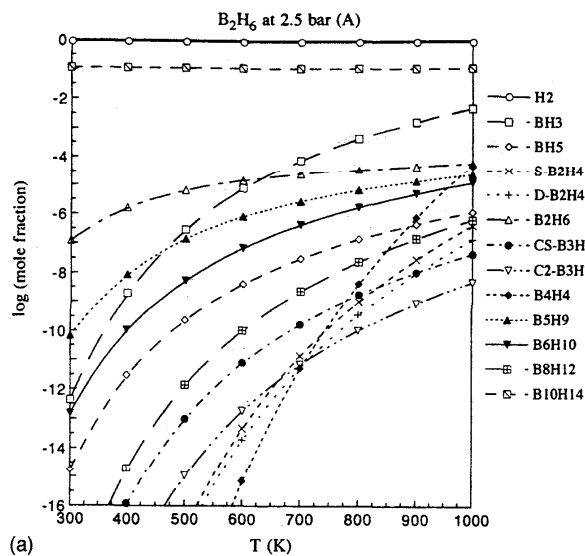, at an initial pressure of 0.03 bar. (B) Computed equilibrium mole fractions for 12 species (excluding the formation of species in condensed phases) for a sample represented by the B/H ratio=0.030, equivalent to a mixture of 98.4% H_2 and 1.6% B_4H_{10}, at an initial pressure of 0.03 bar.

FIG. 2. (A) Computed equilibrium mole fractions for 13 species (excluding the formation of species in condensed phases) for a sample represented by the B/H ratio = 0.030, equivalent to a mixture of 98.4% H_2 and 1.6% B_4H_{10}, at an initial pressure of 0.50 bar. (B) Computed equilibrium mole fractions for 12 species (excluding the formation of species in condensed phases) for a sample represented by the B/H ratio=0.030, equivalent to a mixture of 98.4% H_2 and 1.6% B_4H_{10}, at an initial pressure of 0.50 bar.

tional constants were derived from the data compiled by Beaudet.[148] The vibrational frequencies are those calculated by McKee[173] and are scaled by a factor of 0.90. The enthalpy of formation was estimated empirically[139,162,174] and calculated ab initio;[110] no experimental determinations are available. The spread in the literature values for $\Delta_f H^\circ$ (B_9H_{15}, g, 298.15 K) is large, from 59.41 to 175.73 kJ·mol.[-1] We recommend a value of 147.28 kJ·mol^{-1}, which was calculated from the atomization energy (6948.37 kJ·mol^{-1}) estimated by Herndon and Ellzey.[174] The lower value is not acceptable.

Were that the case, thermal equilibrium calculations (given in Sec. 4) indicated that B_8H_{12} would rival $B_{10}H_{14}$ in composition, in disagreement with observations. Table 26 lists the ideal gas thermodynamic parameters for B_8H_{12}.

2.21. B_9H_{15}

The structure of B_9H_{15} was determined by x-ray diffraction[175] to have C_s symmetry, which is supported by ab initio calculations.[110,170,176] The rotational constants were calculated from structural data compiled by Beaudet.[148] The

FIG. 3. (A) Computed equilibrium mole fractions for 13 species (excluding the formation of species in condensed phases) for a sample represented by the B/H ratio=0.030, equivalent to a mixture of 98.4% H_2 and 1.6% B_4H_{10}, at an initial pressure of 2.5 bar. (B) Computed equilibrium mole fractions for 12 species (excluding the formation of species in condensed phases) for a sample represented by the B/H ratio=0.030, equivalent to a mixture of 98.4% H_2 and 1.6% B_4H_{10}, at an initial pressure of 2.5 bar.

FIG. 4. (A) Computed equilibrium mole fractions for 13 species (excluding the formation of species in condensed phases) for a sample represented by the B/H ratio=0.333, corresponding to B_2H_6, at an initial pressure of 0.5 bar. (B) Computed equilibrium mole fractions for 12 species (excluding the formation of species in condensed phases) for a sample represented by the B/H ratio=0.333, corresponding to B_2H_6, at an initial pressure of 0.5 bar.

scaled vibrational frequencies are those of McKee.[110] Experimental determinations of its enthalpy of formation are not available. McKee[110] proposed $\Delta_f H°$ (B_9H_{15}, g, 298.15 K) =110.88 kJ·mol^{-1}. Housecroft and Wade[162] reported an atomization energy of 6919.9 kJ·mol^{-1}, from which $\Delta_f H°$ (B_9H_{15}, g, 298.15 K) is estimated to be 179.91 kJ·mol^{-1}. Recently, an enthalpy increment at 0 K for the reaction ($B_9H_{15}+BH_3 \rightarrow B_{10}H_{14}+2H_2$) was calculated to be −205.85 kJ·mol^{-1} by McKee.[176] Based on this result and $\Delta_f H°$ ($B_{10}H_{14}$, g, 0 K)=93.98 kJ·mol^{-1} (see next) and $\Delta_f H°$ (BH_3, g, 0 K)=93.05 kJ·mol^{-1}, $\Delta_f H°$ (B_9H_{15}, g, 298.15 K)

was estimated to be 206.77 kJ·mol^{-1}, and $\Delta_f H°$ (B_9H_{15}, g, 0 K)=158.41 kJ·mol^{-1}. These results are used in the present calculations. The ideal gas thermodynamic parameters for B_9H_{15} are given in Table 27.

2.22. $B_{10}H_{14}$

The structure of $B_{10}H_{14}$ was determined by x-ray[177,179] and neutron diffraction[180] (C_{2v} symmetry). The rotational constants were derived from the data compiled by
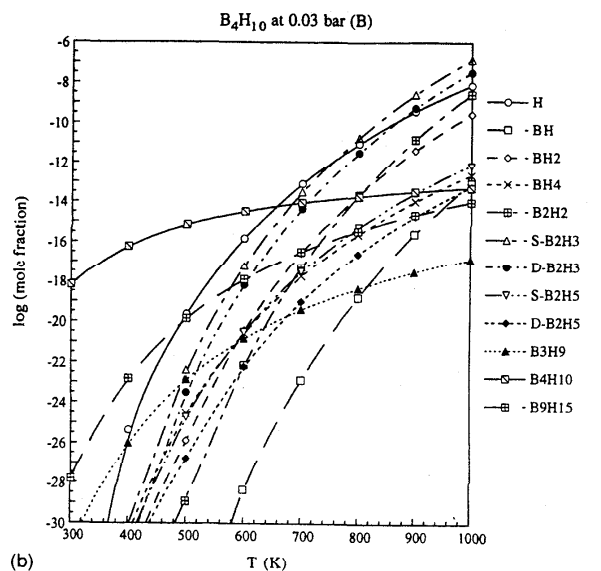
FIG. 5. (A) Computed equilibrium mole fractions for 13 species (excluding the formation of species in condensed phases) for a sample represented by the B/H ratio=0.333, corresponding to B_2H_6, at an initial pressure of 2.5 bar. (B) Computed equilibrium mole fractions for 12 species (excluding the formation of species in condensed phases) for a sample represented by the B/H ratio=0.333, corresponding to B_2H_6, at an initial pressure of 2.5 bar.
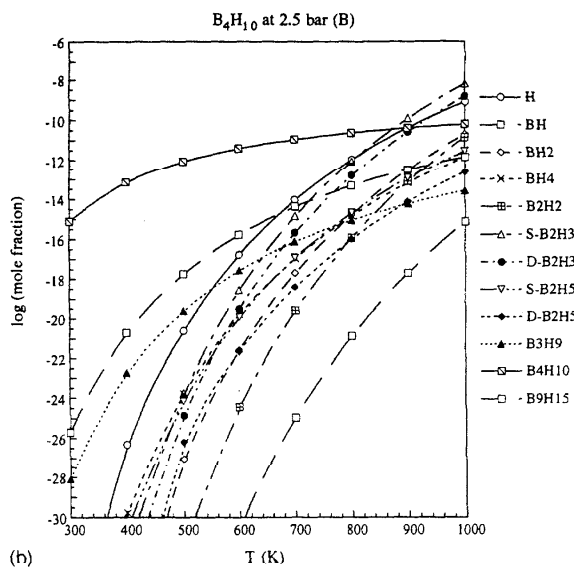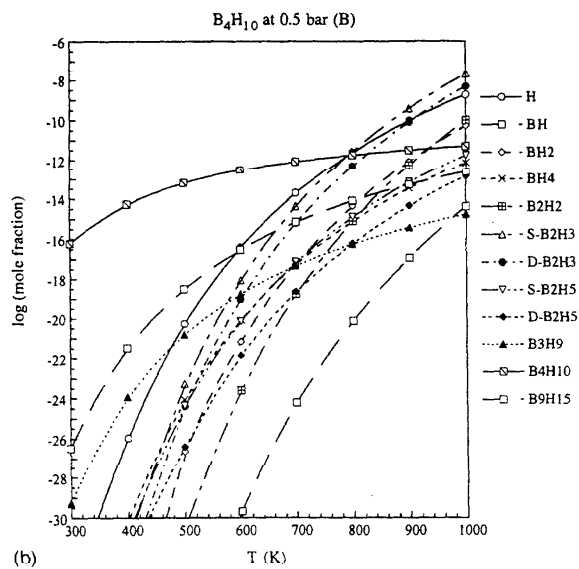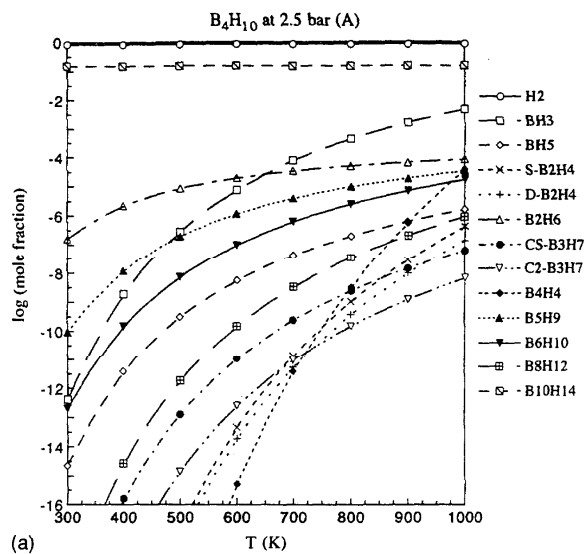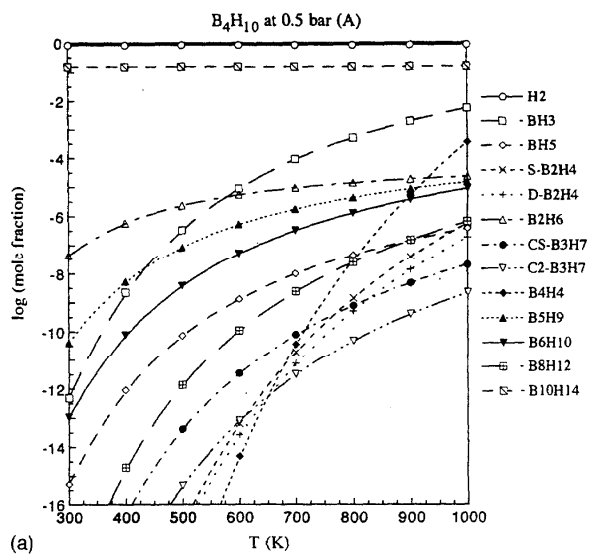

FIG. 6. (A) Equilibrium mole fractions for a sample with B/H=0.40, corresponding to B_4H_{10}, at 0.03 bar. (B) Equilibrium mole fractions for a sample with B/H=0.40, corresponding to B_4H_{10}, at 0.03 bar.

Beaudet.[148] The vibrational frequencies are those calculated by McKee[110] and were scaled by a factor of 0.943.

$\Delta_f H°$ ($B_{10}H_{14}$, g, 298.15 K) was determined experimentally by Johnson et al.[181] (-32.64 kJ·mol^{-1}) and Galchenko et al.[182] (-25.10 kJ·mol^{-1}). An average of -28.87 kJ·mol^{-1} was recommended for $\Delta_f H°$ ($B_{10}H_{14}$, 298.15 K). Based on the measured enthalpy of vaporization by Furukawa and Park[183] and Miller,[184] an average value (47.28 kJ·mol^{-1}) was obtained for $\Delta_f H°$ ($B_{10}H_{14}$, g, 298.15 K) and was accepted in the JANAF tables.[1] However, another experimental determination by Gunn and Kindsvater[185] favored

a somewhat lower value (18.41 kJ·mol^{-1}). Recent ab initio calculations by McKee[176] led to a much lower value (-35.98 kJ·mol^{-1}). Laurie and Perkin[139] and Guest et al.[140] suggested 115.48 and 29.71, kJ·mol^{-1}, respectively. The latter is close to that evaluated by Wagman et al.[63] (31.38 kJ·mol^{-1}). Here we selected the value recommended in the JANAF tables.[1] The ideal gas thermodynamic parameters for $B_{10}H_{14}$ are given in Table 28. The maximum deviations on $C_p°$ and $S°$ between Table 28 and those of the JANAF tables[1] are 2.8 and 3.2 J·K^{-1}·mol^{-1}, respectively.

FIG. 7. (A) Equilibrium mole fractions for a sample with B/H = 0.40, corresponding to B_4H_{10}, at 0.5 bar. (B) Equilibrium mole fractions for a sample with B/H=0.40, corresponding to B_4H_{10}, at 0.5 bar.
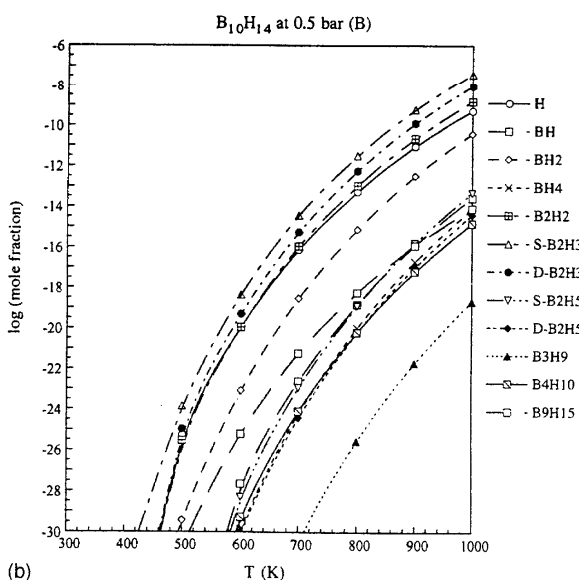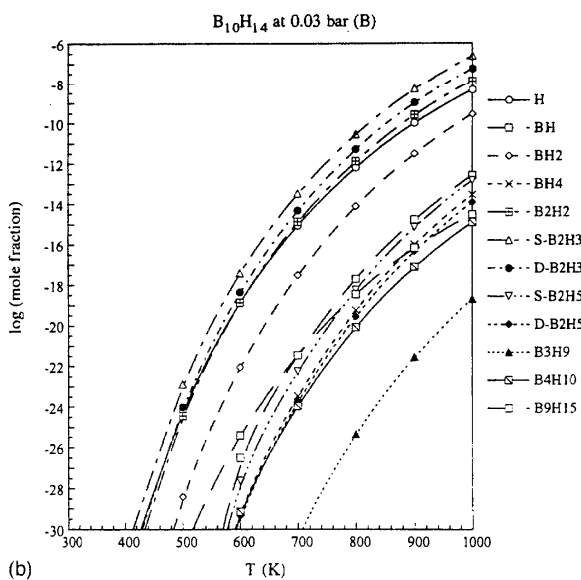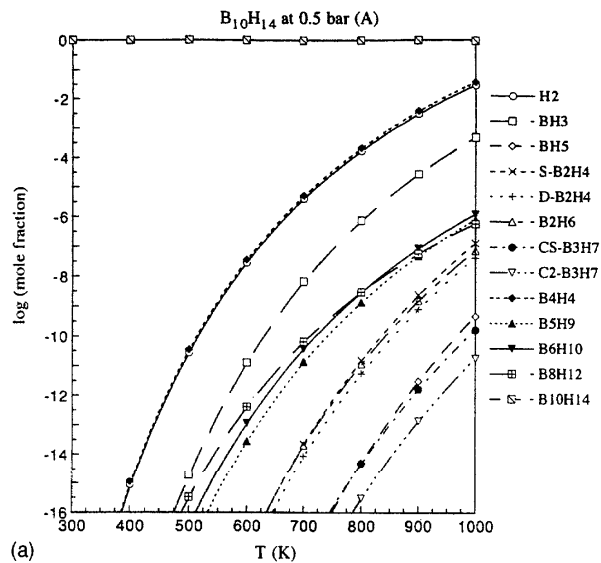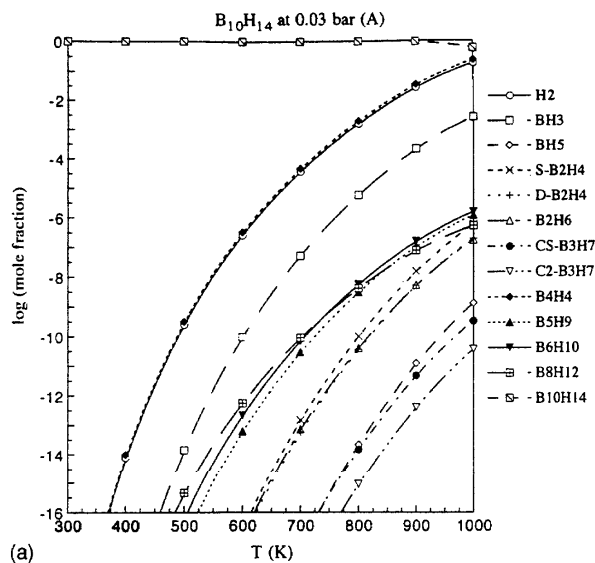
FIG. 8. (A) Equilibrium mole fractions for a sample with B/H=0.40, corresponding to B_4H_{10}, at 2.5 bar. (B) Equilibrium mole fractions for a sample with B/H=0.40, corresponding to B_4H_{10}, at 2.5 bar.

FIG. 9. (A) Equilibrium mole fractions for a sample with B/H=0.714, corresponding to $B_{10}H_{14}$, at 0.03 bar. (B) Equilibrium mole fractions for a sample with B/H=0.714, corresponding to $B_{10}H_{14}$, at 0.03 bar.
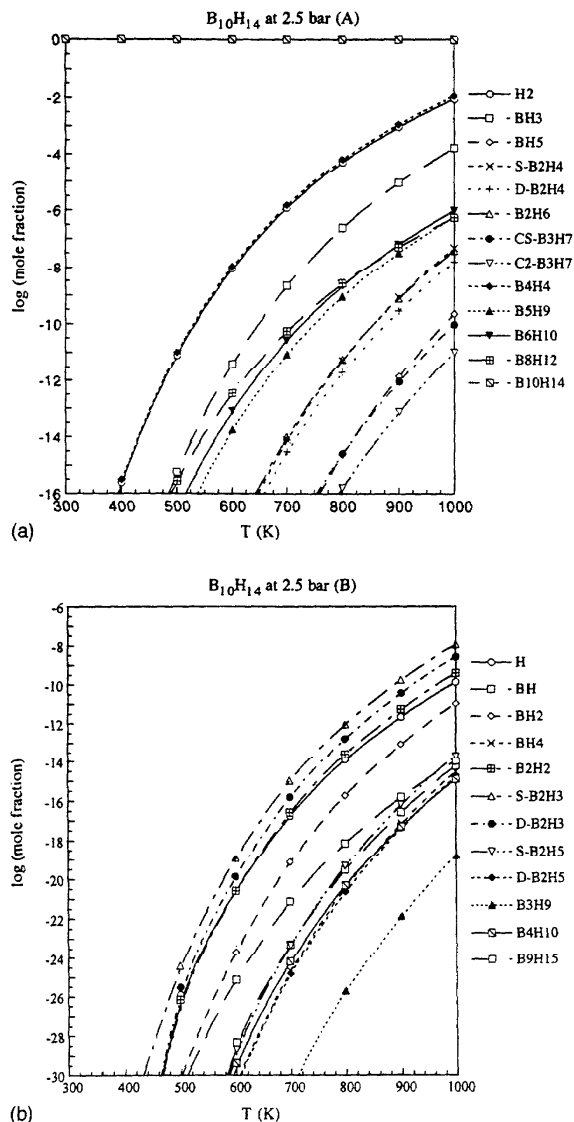
FIG. 10. (A) Equilibrium mole fractions for a sample with B/H=0.714, corresponding to $B_{10}H_{14}$, at 0.5 bar. (B) Equilibrium mole fractions for a sample with B/H=0.714, corresponding to $B_{10}H_{14}$, at 0.5 bar.

(a)

(b)

FIG. 11. (A) Equilibrium mole fractions for a sample with B/H=0.714, corresponding to $B_{10}H_{14}$, at 2.5 bar. (B) Equilibrium mole fractions for a sample with B/H=0.714, corresponding to $B_{10}H_{14}$, at 2.5 bar.

3. Polynomials for Thermodynamic Parameters

The computed values of the thermodynamic variables C_P°, S°, and ΔH° (in Tables 3–28) were fitted by the following (NASA type) polynomials:[3]

$$\frac{C_P^{\circ}}{R} = a_1 + a_2 T + a_3 T^2 + a_4 T^3 + a_5 T^4,$$

$$\frac{S^{\circ}}{R} = a_1 \ln T + a_2 T - \frac{a_3 T^2}{2} + \frac{a_4 T^3}{3} + \frac{a_5 T^4}{4} + a_7.$$

$$\frac{\Delta H^{\circ}_T}{RT} = a_1 + \frac{a_2 T}{2} + \frac{a_3 T^2}{3} + \frac{a_4 T^3}{4} + \frac{a_5 T^4}{5} + \frac{a_6}{T}.$$

These coefficients, for two different temperature ranges, are listed in Table 29. Notice that the "enthalpy," ΔH°_T, given above is defined by:[3]

$\Delta H^{\circ}(T)$ (compound)

$= \Delta_f H^{\circ}(298.15 \text{ K})(\text{compound})$

$+ [H^{\circ}(T) - H^{\circ} (298.15 \text{ K})]\text{compound},$ (1)

and it differs from the enthalpy of formation of the compound, $\Delta_f H^{\circ}(T)$(compound), which is calculated according to the following relation (as used in the JANAF tables[1]):

$\Delta_f H^{\circ}(T)$(compound)

$= \Delta_f H^{\circ} (298.15 \text{ K})(\text{compound})$

$+ [H^{\circ}(T) - H^{\circ}(298.15 \text{ K})(\text{compound})$

$- \Sigma[H^{\circ}(T) - H^{\circ}_{\text{elements}}]$. (2)

The difference between Eqs. (1) and (2) is the term $\{-\Sigma[H^{\circ}(T) - H^{\circ} (298.15 \text{ K})]_{\text{elements}}\}$. Thus, $\Delta H^{\circ}(T)$(compound) derived from NASA polynomials is equal to $\Delta_f H^{\circ}(T)$(compound) only at 298.15 K. However, the NASA procedure does not introduce errors in thermochemical or kinetic calculations, since the terms $\{-\Sigma[H^{\circ}(T) - H^{\circ} (298.15 \text{ K})]_{\text{elements}}\}$ in Eq. (2) cancel in calculating heats of reaction. Moreover, the NASA format provides the advantage of convenience.

4. Comments on the Derived Equilibrium Mole Fractions

The equilibrium mole fractions versus temperatures (300–1000 K) for four B/H ratios at various initial pressures (0.03, 0.50, and 2.50 bar) are given in Figs. 1–11. Inspection of these graphs shows interesting and, in some respects, surprising features. As expected, higher temperatures increase significantly the proportions of the less stable species. Increases in (initial) pressure do not alter the shapes of mole fraction versus temperature dependencies, nor their relative positions. The levels of the minor species generally decrease with increasing pressure. At the same initial pressure, increasing the B/H ratio from 0.333 to 0.714 is hardly noticeable, but the decrease from B/H=0.333 (as in B_2H_6) to B/H=0.03 enhances significantly the mole fractions of most boranes except that of $B_{10}H_{14}$, which is decreased. Indeed, the highest B/H ratio tested differs from the lower three sets; contrast the relative magnitudes of H_2 versus $B_{10}H_{14}$ vs B_4H_4. The thermochemical trend is towards gaseous species with comparable B and H levels, as expressed when the B/H ratio was increased. It is plausible to argue that these aspects reflect the intrinsic thermodynamic instability of the boranes relative to the elements in their standard states. Recall that Figs. 1–11 were calculated under the restriction that no condensed phases were included, but gaseous elementary boron was.

Kinetic constraints versus the thermodynamic imperative become evident upon comparing these calculations with the relative population profiles observed by Greenwood and co-workers.[19,186–191] Their measured time-dependent species concentrations (e.g., Fig. 3 for B_4H_{10} and Fig. 6 for B_6H_{12} in Greenwood[19]) indicate that after about 30 min the relative populations of the various product species appear to approach a steady state, and these differ significantly from the calculated equilibrium proportions. The discrepancies are too large to be ascribed to uncertainties inherent in the present set of thermofunctions. However, it is not entirely unexpected. The conversion of the lower hydrides to decaborane occurs via many steps, through intermediates that are generated at very low levels, in reactions that are generally reversible. Hence, even though the activation barriers may not be particularly high, overall progress toward the equilibrium distribution is slow. Equilibria were not attained in 30 min. The detailed unraveling of the mechanisms involved is a challenging undertaking.

5. References

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