
CHAPTER 21

Aspects of the Estimation of Physical Properties of Boron Compounds by the Use of Isoelectronic and Plemeioelectronic Analogies

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1. INTRODUCTION AND DEFINITIONS

In this chapter aspects of some of the more important physical properties of boron compounds will be discussed. The properties we have chosen are $\Delta H_{\text{vap}}^\circ$ (298.15 K), the heat required to convert 1 mol of liquid to gas (assumed ideal) in the vaporization process at 298.15 K (25°C) and 1 atm pressure; C_p° (g, 298.15 K), the gas phase heat capacity at 298.15 K; S° (g, 298.15 K), the entropy difference of the species at 298.15 K and at 0 K, where the species is assumed to be an ideal gas at both temperatures; the thermal function, H° (298.15 K) - H° (0 K), which is the difference in enthalpy δH at 298.15 K and at 0 K; and *ZPE*, the zero-point energy, ie, the minimal amount of energy a molecule may have because of its nonzero vibrational energy even at 0 K. These properties are discussed because these quantities are precisely those that interrelate the experimentalist's condensed phase, the computationally inclined theoretician's vibrationless molecule at 0 K, and the isolated gas phase molecule. While rarely taken as the reference state, the isolated gas phase molecule is that state that most closely corresponds to our chemical symbols and structures, whether our understanding is derived from gas phase or condensed phase experiment or from calculational theory. It is for this reason that in this chapter we refer all properties ultimately to this idealized state. Since a standard set of conditions has been defined, we opt to thus omit the (g, 298.15) and the superscript ° from the above and will refer to the physical properties of interest by the set of abbreviated symbols, ΔH_v , C_p , S , δH , and *ZPE*.

Rather than "merely" discussing these physical properties, we will endeavor to estimate their numerical values in the following sections. This will allow us to maximize the use of experimental and theoretical results in understanding the chemistry of boron-containing compounds. For example, to the extent we are successful in predicting heats of vaporization and of sublimation, data on liquid and solid phase species become as useful as data on gas phase compounds. A check of the validity of an experimental result on a solid or liquid becomes as facile as for the gas.

Species are said to be "molecular" liquids or solids when they have the same local molecular structure as well as stoichiometry in the gaseous and

liquid or solid state. Since no structural rearrangement of the atoms is associated with the phase change of these species, the heats of vaporization and of sublimation arise only from the changes in longer range order and are conceptually simpler and more feasible to estimate than for nonmolecular liquids and solids. Compounds in which the bonding is essentially short range and covalent and the bonding electrons are localized between the bound atoms are normally molecular solids and liquids. Conversely, ionic bonding corresponds to long-range Coulombic interactions, while metallic bonding corresponds to the electrons responsible for the bonds to be highly delocalized in the condensed phases. Therefore, metals and ionically bonded compounds rarely form molecular solids or liquids. As such, we herein discuss and attempt to predict the experimental heat of vaporization of the covalently bonded boron hydrides, carboranes, and their "hetero" derivatives.

We do not expect to be able to predict the heat of vaporization and of sublimation for ionic species, for unassociated ions, or for species for which the stoichiometries of the gas and the condensed phases do not correspond. Many "high-temperature" species such as B_2O_2 and $AlCl_2$ and most other suboxides and subhalides fall into at least one of these latter categories. For these compounds the quantities of C_p , S , and δH are far more useful than a heat of vaporization as these new data bridge the high-temperature conditions of synthesis, the often low-temperature of matrix isolation, and the "reasonable" temperature of $25^\circ C$ ($298 K$) for which the thermochemistry is generally quoted. Our predictions of these quantities are expected to be useful in determining relatively casually the validity the admittedly sparse and arduously determined experimental results and in providing a beginning understanding of hitherto uninvestigated compounds.

To help us in this chapter, both "isoelectronic" and "plemeioelectronic" analogies will be extensively used. In the chemical literature, one finds that there are many interrelated and often implicit definitions of the term "isoelectronic." In this chapter, we will take two species to be isoelectronic if:

1. They have the same number of valence electrons.
2. They have both the same number of heavy (ie, nonhydrogen) atoms.
3. They have essentially the same connectivity and geometric arrangement of heavy atoms. That is, we choose not to differentiate between species containing two heavy atoms joined by single and multiple bonds, nor between two-center and multicenter bonds.

If the geometries of the heavy atoms are then the same, the species are isoelectronic. We remind the reader that multiple bonds consist of more than one two-center/two-electron bond between a pair of atoms while multicentered bonds consist of more than two atoms bonded by two electrons. Since all these various bond types are considered equivalent in applications of

TABLE 21-1. Some Atomic and Bonding "Tallies" for a Small, Select Collection of X_nH_n ($X = B$ and/or C , $6 \leq n \leq 10$) Species: *arachno*-Tetraborane(10), Both 1,1- and 1,2-Dimethyldiborane(4), Both *n*- and isobutane, Trimethylborane, Isobutene and (*Z*) (or (*E*))-2-Butene, Cyclobutane, 1,3-Butadiene, 2-Butyne and Bicyclobutane

Compound	Tallies ^a								
	<i>b</i>	<i>c</i>	<i>h</i>	<i>sk</i>	<i>s</i>	<i>d</i>	<i>t</i>	<i>m</i>	<i>j</i>
B_4H_{10}	4	0	10	10	1	0	0	4	5
1,1-(CH_3) ₂ B_2H_4	2	2	10	8	2	0	0	2	3
1,2-(CH_3) ₂ B_2H_4	2	2	10	8	2	0	0	2	3
<i>n</i> - C_4H_{10}	0	4	10	6	3	0	0	0	3
<i>i</i> - C_4H_{10}	0	4	10	6	3	0	0	0	3
(CH_3) ₃ B	1	3	9	6	3	0	0	0	3
(CH_3) ₂ C=CH ₂	0	4	8	8	2	1	0	0	3
CH ₃ CH=CHCH ₃	0	4	8	8	2	1	0	0	3
<i>c</i> -(CH ₂) ₄	0	4	8	8	4	0	0	0	4
CH ₂ =CHCH=CH ₂	0	4	6	10	1	2	0	0	3
CH ₃ C≡CCH ₃	0	4	6	10	2	0	1	0	3
(CH) ₂ (CH ₂) ₂	0	4	6	10	5	0	0	0	5

^a The following abbreviations are used: *b*, *c*, and *h* are the numbers of boron, carbon, and hydrogen atoms respectively; *sk* is the number of skeletal electrons (ie, the number of electrons not used in single B—H and/or C—H bonds); *s*, *d*, and *t* are the numbers of single, double, and triple two-center, two-electron bonds between heavy atoms; *m* is the number of pairs of heavy atoms that are connected by multi- (usually three-) center, two-electron bonds; and *j*, the number of joins between any two heavy atoms in the molecule, which we recognize as equaling $s + d + t + m$.

isoelectronic reasoning, we now introduce the word "join" to label an arbitrary type of bond between any pair of bonded heavy atoms.

In a related way we now introduce the new term, albeit not particularly new concept, "plemeioelectronic," which is linguistically derived from two Greek prefixes meaning "adding to" and "taking from." We will take two species to be plemeioelectronic if:

1. They have *different* numbers of valence electrons.
2. They have the same number of heavy (ie, nonhydrogen) atoms.
3. They have fundamentally a similar geometric arrangement of heavy atoms. Criterion 3 in the preceding discussion of isoelectronic species concerning the differences in types of bonds ignored by is again invoked.
4. They have different number of "joins." It is required, however, that all joins in the species that has a smaller total number of joins have counterparts in the species that has more.

To illustrate the concepts of "joins," "isoelectronicity," and "plemeioelectronicity," consider the 4-heavy-atom species B_4H_{10} , 1,1-(CH_3) $_2B_2H_4$, 1,2-(CH_3) $_2B_2H_4$, $n-C_4H_{10}$, $i-C_4H_{10}$, (CH_3) $_3B$, (CH_3) $_2C=CH_2$, (*Z*)- or (*E*)- $CH_3CH=CHCH_3$, $c-(CH_2)_4$, $CH_2=CHCH=CH_2$, $CH_3C=CCH_3$, (CH) $_2(CH_2)_2$. Table 21-1 lists these compounds and the associated number of borons (b), carbons (c), hydrogens (h), skeletal electrons that bind the heavy atoms (sk), single bonds (s), double bonds (d), triple bonds (t), multicenter bonds (m), and joins (j). Table 21-2 pairwise interrelates the same compounds wherein an asterisk means that the species are identical; "pleme" that they are plemeioelectronic; "ielec" that they are isoelectronic; "imerc" isomers; and noirn, that they have no interrelationship.

Isoelectronic and plemeioelectronic reasoning has been highly useful in providing organizing principles for aspects of boron chemistry considerably more elegant and informative than the tables illustrating electron, atom, and bond tallies. While examples may be found in many chapters in this book, we note the importance of such reasoning in the following seminal papers in the chemistry of boron compounds and related species. The first two^{1,2} compare the hydrogen bridging of diborane(6) with the "normalcy" of ethane and offer a self-consistent, simple orbital interpretation to explain the structural differences of these archetypal and plemeioelectronically related hydrides of boron and carbon and their derivatives. From this analysis we gain a fundamental understanding of the differences of two- and multicenter bonding. The third paper³ interrelates the photoelectron spectra of the isoelectronic ethylene and diborane(6) and produces a new understanding of unsaturation and of electron and hydrogen deficiency in molecules. The final two papers^{4,5} incorporate all the concepts developed in the first three in a comparison of the isoelectronic pyramidal carbocation, $C_5H_5^+$, and the *nido*-borane, B_5H_9 . Reference 4 also presents a pioneering study of "bond stretch isomerism" and sets the stage for three-dimensional aromaticity, while Reference 5 offers an early but insightful systematization of boranes and carboranes, and defines the now "classical" prefixes *closo*, *nido*, and *arachno*.⁶ We now turn to our own isoelectronic and plemeioelectronic comparisons in a further attempt to understand the chemistry of boron compounds and related species.

2. ESTIMATION OF THE HEATS OF VAPORIZATION OF SPECIES CONTAINING BORON, HYDROGEN, AND SOMETIMES CARBON

We begin this discussion of physical properties with a study of the heats of vaporization of boron-containing compounds. As noted in the introduction,

TABLE 21-2. Some Conceptual Interrelationships Among the Small but Select Collection of X_4H_n ($X = B$ and/or C , $6 \leq n \leq 10$)^{a,b}
Species Studies in Table 21-1

Compound	B_4H_{10}	$1,1(CH_3)_2B_2H_4$	$1,2(CH_3)_2B_2H_4$	$n-C_4H_{10}$	$i-C_4H_{10}$	$(CH_3)_3B$	$(CH_3)_2C=CH_2$	$CH_3CH=CHCH_3$	$c-(CH_2)_4$	$CH_2=CHCH=CH_2$	$CH_3C\equiv CCH_3$	$(CH)_2(CH_2)_2$
B_4H_{10}	*	pleme	pleme	pleme	pleme	pleme	pleme	pleme	pleme	pleme	pleme	pleme
$1,1(CH_3)_2B_2H_4$		*	imerc	noirn	pleme	pleme	ielec	noirn	pleme	noirn	noirn	pleme
$1,2(CH_3)_2B_2H_4$			*	pleme	noirn	noirn	noirn	ielec	pleme	pleme	pleme	pleme
$n-C_4H_{10}$				*	imerc	noirn	noirn	pleme	pleme	pleme	pleme	pleme
$i-C_4H_{10}$					*	pleme	pleme	noirn	noirn	noirn	noirn	pleme
$(CH_3)_3B$						*	pleme	noirn	noirn	noirn	noirn	pleme
$(CH_3)_2C=CH_2$							*	imerc	imerc	noirn	noirn	pleme
$CH_3CH=CHCH_3$								*	imerc	pleme	pleme	pleme
$c-(CH_2)_4$									*	pleme	pleme	pleme
$CH_2=CHCH=CH_2$										*	ielec	imerc and pleme
$CH_3C\equiv CCH_3$											*	imerc and pleme
$(CH)_2(CH_2)_2$												*

^a The following abbreviations are used: pleme = plemeioelectronic, ielec = isoelectronic, imerc = isomeric, and noirn = no interrelationship except that both species are of the type X_4H_n .

^b Asterisk indicates that species so paired are identical.

in this chapter "heat of vaporization" will be taken to mean that quantity of energy needed to transform 1 mol of compound from the liquid to the ideal gas at 25°C (298 K) and 1 atm pressure. This quantity provides access to the conceptually idealized state of noninteracting molecules. Since most compounds are *not* gases under these conditions, the heat of vaporization is a highly desirable physical quantity. Regrettably, it is usually not available for most species of interest because of problems with insufficient purity, thermal lability, or excessive reactivity. As such, we provide a systematic method to allow the reader to estimate this quantity.

Noting that hydrocarbons have represented paradigms for the study of the energetics of species containing carbon, we start with the formally related binary hydrides of boron. Unlike the case of hydrocarbons in which there exist considerable heat of formation data to complement the heat of vaporization, there is almost no experimental information on the heats of formation and vaporization of the boron hydrides. We are convinced that, the relative ease of studying boron and carbon hydrides aside, this is true because there are far fewer boranes than hydrocarbons. We thus will take whatever data we can find as long as both quantities are known—ie, the temperature need not be exactly 25°C and corrections for nonideality need not have been made. These relaxed standards yield a total of five data points, four species at 25°C (298 K): B₅H₉, 6.79 kcal/mol⁷; B₅H₁₁, 7.19 kcal/mol⁸; B₆H₁₀, 9.15 kcal/mol⁸; B₁₀H₁₄, 12.95 kcal/mol⁷; and one at the slightly lower temperature of 18°C (291 K): B₄H₁₀, 6.1 kcal/mol.⁹ It is casually seen that the heats of vaporization for the two pentaboranes are comparable and that the ratio of the values for tetraborane(10), the two pentaboranes, hexaborane(10), and decaborane(14) is nearly 4 : 5 : 6 : 10, the ratio of the number of borons. This suggests that simple equations, formally related to those we found earlier¹⁰ for hydrocarbons of arbitrary structure, should be applicable here. That is, the heat of vaporization of boron hydrides may be assumed to depend only on the number of boron atoms in the simple functional manner:

$$\Delta H_v = k_1 n_b + RT \quad (21-1)$$

This prediction is tested below. The same reasoning as that earlier enunciated⁴ for the hydrocarbon case forces the intercept to equal RT . The predicted value of k_1 is 1.29(±0.04) kcal/mol; the associated correlation coefficient, r , is 0.9983. The coefficient for boron, k_1 , is somewhat higher than that found earlier for hydrocarbons, $k_2 = 1.1$ kcal/mol. This finding should not be surprising, since it may be remembered that boron hydrides generally have higher dipole moments¹¹ than all but some special highly electronically asymmetric and so particularly polar hydrocarbons.

Turning now to compounds composed of hydrogen, boron, and carbon, let us employ the related functional form:

$$\Delta H_v = k_1 n_b + k_2 n_c + RT \quad (21-2)$$

Following from the above and paralleling our study of the heat of vaporization of hydrocarbons,¹⁰ only the species for which heat of formation data are also available will now be considered. Admittedly, our earlier standards for "quality" of data are ignored here because of the paucity of data of any degree of trustworthiness or reliability. Furthermore, k_1 will be taken to be 1.3 kcal/mol and k_2 1.1 kcal/mol, the values found earlier for the binary hydrides of boron and carbon. Employing this rule first for the relatively spherical *closo*-carboranes, 1,6-B₄C₂H₆ (which has precisely zero dipole moment because of symmetry) and 2,4-B₅C₂H₇, we predict 8.0 and 9.3 kcal/mol. These are rather much higher than those in the experimental literature¹²: 6.0 and 7.4 (± 0.2) kcal/mol. That we estimate high corroborates the seeming importance of the significantly higher dipole moments in the boron hydrides than in the corresponding hydrocarbons. Putting this discrepancy aside, let us turn from these compounds of hydrogen, boron, and carbon with a high B:C ratio to those for which the ratio is low. In particular, consider the heats of vaporization of a collection of so-defined and relevant compounds,¹³ the essentially nonpolar trialkylboranes R₃B, for which the associated dipole moments are presumably small. Table 21-3 presents the experimentally and theoretically derived numbers from Equation 21-2 with k_1 and k_2 still equaling 1.3 and 1.1 kcal/mol.

It is seen that the discrepancies between the predicted and experimental values are generally under 1 kcal/mol and so really quite small. These errors average 0.8 kcal/mol, and many theoretical and experimental values are seen to be equal within experimental error bars. Indeed, from the foregoing

TABLE 21-3. Comparison of Literature Heats of Vaporization (kcal/mol) of Triorganoboranes and Those Calculated Using Equation 21-1

R	$\Delta H_{v,\text{expt}}$	$\Delta H_{v,\text{pred}}$	Difference
CH ₃	4.8 (± 0.1)	5.2	0.4
C ₂ H ₅	8.8 (± 0.1)	8.5	-0.3
<i>n</i> -C ₃ H ₇	10.0 (± 0.3)	11.8	1.8
<i>i</i> -C ₃ H ₇	10.0 (± 0.3)	11.8	1.8
<i>n</i> -C ₄ H ₉	14.8 (± 0.5)	15.1	0.3
<i>i</i> -C ₄ H ₉	14.3 (± 0.5)	15.1	0.8
<i>s</i> -C ₄ H ₉	14.5 (± 0.5)	15.1	0.6
<i>i</i> -C ₅ H ₁₁	17.2 (± 0.6)	18.3	1.1
<i>n</i> -C ₆ H ₁₃	21.2 (± 0.7)	21.7	0.5
<i>n</i> -C ₇ H ₁₅	24.4 (± 0.7)	25.0	0.6
<i>n</i> -C ₈ H ₁₇	27.6 (± 0.7)	28.3	0.7
<i>s</i> -C ₈ H ₁₇	27.0 (± 1.0)	28.3	1.3

experimental heats of vaporization for triorganoboranes and those predicted with Equation 21-2, one may derive Equation 21-3.

$$\Delta H_{v,\text{exp}} = 0.9895 \Delta H_{v,\text{pred}} - 0.613, \quad r = 0.9966 \quad (21-3)$$

The near-unity slope and correlation coefficient are encouraging. However, it is disconcerting that the intercept is nonzero and that most of the discrepancies are of one algebraic sign. Since we used k_1 , the coefficient for boron, only slightly larger than k_2 , that of carbon, this suggests the next approximation—we assume that the ΔH_v of an organic borane will be that of the plemeioelectronic alkane because the contribution to the heat of vaporization of the B in the former is nearly identical to the CH in the latter. Looking more closely at the experimental data for the trialkylboranes in Table 21-1, we see that the experimental values of ΔH_v are generally smaller for alkyl groups that are branched than for their “*n*-” isomers. This finding parallels the heats of vaporization for the unsubstituted hydrocarbons,¹⁴ eg, $(\text{CH}_3)_3\text{CH}$ with a ΔH_v of 4.61 (± 0.02) kcal/mol is lower than that of *n*- C_4H_{10} by 0.4 kcal/mol, and $(\text{C}_2\text{H}_5)_3\text{CH}$ with a ΔH_v of 8.41 ($< \pm 0.02$) kcal/mol is lower than that of *n*- C_7H_{16} by 0.3 kcal/mol. While it may seem trivial, a nonetheless relevant observation is that the hydrocarbon that is plemeioelectronic to the trialkylborane is always branched. As such, the simplest formula for estimating ΔH_v , (Equation 21-3) is expected to result in values somewhat high even if one considered only hydrocarbons. Correcting our estimated ΔH_v by a rough empirical correction of -0.3 kcal/mol for each branch, ie, replacing Equation 21-3 with Equation 21-4:

$$\Delta H_v = 1.1(n_c + n_b) + RT - 0.3(n(\text{branches})) \quad (21-4)$$

results in the values in Table 21-4.

In general, the discrepancies between theory and experiment are markedly reduced from the first equation, and the new errors for the trialkylboranes in fact, reassuringly average 0.0 kcal/mol. There is also the associated Equation 21-5.

$$\Delta H_{v,\text{exp}} = 0.99 \Delta H_{v,\text{pred}} + 0.25, \quad r = 0.9971 \quad (21-5)$$

The primary discordant compound in Table 21-4 is $(n\text{-C}_3\text{H}_7)_3\text{B}$ in that it has a considerably higher predicted value than experimental. However, the experimental value reported is almost certainly incorrect for several reasons. First, the heat of vaporization of the isomeric *i*- C_3H_7 compound is numerically the same. The latter is also in fact predicted much more accurately. Finally, the 1.2 kcal/mol difference in ΔH_v found between $(\text{C}_2\text{H}_5)_3\text{B}$ and $(n\text{-C}_3\text{H}_7)_3\text{B}$ seems too small. Leaving out $(n\text{-C}_3\text{H}_7)_3\text{B}$ results in the new Equation 21-6.

TABLE 21-4. Comparison of Literature Heats of Vaporization of Triorganoboranes and Calculated Heats of Vaporization (kcal/mol) of the Plemeioelectronically Related Hydrocarbon Using Equation 21-4

<i>R</i>	$\Delta H_{v,\text{expt}}$	$\Delta H_{v,\text{pred}}$	Difference
CH ₃	4.8 (±0.1)	4.7 ^a	-0.1
C ₂ H ₅	8.8 (±0.1)	8.0 ^b	-0.8
<i>n</i> -C ₃ H ₇	10.0 (±0.3)	11.3 ^c	1.3
<i>i</i> -C ₃ H ₇	10.0 (±0.3)	10.4 ^d	0.4
<i>n</i> -C ₄ H ₉	14.8 (±0.5)	14.6	-0.2
<i>i</i> -C ₄ H ₉	14.3 (±0.5)	13.7	-0.6
<i>s</i> -C ₄ H ₉	14.5 (±0.5)	13.7	-0.8
<i>i</i> -C ₅ H ₁₁	17.2 (±0.6)	17.0	-0.2
<i>n</i> -C ₆ H ₁₃	21.2 (±0.7)	21.2	0.0
<i>n</i> -C ₇ H ₁₅	24.4 (±0.7)	24.5	0.1
<i>n</i> -C ₈ H ₁₇	27.6 (±0.7)	27.8	0.2
<i>s</i> -C ₈ H ₁₇	27.0 (±1.0)	27.2	0.2

^a The literature value¹⁴ for $\Delta H_v[(\text{CH}_3)_3\text{CH}]$ is 4.6 kcal/mol.

^b The literature value¹⁴ for $\Delta H_v[(\text{C}_2\text{H}_5)_3\text{CH}]$ is 8.4 kcal/mol.

^c The literature value¹⁵ for $\Delta H_v[(\text{C}_3\text{H}_7)_3\text{CH}]$ is 11.5 kcal/mol.

^d The literature value¹⁵ for $\Delta H_v[(i\text{-C}_3\text{H}_7)_3\text{CH}]$ is 10.9 kcal/mol.

$$\Delta H_{v,\text{exp}} = 0.996 \Delta H_{v,\text{pred}} + 0.07, \quad r = 0.9983 \quad (21-6)$$

Alternatively if we estimate ΔH_v of $(n\text{-C}_3\text{H}_7)_3\text{B}$ to be the average of the values for $(\text{C}_2\text{H}_5)_3\text{B}$ and $(n\text{-C}_4\text{H}_9)_3\text{B}$, the equation results in:

$$\Delta H_{v,\text{exp}} = 0.998 \Delta H_{v,\text{pred}} - 0.04, \quad r = 0.9982 \quad (21-7)$$

That the slope is nearly 1 and the intercept nearly 0 for these new equations convinces us that the heat of vaporization of $(n\text{-C}_3\text{H}_7)_3\text{B}$ is in error and leads us to recommend that this quantity be remeasured. (We have opted not to compare any of our values, however, with those of a recent literature highly parameterized model,¹⁶ since we believe it is *too* uncritically dependent on experimental data.)

Our analysis and accompanying equations may be applied more broadly than to triorganoboranes. Because k_1 and k_2 were shown to be so nearly equal, for the rest of the chapter we will make the even simpler assumption that the heat of vaporization of a compound containing boron is the same as its plemeioelectronic analogue. (In the cases of the boron hydrides and carboranes such analogues rarely exist—the structures of the boron-containing and any neutral all-carbon species are generally too different. We must thus

content ourselves with general hydrocarbons that have the same number of heavy atoms.) Using Equation 21-4 and setting the number of branches equal to zero results in predictions for B_4H_{10} , B_5H_9 , B_5H_{11} , B_6H_{10} , and $B_{10}H_{14}$ of 5.0, 6.1, 6.1, 7.2, and 11.6 kcal/mol, values that are 1.1, 0.7, 1.1, 2.0, and 1.3 kcal/mol lower than those experimentally measured. From the earlier discussion, we are confident that this discrepancy is atypically high. The comparable predictions for 1,6- $B_4C_2H_6$ and 2,4- $B_5C_2H_7$, the two carboranes, are 7.2 and 8.3 kcal/mol, and so theory results in values still higher than experiment by 1.2 and 0.9 kcal/mol higher than experiment. (The typical discrepancies of about 1 kcal/mol between theoretical and experimental values of heats of vaporization may appear excessively high. However, this difference is comparable to that found using the related one-parameter approach in Reference 10 for the much more extensive set of the considerably more simple, nonpolar, and "classical" hydrocarbons.) The opposite sign of the errors for carboranes and for boron hydrides and the general reliability of prediction for trialkylboranes encourages us to believe in the foregoing methods. We likewise trust Equation 21-4 and its approximation of $k_1 = k_2$ in the estimation of the heats of vaporization of species containing boron, carbon, and hydrogen and, equivalently, in the approximate equality of the heats of vaporization of arbitrary hydrocarbons, boranes, and carboranes with the same number of heavy atoms.

3. ESTIMATION OF THE HEATS OF VAPORIZATION OF BORON-CONTAINING SPECIES WITH "HETERO"-ATOMS

Extending the logic used in Section 2, we turn now to compounds that contain "hetero"-atoms, ie, atoms other than boron, carbon, and hydrogen, commencing with oxygen-containing compounds. Our motivation to allow for the use of condensed phase data remains. Furthermore, owing to the increased complexity and diversity of compounds discussed now, our casual acceptance in Section 2 of a 1 kcal/mol discrepancy between theory and experiment will, if anything, be somewhat relaxed here. Let us start now with a discussion of the heats of vaporization of the alkoxyboranes $(CH_3O)_2BH$, $(CH_3O)_3B$, and $(C_2H_5O)_3B$, which are expected to be comparable to those of the related alkoxyethanes, $(CH_3O)_2CH_2$, $(CH_3O)_3CH$, and $(C_2H_5O)_3CH$. The three alkoxyborane heats of vaporization are 6.1 (± 0.3), 8.3 (± 0.5), and 10.5 (± 0.5) kcal/mol, while the corresponding three alkoxyethane values are 6.9 (± 0.1), 9.5, and 11.43 (± 0.02) kcal/mol (last two numbers from Reference 17). In all three cases, the values for the plemeioelectronic all-carbon ethers (ie, no-boron compounds) are higher than the boron-containing species by about 0.8 kcal/mol. We wonder if this is due to comparatively strong C—H...O hydrogen bonds found only in the ethers. Alternatively, the net polarity of the B—O bonds is no doubt smaller than

simple electronegativity logic would suggest because of B—O π bonding. There are literature data on some higher trialkoxyboranes. However, these will not be discussed here because (a) we are suspicious of the data and (b) there are no data for the corresponding trialkoxymethanes. More precisely with regard to the former, it seems unreasonable to us that the quoted heats of vaporization of triethoxy, tri-*n*-propoxy, and tri-*n*-butoxyboron [10.5 (± 0.5), 11.8 (± 1.0), and 12.5 (± 1.0) kcal/mol] vary so little. Indeed, the small incremental increases associated with adding three carbons at once as one proceeds from the *tri*-ethoxy, propoxy, and *n*-butoxy cases are comparable to the increase of one carbon for the *mono*-ethoxy, *n*-propoxy, and *n*-butoxymethanes [5.0, 6.66 (± 0.05), and 7.77 (± 0.02) kcal/mol]. The value for the first monoether, ethoxymethane, was estimated by setting the heat of vaporization of an ether equal to that of the isoelectronic alkane. For calibration, the heats of vaporization of the corresponding *n*-butane, *n*-pentane, and *n*-hexane are 5.02 (± 0.02), 6.38 (± 0.04) and 7.53 ($< \pm 0.02$) kcal/mol. The earlier mentioned $(\text{CH}_3\text{O})_2\text{CH}_2$, $(\text{CH}_3\text{O})_3\text{CH}$, and $(\text{C}_2\text{H}_5\text{O})_3\text{CH}$, with their heats of vaporization of 6.9, 9.1, and 11.4 kcal/mol, are paralleled by those of the related hydrocarbons $(\text{CH}_3\text{CH}_2)_2\text{CH}_2$, $(\text{CH}_3\text{CH}_2)_3\text{CH}$, and $(\text{C}_2\text{H}_5\text{CH}_2)_3\text{CH}$, with their highly accurate heats of vaporization of 6.38 (± 0.05),¹⁴ 8.41 ($< \pm 0.02$),¹⁴ and 11.6¹⁵ kcal/mol.

The aforementioned comparison of hydrocarbons and ethers now allows consideration of boron–oxygen compounds. Table 21-5 so compares the heats of vaporization of $(\text{RO})_3\text{B}$ and the isoelectronic $(\text{RCH}_2)_3\text{B}$. Agreement of the values for these isoelectronic trialkoxy and alkylboranes is however surprisingly poor. This, in combination with our earlier observation that the heats of vaporization of $(\text{RO})_3\text{B}$ ($\text{R} = \text{C}_2\text{H}_5$, C_3H_7 , C_4H_9) are nearly the same, makes us suspect that the values of heats of vaporization of $(\text{C}_3\text{H}_7\text{O})_3\text{B}$ and $(\text{C}_4\text{H}_9\text{O})_3\text{B}$ are incorrect. We suggest remeasurement. Turning to the one “diboron” compound, $(\text{CH}_3\text{O})_2\text{B}-\text{B}(\text{OCH}_3)_2$, its heat of vaporization of 10.68 (± 0.05) kcal/mol is somewhat lower than its plemeioelectronic analogue $(\text{CH}_3\text{CH}_2)_2\text{CH}-\text{CH}(\text{CH}_2\text{CH}_3)_2$ with its value⁹ of 11.4 kcal/mol. This parallels the relative heats of vaporization of $(\text{CH}_3\text{O})_2\text{BH}$ and $(\text{CH}_3\text{O})_3\text{B}$ and their plemeioelectronic alkanes. It would seem that predictions of the heat of vaporization of organic boron–oxygen compounds may be reliably and easily made.

For the two liquid trihaloboranes, BCl_3 and BBr_3 , the values of ΔH_v are 5.6 and 8.1 kcal/mol. These are to be compared with the plemeioelectronically related trihalomethanes CHCl_3 and CHBr_3 , and their values of 7.3 (± 0.1) and 10.9 kcal/mol (the latter value is derived from Reference 8). The values for the related carbon compounds are higher than expected. The two mechanisms noted earlier for oxygen compounds of π bonding and/or formation of hydrogen bonds are clearly applicable in these cases. It is also the case that while most conformers of the trialkylboranes and trialkoxyboranes have, in fact, nonzero dipoles, BCl_3 and BBr_3 are strictly nonpolar. For the diboron case of B_2Cl_4 we find a heat of vaporization of 10.2 kcal/mol for

TABLE 21-5. Comparison of Literature Heats of Vaporization (kcal/mol) of Trialkoxy and Trialkylboranes

R	$\Delta H_v(RO)$	$\Delta H_v(RCH_2)$	Difference
CH ₃	8.3	8.8	0.5
C ₂ H ₅	10.5	10.0 ^a	-0.5
C ₃ H ₇	11.8	14.7	-2.9
C ₄ H ₉	12.5	18.0 ^b	-5.5

^a The reader will recall our suspicion enunciated earlier of the value of the heat of vaporization of this compound, which is more commonly recognized by the name tri-*n*-propylboron. Equating values for plemeioelectronic boron and carbon compounds results in a value of 11.4 kcal/mol, and so the difference of heats of vaporization of the C₂H₅O and C₂H₅CH₂ compounds is 0.9 kcal/mol. This difference is comparable to that for the R = CH₃ case.

^b The heat of vaporization of (C₄H₉CH₂)₃B was estimated using the following procedure.

1. Take that of its isomer [(CH₃)₂CHCH₂CH₂]₃B and add 0.3 kcal/mol per branch to get 18.1 kcal/mol.
2. Take the value of plemeioelectronic hydrocarbon using our hydrocarbon estimation procedure to get 18.2 kcal/mol.
3. Modify the values for (C₄H₉)₃B and (C₆H₁₃)₃B by adding and subtracting 3 × 1.1 kcal/mol for three CH₂'s to get 18.1 and 17.9 kcal/mol, respectively.
4. Interpolate between (C₄H₉)₃B and (C₆H₁₃)₃B to get 18.0 kcal/mol.

which there are two plemeioelectronic analogues, C₂Cl₄ and CHCl₂CHCl₂. Their heats of vaporization are 9.5 (±0.2) and 10.9 (±0.1) kcal/mol, respectively. We are encouraged that the value for the hydrogen-containing organic species is meaningfully higher than the value for species lacking hydrogen and additionally note that C₂Cl₄ is as nondipolar as B₂Cl₄ precisely because of symmetry in both cases. It would appear that differences in polarity and hydrogen bonding constitute important means of distinguishing haloboranes and related halocarbons.

Consider now the three halo-di-*n*-butylboranes, (C₄H₉)₂BX (X = Cl, Br, I) with their heats of vaporization of 12.0 (±0.3), 12.5 (±0.3), and 13.0 (±0.6) kcal/mol. We know of no corresponding data for the plemeioelectronically related 5-halononanes. However, these may be simply estimated by adding to the values for the 2-halopropanes the contribution to the heat of vaporization of six carbons. The predicted values are 13.1, 13.8, and 14.8 kcal/mol. These are in the proper order and are comparable to the experimental values

but are again somewhat higher. Thus for X taken to be OH we would thus predict likewise a reduced heat of vaporization for the boron compound. In addition, the presence of the relatively positive oxygen in the boron compound would mitigate against favorable O—H...O hydrogen bonding as found in the plemeioelectronic alcohol, and so the heat of vaporization should be still lower than the carbon compound. This is indeed what is found as the value predicted without consideration of these features is 17.4 kcal/mol, while the experimental value is 15.0 (± 2.0) kcal/mol.

Consider now the phenyl-containing $(C_6H_5)_2BX$ and $C_6H_5BX_2$ species (X = Cl, Br) and let us compare our predicted heats of vaporization with the values presented in the literature.¹⁸ The two diphenyl monohaloboranes have heats of vaporization of 9.9 (± 0.2) and 14.4 (± 0.5) kcal/mol, while the two monophenyl dihaloboranes have corresponding values of 8.1 (± 0.5) and 10.5 (± 0.5) kcal/mol. (Not surprisingly, all four values were used as paradigms, ie, sources of parameters, for Reference 16.)

We know of no experimental data on the plemeioelectronic "all-carbon" compounds and so will make necessary estimates. Proceeding sequentially through the four compounds, we are convinced that the value for $(C_6H_5)_2BCl$ cannot be correct—Why should the heat of vaporization of this compound be so much less than the 13.2 kcal/mol contribution of "just" the carbons? The value for $(C_6H_5)_2BBr$ is more plausible but it is also low. Simply using our rule of equating heats of vaporization of boron compounds with corresponding plemeioelectronic hydrocarbon derivatives would give a heat of vaporization of 14.3 kcal/mol with the assumption that the Br does not contribute at all. Noting that hydrocarbons containing benzene rings usually have comparatively high heats of vaporization compared to other hydrocarbons, eg, $\Delta H_v(\text{benzene}) = 8.08$ ($< \pm 0.02$) kcal/mol but $\Delta H_v(n\text{-hexane}) = 7.53$ ($< \pm 0.02$) kcal/mol, we doubt that addition of four carbons (and the associated introduction of two benzene rings) increases the heat of vaporization of $(n\text{-}C_4H_9)_2BBr$ by only 1.9 kcal/mol, as required to produce the result given for $(C_6H_5)_2BBr$. By the same reasoning, the value for $C_6H_5BCl_2$ must be in error and the value for $C_6H_5BBr_2$ is suspect. More work is sorely needed on these phenyl boron halides.

We may even look at chlorooxygen derivatives of organic boron compounds. In the particular, consider $(CH_3O)_2BCl$, $(C_2H_5O)_2BCl$, and $C_2H_5OBCl_2$. By equating the heats of vaporization of plemeioelectronic boron- and carbon-containing species and then of isoelectronic ethers and hydrocarbons, the first two compounds would naturally be compared with $(C_2H_5)_2CHCl$ and $(n\text{-}C_3H_7)_2CHCl$. We would thus predict values of 8.7 and 10.9 kcal/mol, derived by adding the heat of vaporization contribution of two and four carbons, respectively, to $(CH_3)_2CHCl$ by the method of Section 2. Our earlier experience suggests these values are somewhat higher than the experimental for $(CH_3O)_2BCl$ and $(C_2H_5O)_2BCl$. These predictions are confirmed, the literature values are 8.2 (± 0.3) and 9.3 (± 0.2) kcal/mol. The last species can be naturally compared with $n\text{-}C_3H_7CHCl_2$ for which, however,

we have no data. However, likewise simply correcting the value for CH_3CHCl_2 for the addition of two carbons results in the desired value of 9.3 kcal/mol. This value is to be compared with the experimental value of 8.3 (± 0.2) kcal/mol.

Turning now to compounds containing nitrogen, we note that the heats of vaporization of $[(\text{CH}_3)_2\text{N}]_3\text{B}$ and $\mu\text{-N}(\text{CH}_3)_2\text{B}_2\text{H}_5$, 11.7 (± 0.2) and 6.9 (± 0.1) kcal/mol, are comparable to those of the plemeioelectronic hydrocarbons $[(\text{CH}_3)_2\text{CH}]_3\text{CH}$ and $\text{C}(\text{CH}_3)_4$, 10.9 (Reference 15) and 5.4 (± 0.1) kcal/mol. That the boron-nitrogen compounds have somewhat higher heats of vaporization is preceded by the observation of tertiary amines generally having a somewhat higher heat of vaporization than the isoelectronically related hydrocarbons. For example, $(\text{CH}_3)_3\text{CH}$ and $(\text{CH}_3)_3\text{N}$ have heats of vaporization of 4.61 (± 0.02) and 5.26 (± 0.02) kcal/mol, respectively. Analogously, the value of ΔH_v of $n\text{-C}_4\text{H}_9\text{B}(\text{OCH}_3)\text{N}(\text{C}_2\text{H}_5)_2$ is reported to be 13.9 (± 0.6) kcal/mol, a value comparable to, but comfortably larger than its plemeioelectronic analogue, $n\text{-C}_4\text{H}_9\text{CH}(\text{CH}_2\text{CH}_3)\text{CH}(\text{C}_2\text{H}_5)_2$, for which we predict a ΔH_v of 13.2 kcal/mol. In general, it would appear that boron-nitrogen compounds have heats of vaporization somewhat higher than their analogues, a finding compatible with the comparatively highly polar nature because of backbonding in the B—N bonds. In summary, use of Equation 21-4 and the appropriate isoelectronic and plemeioelectronic analogies allows for the easy and reliable estimation of the heats of vaporization of boron compounds of diverse structure and composition.

4. ESTIMATION OF HEATS OF SUBLIMATION OF BORON-CONTAINING SPECIES

The reader who noted that we previously spoke solely of the heat of vaporization, the energy needed to convert a liquid into the corresponding gas, may have questioned why we did not also deal with the heat of sublimation, the energy needed to convert a solid directly into the gas. The simplest answer is that there appears to be no general way of directly predicting heats of sublimation with the same degree of accuracy and/or generality as predicting heats of vaporization. Considering that so many compounds of interest are solids, particularly in the case of carborane derivatives, this is insufficient reason to ignore the topic entirely. Following literature precedent on hydrocarbons,¹⁹ we introduce the approximate equality,

$$\Delta H_{\text{sub}} \cong \Delta H_v + \Delta H_{\text{fus}} \quad (21-8)$$

an expression that becomes exact when the heats of sublimation, of vaporization, and of fusion are measured at the same pressure and temperature. For most species, ΔH_{fus} is considerably less than ΔH_v . Thus a simple esti-

mate of ΔH_v should provide a convenient and generally reliable lower bound to ΔH_{sub} . The remainder of this section is a test of this assertion.

We start with the three isomeric carboranes: *o*- (ie, 1,2), *m*- (ie, 1,7), and *p*- (ie, 1,12) $B_{10}C_2H_{12}$. To first approximation their heats of sublimation should be identical because they are isoelectronic, isostructural, and isosteric species. As such, knowledge of the value for one provides an estimate of the values of the other two. Since their respective values are 15.6 (± 0.2), 14.0 (± 0.2), and 14.7 (± 0.2) kcal/mol, these assertions are true. No simple understanding exists for the small differences given that all three molecules are nearly spherical but only the last, whose value is intermediate, has no dipole moment. However, our simple estimate is quite valid in that a lower bound of 13.8 kcal/mol would have been suggested.

Turning now to the mono (*C*-) and dimethyl (*C,C'*-) derivatives of *o*-carborane, we would estimate a lower limit of 14.9 and 16.0 kcal/mol to be compared with experimental values of 15.2 (± 0.1) and 15.6 (± 0.2) kcal/mol. That methylation should have such a small effect on the heat of sublimation is surprising but may be said to be preceded by the decrease of the heat of sublimation of naphthalene on monomethylation. Clearly methylation can "ruin" crystal packing. Interestingly, the *n*-hexyl (*C*-) derivative of *o*-carborane has an experimental heat of sublimation of 20.6 (± 0.3) kcal/mol, while the estimated lower limit is 20.4 kcal/mol. Regrettably, there appears to be no sublimation data on either 1- or 2-*n*-hexylnaphthalene.

Considering "hetero" derivatives and their heats of sublimation, we start with the *C*-hydroxymethyl derivatives of *o*-, *m*-, and *p*-carborane. Neglecting hydrogen bonding and approximating the effect of $-CH_2OH$ by the isoelectronic $-CH_2CH_3$, the predicted heats of vaporization of all three isomers would be 16.0 kcal/mol, as contrasted with the experimental values of heats of sublimation of 18.4 (± 0.3), 18.7 (± 0.3), and 20.1 (± 0.3) kcal/mol. The increase in ΔH_{sub} by about 3 kcal/mol upon replacing a CH_3 by an OH group is not unexpected; ie, it is a little less than the energy contribution expected from an intermolecular hydrogen bond.

We close this section with a discussion of the heats of sublimation of the *o*-, *m*-, and *p*-carborane carboxylic acids. To first approximation, all three quantities should be the same and equal to that of the plemeioelectronic isopropylcarborane. For any of the three isomers of this last species, we estimate a value of heat of vaporization of 17.1 kcal/mol as a lower limit for the experimental values of heats of sublimation of 23.2 (± 0.4), 23.4 (± 0.2), and 23.0 (± 0.2) kcal/mol. The near equality of the numbers for the three isomers is experimentally reconfirmed and the discrepancy between theory and experiment (≈ 6 kcal/mol) is not unexpected; ie, it is a little more than the energy contribution expected from an intermolecular hydrogen bond.

In summary, the use of the approximate Equation (21-4) for deriving heats of vaporization and the fact that the heat of vaporization is a generally close lower bound to the heat of sublimation provide us with a satisfactory method for estimating the heats of sublimation of boron-containing species.

5. ISOELECTRONIC COMPARISONS OF BORON- AND ALUMINUM-CONTAINING SPECIES

Let us now make some comparisons between boron and aluminum and their simple compounds. It is clear that many fundamental differences exist between these formally isoelectronically relatable classes of compounds including the following.

1. Bonds involving aluminum are generally ionic while those with boron are generally covalent or polar.
2. Aluminum is found as the hexa-coordinated $3+$ cation in many salts while boron is usually tetracoordinated and but rarely cationic.
3. Boron forms an extensive collection of binary hydrides while aluminum does not.
4. Boron forms numerous compounds with extensive multicenter bonding, including the hydrides above, while aluminum forms but few. Relatedly, elemental boron has extensive multicenter bonding while elemental aluminum is metallic.
5. Both boron and aluminum form acidic hydroxides, and while numerous salts of the former contain discrete oxyanions, the corresponding salts of the latter are generally better described as mixed oxides.

Nonetheless, despite these generally major differences between compounds of boron and aluminum, we may still ask, What are the similarities and differences of *truly* isoelectronic compounds of these elements? In particular, we will consider species only in their gaseous state and deal only with the thermodynamic quantities: heat capacity (C_p), entropy (S), and the thermal function (δH). Table 21-6 presents a collection of these numbers for such species, where E is B and Al.

Examination of Table 21-6²¹ leads to the following general rules useful for estimating the properties of Al compounds from those of B.

1. The value of C_p increases by approximately 0.5 cal/K-mol for species with two heavy atoms, 1.5 for three, and 2.5 with four, where we remind the reader that "heavy atom" refers to any nonhydrogen atom in the molecule.
2. The value of S increases by approximately 3.5 cal/K-mol for species with two heavy atoms, somewhat more with three heavy atoms, and about 5 cal/K-mol with four heavy atoms.
3. The value of δH is always small but increases with the number of heavy atoms by about 0.2 kcal/mol per heavy atom.

There are, however, some large—but understandable—exceptions to these generalities. In particular, we note the following.

TABLE 21-6. Values of the Heat Capacity, Entropy, and Thermal Function of Isoelectronic Boron and Aluminum Species in Their Gaseous State

Species	Heat capacity (cal/K-mol)		Entropy (cal/K-mol)		Thermal function (kcal/mol)	
	$C_p(B)$	$C_p(Al)$	$S(B)$	$S(Al)$	$\delta H(B)$	$\delta H(Al)$
E	5.0	5.1	36.7	39.3	1.5	1.7
EBO ₂	13.7	12.6	58.0	64.4	3.0	2.9
EBr	7.8	8.5	53.8	57.2	2.2	2.3
EBr ₃	16.2	18.0	77.5	83.4	3.8	4.3
EC	7.1	7.7	49.8	53.4	2.1	2.1
ECl	7.6	8.3	50.9	54.4	2.1	2.2
ECl ⁺	7.6	8.1	52.3	55.5		
ECIF	10.2	11.7	63.2	67.6	2.6	2.9
ECIF ₂	13.0	15.6	65.7	71.2	3.0	3.5
ECIO	10.8	12.0	56.7	59.5	2.5	2.7
ECl ₂	11.3	12.3	65.1	69.1	2.8	3.1
ECl ₂ ⁺	12.7	13.2	61.6	64.1		
ECl ₂ ⁻	11.1	12.6	63.6	68.3		
ECl ₂ F	14.1	16.4	68.7	74.4	3.2	3.8
ECl ₃	14.9	17.2	69.3	75.1	3.4	4.0
EF	7.1	7.6	47.9	51.4	2.1	2.1
EFO	9.8	11.2	53.7	56.7	2.4	2.6
EF ₂	9.7	11.0	59.0	63.1	2.5	2.8
EF ₂ ⁺	10.6	11.8	53.8	57.2		
EF ₂ ⁻	9.6	11.1	57.5	61.1		
EF ₂ O	12.0	15.2	64.0	69.9	2.8	3.4
EF ₃	12.1	14.9	60.8	66.2	2.8	3.4
EH	7.0	7.0	41.0	44.5	2.1	2.1
HEO	8.6	8.3	48.4	51.5	2.2	2.2
EHO ₂	10.1	12.0	57.3	60.8	2.6	2.8
EI	8.0	8.6	55.6	59.2	2.2	2.3
EI ₃	16.9	18.3	83.3	86.8	4.0	4.4
EN	7.0	7.4	50.7	50.6	2.1	2.1
EO	7.0	7.4	48.6	52.2	2.1	2.1
EO ₂	10.3	11.7	54.9	58.6	2.6	2.7
EO ₂ ⁻	9.4	11.1	55.5	58.6		
E ₂ O	9.2	10.9	54.4	62.0	2.5	2.8
E ₂ O ₂	13.7	15.3	58.0	66.0	3.0	3.3
ES	7.2	8.0	51.6	55.1	2.1	2.2

1. The value of S for BN is higher than for AlN. However, let us make some standard statistical mechanical corrections for the electronic (spin) contribution to the total molecular entropy. We note that BN has a $^3\Pi$ ground state while AlN is $^1\Sigma$. Therefore, the electronic contribution to the entropy is $R \ln 6$ higher for BN than for AlN. Subtracting this factor of 3.6 from the entropy of BN results in 47.1 cal/K-mol, a much more "reasonable" number that may be meaningfully expected to equal that of AlN.

2. The C_p for AlBO_2 is somewhat less than for B_2O_2 , rather than somewhat more. We note that the geometry of AlBO_2 has a bent Al—O—B linkage corresponding to Al—O—B=O , while that of B_2O_2 is linear corresponding to O=B—B=O . As such, these compounds are not truly isoelectronic and their bonding types most likely quite different. Deviation from our simple rules is thus not unexpected, although it is not obvious how to "correct" this.
3. The increase of C_p and δH in going from B_2O_2 to Al_2O_2 is much less here than for most other cases of going from B to the related compound of Al, especially if correction is made for the presence of two B atoms changed to two of Al. (If this correction is made, then the increase in S is also quite low.) We note that while the geometry of B_2O_2 is linear corresponding to a covalent O=B—B=O structure isoelectronic with the covalent C_2N_2 , Al_2O_2 has been suggested to have a square, alternating Al—O geometry reminiscent of much more polar species such as the alkali halide and alkaline earth oxide dimers. Deviation from our simple rules is thus not disturbing, although still "uncorrected."

It is thus seen that thermochemically meaningful comparisons may generally be made between isoelectronically related compounds of boron and aluminum. Equivalently, thermochemical comparisons allow one to make simple structural comparisons between formally related species of boron and aluminum to ascertain whether they have essentially the same structure or "merely" have the same number of valence electrons and the same formal stoichiometry.

6. PLEMEIOELECTRONIC COMPARISONS OF BORON- AND CARBON-CONTAINING SPECIES

Let us now make some comparisons between compounds of boron and of carbon. As in the boron-aluminum case, it is clear that many fundamental differences exist between boron- and carbon-containing species, and so plemeioelectronically relatable classes of compounds with meaningful comparisons are somewhat rare. These differences include the following.

1. Carbon almost always forms compounds with four bonds per carbon, while in numerous boron-containing compounds, boron has but three [eg, BF_3 vs CHF_3 (3 vs 4)]. Likewise, carbon forms numerous compounds with four or fewer bonding partners, while boron forms many with four or more [eg, $\text{B}_6\text{H}_6^{2-}$ vs C_6H_6 (cf. benzene, 5 vs 3)].
2. Multiple bonding is rarely found in compounds of boron but is common for those of carbon; multicenter bonding is common for compounds of boron but rare for those of carbon.

3. Boron forms an extensive collection of binary hydrides when compared to most elements, but the number pales in comparison to that of carbon hydrides. Carbon-carbon (two-center, two-electron) single bonds are found in most carbon hydrides but are a rare feature in those of boron. Furthermore, boron hydrides are generally both kinetically and thermodynamically unstable relative to those of carbon.
4. While both boron and carbon form acidic oxides, the former is a solid while the latter is a gas under ambient conditions. Furthermore, numerous boron salts contain oligomeric oxyanions, while the corresponding salts of carbon are limited to the monomeric HCO_3^- and CO_3^{2-} . The analogous difference of phase is also found in the binary nitrides and sulfides, where we may compare the solid BN and gaseous C_2N_2 , and the solid B_2S_3 and gaseous CS_2 .

Nonetheless, despite these major differences, we may still ask, What are the similarities and differences of truly plemeioelectronic compounds of boron and carbon? In particular, we again consider species only in their gaseous state and again focus the thermodynamic quantities: heat capacity (C_p), entropy (S), and the thermal function (δH). B is plemeioelectronically related to both C and to CH. Both comparisons are meaningful and so will be made wherever possible. In the name of brevity, however, only compounds containing either one or two borons are considered here.

From examination of Table 21-7²¹ and in accord with both statistical mechanical analysis and qualitative precedent in the thermochemical literature,²² we find that compounds in which C and B are plemeioelectronically exchanged have very similar values for the properties of interest. More precisely, the values of C_p and δH are nearly identical. The difference of the two values of entropy can be understood in terms of different symmetry numbers and/or electronic degeneracies and so the reader may thus be implicitly reminded of the concept of "symmetryless"^{23a} (or "intrinsic"^{23b}) entropy, defined as follows:

$$S^* = S + R \ln(\sigma) \quad (21-9)$$

The plemeioelectronic exchange of B by CH produces negligible changes in δH and changes in C_p of larger than about 1 and of about 4 cal/K-mol in S are quite rare. The biggest changes are found for the species with the fewest atoms. The change in S is quite small, but it should be remembered that the number of unpaired electrons (and so spin degeneracy) of plemeioelectronically related B- and CH-containing species is usually the same. As such, the entropy increase is small and the entropy is comparable for species with any of the B, C, and CH centers.

In summary, after making the quite simple corrections for geometric symmetry and electronic degeneracy to the total entropy, it is generally safe to equate the values for plemeioelectronically related species containing B, C,

TABLE 21-7. Literature Values of Heat Capacity, Entropy, and Thermal Function of Plemeioelectronic Boron and Carbon Compounds^a

Species	Heat capacity (cal/K-mol)			Entropy (cal/K-mol)			Thermal function (kcal/mol)		
	$C_p(B)$	$C_p(C)$	$C_p(CH)$	$S(B)$	$S(C)$	$S(CH)$	$\delta H(B)$	$\delta H(C)$	$\delta H(CH)$
E	5.0	5.0	7.0	36.7	37.8	43.7	1.5	1.6	2.1
EB	7.3	7.1		48.2	49.8		2.1	2.1	
EBr	7.8	8.5		53.8	55.8		2.2	2.3	
EBrCl ₂	15.4		16.1*	74.2		75.6*	3.5		3.5*
EBrF ₂	13.5		14.0*	68.4		70.6*	3.1		3.1*
EBr ₂ Cl	15.8		16.5*	76.9		78.3	3.6		3.6*
EBr ₂ F	14.9		15.6*	74.1		75.7*	3.4		3.4*
EBr ₂ H	12.7		13.1*	69.8		70.1*	3.0		3.0*
EBr ₃	16.2		17.0*	77.5		79.1*	3.8		3.8*
EC	7.1	10.3	6.9	49.8	53.4	49.6	2.1	2.1	2.2
ECl	7.6	7.7	8.8	50.9	53.6	56.1	2.1	2.2	2.4
ECIF ₂	13.0		13.6	65.7		67.1	3.0		3.0
ECIO	10.8	10.8		56.7	63.5		2.5	2.8	
ECl ₂	11.3	11.1		65.1	63.4		2.8	2.7	
ECl ₂ F	14.1		14.6	68.7		70.1	3.2		3.2
ECl ₂ H	11.9		12.2#	64.1		64.6#	2.8		2.8*
ECl ₃	14.9	15.2	15.6	69.3	70.9	70.6	3.4	3.4	3.4
EF	7.1	7.2	8.3	47.9	50.9	53.4	2.1	2.2	2.4
EFO	9.8	9.3	9.7	53.7	59.4	59.0	2.4	2.5	2.5
EF ₂	9.7	9.3		59.0	57.5		2.5	2.5	
EF ₂ H	10.1		10.3#	58.3		58.9#	2.6		2.6*
EF ₂ O	12.0	11.3		64.0	61.9		2.8	2.6	
EF ₃	12.1	11.9	12.2	60.8	63.3	62.0	2.8	2.8	2.8
EH	7.0	7.0	8.3	41.0	43.7	46.3	2.1	2.1	2.4
EH ₂	8.1	8.3	8.5	43.0	46.3	46.4	2.2	2.4	2.4
EH ₃	8.7	8.5		44.9	46.4		2.4	2.4	
HEO	8.6	8.3	8.5	48.4	53.7	52.3	2.2	2.4	
EHO ₂	10.1		10.8#	57.3		59.5#			
EH ₃ CO ^b	14.2*		13.1#	59.6		63.2#	3.1*	3.1	
EI ₃	16.9		17.9*	83.3		85.1*	4.0		4.1*
EN	7.0	7.4	8.6	50.7	48.4	48.2	2.1	2.0	2.2
EO	7.0	7.0	8.3	48.6	47.2	53.7	2.1	2.1	2.1
EO ₂	10.3	8.9		54.9	51.1		2.6	2.2	
E ₂	7.3	10.3	10.5	48.2	47.6	48.0	2.1	2.5	2.4
E ₂ Cl ₄ ^c	22.7	22.8	24.0*	85.8	82.1	86.7*	3.8	3.8	
E ₂ F ₄ ^c	18.4	19.2		76.1	71.7		2.9	3.0	
E ₂ H ₆	13.9	12.6*		55.7	54.9*		2.9	2.8*	
E ₂ O ^d	9.2	10.3	12.3*	54.4	55.7	59.2*	2.5	2.5	2.8*
E ₂ O ₂ ^e	13.7	13.5		58.0	58.0		3.0	3.0	
ES	7.2	7.1		51.6	50.3		2.1	2.1	

^a All data are implicitly from Reference 7, except those marked by *, which are from Reference 8, and by #, which are from Reference 20.

^b The plemeioelectronic analogue with CH is taken to be CH₃CHO.

^c Note that δH refers to the difference at 100 and 298 K.

^d Because there are two E atoms, the plemeioelectronic CH analogue is taken to be CH₂CO. Admittedly, however, B₂O has a bent B—O—B structure and not B—B=O.

^e The values given for C₂O₂ are taken as the average of those for the plemeioelectronic C₂N₂ and C₂F₂.

and CH. Indeed, these corrections are generally small enough that they may be ignored in a usefully accurate, but admittedly first, approximation.

7. ARE THERE ISOLABLE ISOMERS OF B_4H_{10} ?

In recent years there have been several high-quality quantum chemical calculations²⁴⁻²⁷ on the energy difference between the long experimentally known arachno (or "butterfly") form of tetraborane(10) and its still unknown isomer, bis-diborane, $(B_2H_5)_2$.²⁸ As is usually the case in theoretical studies of molecular stability, these calculations referred directly to the energy difference of the hypothetical vibrationless molecules at 0 K. To aid in future studies of these two species, be they experimental or theoretical, we explicitly consider below the following energy quantities: the "symmetryless"^{23a} or "intrinsic"^{23b} entropy (S^*), the thermal function (δH), the heat capacity at 298 K (C_p), and the zero-point energy (ZPE). The reader should note that there are few relevant published pieces of thermochemical data on the butterfly form of B_4H_{10} and save the calculated energy difference above, none at all for its isomer $(B_2H_5)_2$.

In what follows we will use isoelectronic, plemeioelectronic, and generalized isomerism analogies to attempt to compare these two species. To demonstrate that these analogies are valid, we will start with the smaller and thus presumably simpler species B_2H_6 . The first comparison is with the plemeioelectronic C_2H_6 . Their values of ZPE and δH (in kcal/mol), and S^* and C_p (in cal/K-mol) are given below:

	ZPE	δH	S^*	C_p
B_2H_6	38.6	2.90	58.5	13.9
C_2H_6	45.2	2.84	60.6	12.6

Except for the zero-point energy, the various energy quantities are comparable for these two substances. The second comparison of all four quantities involve B_2H_6 and the isoelectronically related C_2H_4 . (For completeness, we also include N_2H_4 , which we identify as both plemeioelectronic to C_2H_4 and isoelectronic to the earlier discussed C_2H_6 .)

	ZPE	δH	S^*	C_p
B_2H_6	38.6	2.90	58.5	13.9
C_2H_4	30.9	2.53	55.2	10.4
N_2H_4	29.8	2.75	59.8	12.1

It is seen that the plemeioelectronic C_2H_4 and N_2H_4 have more nearly equal values of ZPE , δH , and C_p than do the isoelectronic B_2H_6 and C_2H_4 . The symmetryless entropy of C_2H_4 is somewhat closer to B_2H_6 than it is to N_2H_4 ,

although the net spread of the contribution of the entropy terms to the Gibbs free energy at 298 K of all three species is but 1 kcal/mol. The effect of δH and S^* is correspondingly small. By far the biggest difference is again that of the zero-point energies.

If energy differences are rather small for a set of isoelectronic and plemeioelectronic species, they are likewise expected to be small for species that are in fact isomeric. Let us now consider four isomers of a species that is isoelectronic to B_4H_{10} , C_4H_6 . Three of these new compounds are bicyclobutane, 1,3-butadiene, and 2-butyne. For the fourth, we also consider a "disconnected isomer," $[2C_2H_4 + C_2H_6 - 2CH_4]$, a species that is defined as being composed of the same number and type of atoms and also has the same net number of molecules [$1 = 2(1) + 1 - 2(1)$]. (See Table 21-8). It would appear that sets of isomers have comparable values of ZPE as well as δH and C_p . Even the entropies are comparable, although that of bicyclobutane is low, presumably less than expected because of the cyclic structure.

What does the foregoing tell us about the two isomeric forms of B_4H_{10} ? The comparison of the four isomers of C_4H_6 suggests that the zero-point energies of the two isomers of B_4H_{10} should be nearly equal. The comparisons of B_2H_6 and C_2H_6 , and of C_2H_4 and N_2H_4 suggest that δH and C_p for the two isomers of B_4H_{10} should be also nearly the same. Numerically, these may be estimated by equating these quantities to those of either of the two conventional isomers of C_4H_{10} — $CH_3CH_2CH_2CH_3$ and $CH(CH_3)_3$ —or to a "disconnected isomer," $[3C_2H_6 - 2CH_4]$. The values for δH so derived are 4.6,²⁹ 4.3,²⁹ and 3.7 kcal/mol, respectively, and for C_p are 23.5,²⁹ 23.1,²⁹ and 20.7 cal/K-mol. The values of S^* of the three isomers of C_4H_{10} are 79.9,²⁹ 79.4,²⁹ and 82.8 cal/K-mol. Equating the values of δH and C_p of either

TABLE 21-8. Values of Zero-Point Energy, Thermal Function, "Intrinsic" Entropy, and Heat Capacity for a Collection of C_4H_6 Isomers

Isomer	ZPE (kcal/mol) ^a	δH (kcal/mol)	S^* (cal/K-mol) ^b	C_p (cal/K-mol)
Bicyclobutane	52.0	3.02 ^c	63.9	
1,3-Butadiene	51.4	3.63 ^d	68.0	19.0
2-Butyne	51.1	3.96 ^d	73.5	19.0
$[2C_2H_4 + C_2H_6 - 2CH_4]$	52.9	3.10	72.0	17.7

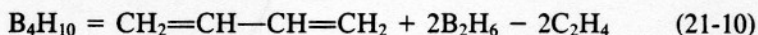
^a These values were obtained by summing over all $3N - 6$ frequencies, i.e., $ZPE = \frac{1}{2} \sum_i h\nu_i$, where the individual frequency values were taken from Shimanouchi, T. "Tables of Molecular Vibrational Frequencies," consolidated Vol. 1, National Standard Reference Data Service, NSRDS-NBS 39, 1972.

^b These values come from correcting the experimental entropies given in Reference 20. Srinivasan, R.; Levi, A. A.; Haller, I. *J. Phys. Chem.* **1965**, *69*, 1775.

^d These values for 1,3-butadiene and 2-butyne are from tables 25r, pt. 1, 1952 and 12r, 1945, respectively of the API44 tables (American Petroleum Institute Project 44) "Selected Properties of Hydrocarbons and Related Compounds" (Thermodynamic Research Center: College Station, Tex.).

isomer of B_4H_{10} with any of the isomers of C_4H_{10} , we thus deduce values of about 4.0 kcal/mol and 23 cal/K-mol, respectively. The value of S^* for the acyclic, noncage bis-diborane is expected to be 76 cal/K-mol, or about 4 less than the value of 80 found for the hydrocarbons by analogy to the fact that S^* for B_2H_6 is about 2 cal/K-mol less than for C_2H_6 . If the difference of the ring and acyclic isomers for C_4H_6 , bicyclobutane, and any of its three isomers is assumed to be comparable to that for the arachno, butterfly B_4H_{10} form and its acyclic isomer, the arachno isomer should have a value of entropy of about 6 (± 2) cal/K-mol lower.

At the risk of "overkill," we note several more approaches to the thermochemistry of bis-diboranyl. Values for the acyclic bis-diborane itself may be obtained using isodesmic reactions³⁰:



with δH , C_p , and S^* deduced to be 4.4 kcal/mol, 26 cal/K-mol, and 74.6 cal/K-mol, respectively, and



with δH , C_p , and S^* deduced to be 4.7 kcal/mol, 26 cal/K-mol, and 75.7 cal/K-mol.

In summary, from our analysis, we deduce that the values for δH , C_p , and ZPE for the two isomers of B_4H_{10} should be nearly identical and that the entropy of the unknown isomer should be about 6 cal/K-mol higher than the known species. This corresponds to but 2 kcal/mol or so for our total thermochemical and zero-point energy corrections to the literature calculations on the two isomers of B_4H_{10} . We eagerly await experimental studies on bis-diborane.

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