THE ABSOLUTE ENTROPIES OF ALKALI METAL BORIDES. SIMPLE PATTERNS AND HIGH-LEVEL CALCULATIONS

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Dedicated to Professor Jaroslav Koutecký, who pioneered the establishment of the famous quantum chemistry school in the former Czechoslovakia.

The validity of the recently enunciated average-entropy equation, using symmetry-corrected absolute entropies, was tested against the values obtained from the literature and from accurate quantum chemical calculations. We analyze this validity for the series of yet unexplored alkali metal borides MeB (Me = Li, Na, K, Rb, Cs).

Keywords: Entropy; Pair additivity; Alkali metal borides; Diatomics; Thermodynamics; Ab initio calculations.

Entropy is a useful and fundamental concept in our understanding of chemistry. In a recent paper[1] we earlier discussed the validity of the following "average entropy equation"

$$S^*(\mathrm{XY}) = 1/2[S^*(\mathrm{X}_2) + S^*(\mathrm{Y}_2)] \qquad (1)$$

where S^* is the symmetry corrected absolute entropy. Using this equation we studied in our earlier paper[1] the trends in absolute entropy in the series of the homonuclear and heteronuclear dimers XY (X, Y = H, F, Cl, Br, I, Li, Na, K, Rb, Cs; and B and Al). How valid is Eq. (*1*)? Values from the literature and from our quantum chemical calculations will be discussed for the all but unexplored series MeB (Me = Li, Na, K, Rb, Cs).

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In paper[1] we presented atomic equivalents for S^*, i.e. quantities to be summed to obtain the desired molecular quantity. We included these quantities for B and Al. In that $S^*(\mathrm{B}) = 100.5$ J mol^{-1} K^{-1}, the symmetry-corrected absolute entropy for B_2, equals twice this quantity: $S^*(\mathrm{B}_2) = 201.0$ J mol^{-1} K^{-1}. Relatedly, $S^*(\mathrm{Al}) = 115.8$ J mol^{-1} K^{-1}, $S^*(\mathrm{Al}_2) = 231.6$ J mol^{-1} K^{-1}. From the archival literature[2], we find values of the absolute entropy $S°$ of 202.07 ± 0.17 and 233.5 ± 0.3 J mol^{-1} K^{-1} for B_2 and Al_2, respectively. These derived[1] and literature[2] values are in pleasantly good agreement until it is recognized that

a) we need to correct the $S°$ values by symmetry number correction $R \ln 2$, namely 5.8 J mol^{-1} K^{-1}, because these diatomics are homonuclear;

b) the literature values are for the triplet ground states of the diatomics while our calculation assumes we have the term symbol $^1\Sigma$ for the diatomics of interest. Are we not talking about different species in the two different sources of information?

The former correction is numerically easy to make resulting in $S^*(\mathrm{B}_2) = 207.8$ J mol^{-1} K^{-1} and $S^*(\mathrm{Al}_2) = 239.3$ J mol^{-1} K^{-1}. Our good agreement is seemingly lost by making this correction. What does this say about the earlier enunciated validity of Eq. (*1*)? And what do we do about the latter correction? How do we test this validity?

Recall that within the well-established Born–Oppenheimer approximation,

$$S° = S°_{\mathrm{trans}} + S°_{\mathrm{rot}} + S°_{\mathrm{vib}} + S°_{\mathrm{elec}} + S°_{\mathrm{spin}} \, . \tag{2}$$

For all of the species explicitly discussed in ref.[1], $S°_{\mathrm{spin}} = 0$. (The species were chosen to be all singlets, the multiplicity or spin degeneracy of the species, g, equals unity, and this additional entropy contribution is the product of R and $\ln g$.) For triplet state species, we must therefore decrease their entropy by $R \ln 3$, namely 9.13 J mol^{-1} K^{-1}. This decremental procedure numerically reduces $S^*(\mathrm{B}_2)$ and $S^*(\mathrm{Al}_2)$ to 198.7 and 230.2 J mol^{-1} K^{-1} where the superscripted * refers henceforth in this text to spin as well as symmetry number-corrected entropies.

$S°_{\mathrm{trans}}$ is the same for an arbitrary species and any of its excited states because it depends only on the mass. $S°_{\mathrm{rot}}$ depends on the masses of the atoms and their location. The masses are always the same for ground and excited state species. For our diatomic molecules within the current model, the masses are always located at opposite ends of a rigid rod that we recognize as the B–B and Al–Al bond. The rotational entropy depends only logarithmically on bond length – presumably the difference of the bond lengths for ground and low-lying excited states is not too great and so $S°_{rot}$ is roughly unchanged on excitation. The vibrational entropy of an arbitrary molecular species, has a rather much more complicated dependence on the component quantities, the various vibrational frequencies. However, we have but one frequency to consider here and, in any case, $S°_{vib}$ is usually smaller than the translational and rotational entropy components. Accordingly, the aforementioned values of 198.7 and 230.2 J mol^{-1} K^{-1} for $S^*(B_2)$ and $S^*(Al_2)$ are suggested for the $^1\Sigma$ states of B_2 and Al_2 in satisfactory agreement with our earlier suggested values.

METHODS

We are interested in the trends in entropies, not only for a given set of diatomics, but also for all conceivable borides across the rows and columns of periodic system. To further check the additivity assumption discussed briefly in the introduction we have opted for the following strategy. For the tested set of the molecules we have used a rather pragmatic approach selecting very simple level of calculation – Hartree–Fock approximation with economical 3-21G* basis set[3–5] (HF/3-21G*) within the SPARTAN suite of programs[6]. We have not included CsB with SPARTAN. As we will show later, for the HF/3-21G* approximation the deficiencies in the method (namely the absence of electron correlation and for heavier elements also scalar relativistic effects) and the lower flexibility of the basis set have opposite effect and the cancellation of these errors (cf., e.g., ref.[7]) results in reasonable agreement with available experimental data. For our selected series of diatomics MeB (Me = Li, Na, K, Rb, Cs) we have applied also the higher-level method – coupled cluster singles and doubles augmented with perturbative triples correction – CCSD(T)[8,9]. For heavier members in this set of molecules (e.g., RbB and CsB), scalar relativistic effects can play some role; thus we have included them systematically for the whole set within the Douglas–Kroll–Hess scheme[10–12] as implemented in the MOLCAS program system[13]. We have used the ANO-RCC basis set[14,15] with maximum contraction, namely: B(14s9p5d3f)/[9s8p5d3f], Li(14s9p4d3f)/[8s7p4d2f], Na(17s12p5d4f)/[9s8p5d4f], K(21s16p5d4f)/[10s9p5d3f], Rb(23s19p11d4f)/[10s10p5d4f], Cs(26s22p15d4f/9s8p7d3f). This will allow us to check the reliability of the simplified HF/3-21G* approach and also to calculate the entropy of CsB (not included in the HF/3-21G* set).

The individual contributions to *S* in Eq. (*2*) were calculated using the standard rigid-rotor-harmonic-oscillator scheme. For the high-level coupled-cluster data we have included in the calculations of vibrational entropies also anharmonicity constants and first-order rotation-vibration interaction constants to check the anharmonicity effects. In the calculations of anharmonicity corrections we have used the formula for vibrational entropy published in JANAF thermochemical tables[2].

Since our set of the molecules consists only of singlets and we are computing the entropies at room temperature, the electronic contribution to the partition functions arising from higher electronic singlet states is expected to be negligible.

RESULTS AND DISCUSSION

What do quantum chemical calculations tell us? First we tried $^1\Sigma$ B_2 and Al_2 at the HF/3-21G* level, these trial calculations gave the values 195.7 and 230.6 J mol^{-1} K^{-1}. Even though the calculational level is comparatively low, the results are compatible with those suggested before. This gives us confidence to consider other diatomic species containing boron and alkali metal and defer also consideration of those of their heavier congeners Al, Ga and In.

Table I presents the symmetry number-corrected entropies S^* for species of the type XB, with X = Li, Na, K, Rb and Cs and Table II presents calculated HF/3-21G* data for the same species but without caesium boride.

TABLE I

Symmetry number-corrected entropies S^*. Experimental entropies from refs[2,16,17] except for data in italics[a]. Values in J mol^{-1} K^{-1}

Element	Li	Na	K	Rb	Cs	B
Li	202.8	219.2	228.4	237.7	243.5	*201.6*
Na	219.2	236.0	245.7	254.4	259.8	*218.5*
K	228.4	245.7	255.5	264.2	269.9	*227.7*
Rb	237.7	254.4	264.2	276.9	283.3	*238.2*
Cs	243.5	259.8	269.9	283.3	290.5	*244.9*
B	*201.6*	*218.5*	*227.7*	*238.2*	*244.9*	198.7[b]

[a] MBPT(4)/6-311G* entropies taken from ref.[1]. [b] This value is not predicted; the experimental value for B_2 was derived from the analysis of the data in ref.[2]

Table II gives also the differences between the entropies from Table I and theoretical values. It is to be seen that our calculations generally reproduce experimental values to within 5 J mol^{-1} K^{-1}, most values being even in better agreement. In that, calculations and prior experience are in concurrence, we now present in Table III the entropies derived from the average entropy equation (*1*) using the HF/3-21G* entropies of alkali metal dimers and B_2. Comparison with Table I as well as with Table II offers the possibility to test the predictions of Eq. (*1*). Good agreement is found for all of our investigated species. Why is the agreement so good for so simple approximation?

TABLE II
HF/3-21G* absolute entropies S^* and deviations (in parentheses) from earlier "additive" values suggested in ref.[1]. Values in J mol^{-1} K^{-1}

Element	Li	Na	K	Rb	B
Li	203.6 (–0.8)	220.0 (–0.8)	230.5 (–2.1)	241.5 (–3.8)	199.7 (1.9)
Na	220.0 (–0.8)	237.4 (–1.4)	246.7 (–1.0)	257.1 (–2.7)	216.6 (1.9)
K	230.5 (–2.1)	246.7 (–1.0)	256.7 (–1.2)	267.4 (–3.2)	226.4 (1.3)
Rb	241.5 (–3.8)	257.1 (–2.7)	267.4 (–3.2)	278.3 (–1.4)	243.0 (–4.8)
B	199.7 (1.9)	216.6 (1.9)	226.4 (1.3)	243.0 (4.8)	195.7 (3.0)

TABLE III
Absolute entropies S^* from the average entropy equation (*1*) using the Me_2 and B_2 HF/3-21G* data and deviations (in parentheses) from earlier "additive" values suggested in ref.[1]. Values in J mol^{-1} K^{-1}

Element	Li	Na	K	Rb	B
Li	203.6 (–0.8)	220.5 (–1.3)	230.1 (–1.7)	240.9 (–3.2)	199.6 (2.0)
Na	220.5 (–1.3)	237.4 (–1.4)	247.0 (–1.3)	257.8 (–3.4)	216.5 (2.0)
K	230.1 (–1.7)	247.0 (–1.3)	256.7 (–1.2)	267.5 (–3.3)	226.2 (1.5)
Rb	240.9 (–3.2)	257.8 (–3.4)	267.5 (–3.3)	278.3 (–1.4)	237.0 (1.2)
B	199.6 (2.0)	216.5 (2.0)	226.2 (1.5)	237.0 (1.2)	195.7 (3.0)

The cynic may wonder about the accuracy of the above quantum chemical calculations. Where earlier studied, the alkali metal trellides are not correctly described as Me–B: indeed, they are found to be ground-state triplets. So, we are dealing with excited state species – is that a computational or conceptual problem? Conceptually no, for we have defined Eq. (*1*) only to apply to $^1\Sigma$ species of the type X–Y. To ameliorate the calculational framework, and any resultant anxiety or dismay, we have also employed state of the art CCSD(T)/ANO-L calculations (Tables IV and V). They enable us to

TABLE IV
CCSD(T)/ANO-L[a] equilibrium distances, harmonic frequencies and absolute entropies for $^1\Sigma^+$ states of MeB

Metal		R_e Å	ω_e cm^{-1}	S_{trans} J mol^{-1} K^{-1}	S_{rot} J mol^{-1} K^{-1}	S_{vib} J mol^{-1} K^{-1}	$S°_{qsm}$ (S^*_{qsm}) J mol^{-1} K^{-1}	S^*_{add} J mol^{-1} K^{-1}	δ
Li	SCF	2.400	472	144.8	55.7	3.2	203.7	201.6	–2.1
	CCSD	2.396	434		55.7	3.7	204.2		–2.6
	CCSD(T)	2.394	426		55.7	3.8	204.3		–2.7
Na	SCF	2.709	319	152.7	62.3	5.6	220.7	218.5	–2.2
	CCSD	2.698	299		62.2	6.1	221.1		–2.6
	CCSD(T)	2.704	287		62.3	6.4	221.4		–2.9
K	SCF	3.199	247	157.5	66.3	7.4	231.2	227.7	–3.5
	CCSD	3.161	233		66.1	7.9	231.5		–3.8
	CCSD(T)	3.172	220		66.1	8.4	232.0		–4.3
Rb	SCF	3.357	221	165.7	68.1	8.3	242.1	238.2	–3.9
	CCSD	3.319	203		67.9	9.0	242.6		–4.4
	CCSD(T)	3.333	191		68.0	9.5	243.2		–5.0
Cs	SCF	3.576	197	170.7	69.5	9.1	249.3	244.9	–4.4
	CCSD	3.542	181		69.4	9.8	249.9		–5.0
	CCSD(T)	3.561	168		69.4	10.4	250.6		–5.7

[a] Frozen shells on Me atoms in CC calculations: lithium and sodium K, potassium KL, rubidium KLM[4s], cesium KLMN[5s].

get an insight into the interplay of different contributions (SCF, CCSD, CCSD(T)) giving the total entropies. In addition, for vibrational entropies we can compare the RRHO approach and the approach refined by anharmonicity corrections. First, we stress that in our CC calculations we analyzed carefully the mono- and biexcitation amplitudes from CCSD part of the calculation and no extremely or dangerously large values were observed. So for all our excited states the single-reference wave function is adequate.

Table IV summarizes our high-level calculated values of bond distances R_e, the stretching frequency ω_e and the derived entropy, $S°_{qsm}$ (or just as well S^*_{qsm}, given these species are heteronuclear). We also include the values earlier suggested in previous paper[1] which explicitly made use of our additivity estimate, here designated as S^*_{add} with no correction made for the small change in recommended values of B_2 discussed earlier in this text. In Table IV we can follow the trends in three principal levels of calculations: SCF, CCSD and CCSD(T). This reveals the role of electron correlation contribution arising from iterative singles and doubles (CCSD) and non-iterative triple-excitation contribution.

In Table V we present the entropies including the anharmonicity corrections. At given temperature of 298 K they represent but a few per cent of the S_{vib} values, however, their effect on the absolute entropies, $S°_{qsm}$, is negligible.

TABLE V
CCSD(T)/ANO-L rotational constants, vibrational anharmonicity constants, first-order rotation-vibration interation constants and corrections to absolute entropies for $^1\Sigma^+$ states of MeB

Metal	B_e	$\omega_e x_e$	α_e	S_{anh}	$S_{vib,anh}$	$S°_{qsm,anh}$
		cm^{-1}		J mol^{-1} K^{-1}		
Li	0.696	5.01	0.010	0.2	4.0	204.5
Na	0.314	3.80	0.004	0.4	6.8	221.8
K	0.198	2.60	0.002	0.4	8.8	232.4
Rb	0.158	2.70	0.002	0.6	10.1	243.8
Cs	0.133	1.70	0.001	0.5	11.0	251.1

We now may compare the entropies of the singlet states of LiB, NaB, KB, RbB and CsB calculated at crude approximation HF/3-21G* and at the CC-level. The comparison reveals that:

1. Combination of the HF method with the small split-valence basis set 3-21G* leads to entropies that are mostly underestimated (except for RbB) compared to HF/ANO-RCC data, but fortuitously close to "additive" ones. This is caused by the differences in geometries provided by the HF/3-21G* model with respect to HF/ANO-RCC one, affecting slightly rotational constants and, consequently, rotational entropies in both models.

2. The differences within high-level set, i.e., between SCF, CCSD and CCSD(T) entropies obtained with the large basis set are marginal (barely exceeding 1 J mol^{-1} K^{-1}).

3. While translational entropy plays merely "spectators role" being independent of the method/basis set, the rotational entropy has more weight than vibrational entropy (Table IV). The key factors are then S_{rot} and S_{vib}, whereas the former is usually an order of magnitude larger than the latter. Thus the accurate geometry determination has greater impact than accurate harmonic frequency.

4. High-level calculations in connection with RRHO approximation lead to slightly larger entropies but the differences with respect to "additive" values suggested in ref.[1] are still small. If one tries to model $T\delta S$ term at room temperature based on δ's from Table IV, it is still on the level of 1 kJ mol^{-1}.

Thus, the two sets of absolute entropies are in good agreement. We may understand the discrepancies in terms of the "real" alkali metal borides being less bound than we might have expected and so the bond length is longer and the stretching frequency lower than expected. These "corrections" to longer and weaker bonds increase the rotational and vibrational entropy components, respectively, and so the "real" absolute entropies are underestimated by our earlier additivity estimate.

In conclusion, we note that the absolute entropy for the alkali metal borides is significantly greater than for the related boron halides with very much the same molecular weight and therefore the translational entropies are nearly equal. Comparison of the pairs BF (200.5) and NaB (218.5), BCl (213.2) and KB (232.4), BBr (225.0) and RbB (243.0), BI (232.6) and CsB (250.6), all in J mol^{-1} K^{-1}, documents the weak, long and floppy bonds of the alkali metal borides. Work is in progress on additional consequences of such nearly "isobarimeric" relations for larger set of exotic molecules including alkali halides and the dialkalis and dihalogens, e.g., NaI, CsF, CsNa and IF. Is it merely coincidental that the entropy difference for the alkali metal borides and corresponding boron halides is nearly constant, approximately 18–19 J mol^{-1} K^{-1}? It would be interesting to find the entropy trends for the related alkali metal aluminides and aluminum halides, and the corresponding species containing Ga, In and Tl. And what about species containing the heaviest alkali metal and halogen, namely Fr and At? Our continuing studies will illuminate the thermochemistry of the species enunciated above as well as provide better understanding of our average entropy rule.

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