ADDITIVITY OF ABSOLUTE ENTROPIES

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Dedicated to Professor Rudolf Zahradník on the occasion of his 75th birthday to admire his passion
for sense and sensitivity in science.

Symmetry number-corrected entropies for a series of inorganic diatomic molecules were ana-
lyzed. We have considered molecules XY (X, Y = H, F, Cl, Br, I, Li, Na, K, Rb, Cs, B and Al).
Based on the assumption of elemental additivity, the prediction of known entropy data is
quite satisfactory (except for H_2) and provides fairly reasonable estimates for data currently
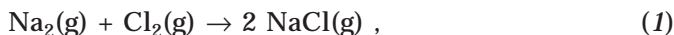unavailable.
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How additive are thermochemical properties? Certainly if enthalpy and en-
tropy were exactly additive, Gibbs energies also would be additive and the
Gibbs energy change for any reaction would be zero. Such is obviously not
the case. While we ultimately care about entropies, we start our discussion
with that of enthalpies: they are a much better known thermodynamic
quantity than entropies (this is particularly true for organic materials)[1]. It is
well established that enthalpies, in general, are not simply additive. That is,
one cannot simply sum atomic enthalpies of formation to generate molecu-
lar enthalpies of formation. If that was the case, molecules would ulti-
mately fall apart to atoms: because the entropy of a molecule is less than

that of the sum of its component atoms, the Gibbs energy of a molecule would always be more positive than its constituent atoms at any non-zero temperature. Nor can one sum the entropies of the component oxides, which make up a multiple oxide phase to estimate its entropy. The very fact that all possible materials are not stable under all conditions implies deviation from additivity. However, for organic molecules one can construct groups composed of one or more atoms (*e.g.* CH_3) and barring "special" effects such as destabilizing strain and stabilizing aromaticity, one can sum the enthalpies of formation of these groups to reliably estimate enthalpies of formation of the entire molecule. The same applies to entropies as well, or more precisely, after corrections for symmetry numbers are made. The thermochemistry of large organic molecules becomes accessible for "normal" species[2].

Entropy of Gas Phase Diatomic Molecules

Let us, however, consider small inorganic molecules, always implicitly in the gas phase. In the particular, what about very small species, namely diatomics? Enthalpies of formation are clearly not additive: we are neither surprised nor disappointed. After all, it was the non-additivity of the bond energies (and equivalently, enthalpies of formation) found for numerous sets of molecules such as Na_2, Cl_2 and NaCl, *i.e.*, the non-thermoneutrality of the reaction

$$Na_2(g) + Cl_2(g) \rightarrow 2\ NaCl(g)\ , \tag{1}$$

from which the concept of electronegativity quantitatively first arose[3]. And, as if to add insult to injury, groups are generally much less apparent within the framework of inorganic compounds[4].

What compounds will we discuss? In the following, we limit our attention to neutral diatomic molecules, those with $^1\Sigma$ ground states derived from ^2S and/or ^2P univalent atomic constituents. In other words, we shall consider the diatomic molecules XY wherein X and Y are either H, the group 17 nonmetal halogens (generically written X, specifically F, Cl, Br and I), the alkali or group 1 metals (generically written M, specifically Li, Na, K, Rb, Cs), and/or the trellides or group 13 metalloid/metals (generically written Tr, specifically B and Al).

Entropies of Diatomic Gases

We recognize the homonuclear diatomic molecules as generally weakly bound except for the case of dihydrogen, X = Y = H, XY = H_2. The heteronuclear cases are of five different types. The first type is that of the alkali metal halides, MX, such as LiF and NaCl which are strongly bound and highly polar. The second class is composed of the alkali metal hydrides, MH, all of which are highly polar but are quite weakly bound. The third class are the hydrogen halides, HX, which start out with HF that is strongly bound and highly polar, and end up with HI which is weakly bound and rather nonpolar. The interhalogens, XX′, such as ClF and IBr are not that different from the homonuclear dihalogens, X_2 and so we consider these together as yet another class. The penultimate class is composed of the weakly bound homonuclear and heteronuclear alkali metal dimers, MM′. Their experimental chemistry is complicated by the fact that any temperature that is hot enough for alkali metals to vaporize is hot enough for the $T\Delta S$ term in the Gibbs energy to encourage atomization of the dimer.

Consider the species containing the lighter trellides, B and Al. All of their monohydrides and monohalides have $^1\Sigma$ ground states and so would naturally appear here. However, B_2, AlB and Al_2 do not have such ground states[5]. Because the $^1\Sigma$ state is an excited state of these diatomics, we have placed these B- and Al-containing species in another category. It is not obvious what is the ground state for alkali metal trellides[6] and so we put them in a different category as well. Quantum chemical calculations of these ditrellides and alkali metal trellides at a uniform methodological level remains to be done: indeed, the literature only discusses the lithium- and sodium-containing species. As such, we will but briefly discuss these species in the current study.

However numerous are our species, there are additional $^1\Sigma$ species we ignore: the neutrals C_2, CO, N_2, the ions HeH^+, CN^-, XeF^+ and the second (i.e., b) excited state of O_2, SO and S_2. These we ignore for diverse reasons. The first set of neutrals is ignored because the monoatomic fragments are not ^2S and/or ^2P, the second set because they are ions, and the third one because they are excited state species as well as having the "wrong" monoatomic fragments.

Absolute Entropies: Expectations and Symmetry Corrections

So, what about absolute entropy of diatomic molecules? How useful do we find the division into the same classes of diatomic molecules as enunciated

above? At the very least, since we will be discussing heteronuclear and homonuclear species, correction should be made for symmetry numbers. We thus automatically add a symmetry number correction of $R \ln 2$, or numerically 5.8 J mol^{-1} K^{-1}, to values for homonuclear species to reflect their $D_{\infty h}$ symmetry ($\sigma = 2$) as opposed to $C_{\infty v}$ symmetry for the heteronuclear species ($\sigma = 1$): we thus study the quantity S^* instead of S^o. Bonds with high dissociation energies are expected to be tight: we expect tight bonds to be accompanied by low entropy. Alkali metal halides and (the lighter) hydrogen halides are thus expected to have comparatively low entropy. The interhalogens, alkali metal hydrides and alkali dimers are expected to have high entropy. It is not obvious what to expect of trellide-containing compounds.

RESULTS AND DISCUSSION

What is found? We use the archived data[7–9] where those in ref.[7] are preferred over ref.[8] and, in turn, data in ref.[8] are preferred over those in ref.[9] We also present "isolated" results from the literature, and from some of our own quantum chemical calculations[10]. Table I presents the assembled data for the symmetry number-corrected absolute entropies, S^* (J mol^{-1} K^{-1}), where superscripts of 7, 8 or 9 are affixed to each value to assign its reference source. It is to be acknowledged that, in general, values from the different archives have less than a 0.3 J mol^{-1} K^{-1} discrepancy between them, corresponding to a difference in Gibbs energy of safely less than 0.1 kJ mol^{-1} at 298 K.

Regularities in the Data

There are some intriguing regularities within the data (Table II). The first is that the difference of pairs of alkali metal species, MY and M′Y, is essentially independent of the atom Y. For example, the difference of LiY and NaY starts at 17.5 J mol^{-1} K^{-1} for Y = H and monotonically dribbles down to 16.7 for Y = I: let us choose a consensus value of 17.1, taken as the average of these two numbers. It may be argued that these are all halides, hydrogen behaving as the lightest halogen in its anionic role as hydride. However, consider LiNa. If this equality was valid, then

$$S^*(\text{NaLi}) - S^*(\text{LiLi}) = S^*(\text{NaNa}) - S^*(\text{LiNa}) = \delta S^*(\text{Na, Li}) ,$$

$$(2)$$

TABLE I

Symmetry number-corrected absolute entropies S* (in J mol⁻¹ K⁻¹): all data are from refs[7–9] and are designated as such with the reference citation appended as a superscript to each individual number[a]

Element	H	F	Cl	Br	I	Li	Na	K	Rb	Cs	B	Al
H	136.5[7]	173.8[7]	186.9[7]	198.7[7]	206.6[7]	170.9[7]	188.4[7]	198.0[7]	208.4[9]	215.2[7]	171.9[8]	187.9[7]
F	173.8[7]	208.4[7]	217.9[7]	229.0[7]	236.1[7]	200.3[7]	217.6[7]	226.6[7]	237.1[8]	243.2[7]	200.5[7]	215.2[8]
Cl	186.9[7]	217.9[7]	228.9[7]	240.0[7]	247.6[7]	212.9[7]	229.8[7]	239.1[7]	249.6[8]	256.1[7]	213.2[7]	228.0[7]
Br	198.7[7]	229.0[7]	240.0[7]	251.3[7]	259.0[7]	224.3[7]	241.2[7]	250.5[7]	261.0[8]	267.4[8]	225.0[7]	239.6[7]
I	206.6[7]	236.1[7]	247.6[7]	259.0[7]	266.5[7]	232.3[7]	249.0[8]	258.3[7]	268.8[7]	275.3[8]	232.6[9]	247.8[7]
Li	170.9[7]	200.3[7]	212.9[7]	224.3[7]	232.3[7]	202.8[7]	219.2[9]	228.4[9]	237.7[9]	243.5[9]	201.6	216.9
Na	188.4[7]	217.6[7]	229.8[7]	241.2[7]	249.0[8]	219.2[9]	236.0[7]	245.7[9]	254.4[9]	259.8[9]	218.5	233.8
K	198.0[7]	226.6[7]	239.1[7]	250.5[7]	258.3[7]	228.4[9]	245.7[9]	255.5[7]	264.2[9]	269.9[9]	227.7	243.0
Rb	208.4[9]	237.1[8]	249.6[8]	261.0[8]	268.8[7]	237.7[9]	254.4[9]	264.2[9]	276.9[7]	283.3[9]	238.2	253.5
Cs	215.2[7]	243.2[7]	256.1[7]	267.4[8]	275.3[8]	243.5[9]	259.8[9]	269.9[9]	283.3[9]	290.5[7]	244.9	260.2
B	171.9[8]	200.5[7]	213.2[7]	225.0[7]	232.6[9]	201.6	218.5	227.7	238.2	244.9	201.0	216.3
Al	187.9[7]	215.2[7]	228.0[7]	239.6[7]	247.8[7]	216.9	233.8	243.0	253.5	260.2	216.3	231.6

[a] Data in italics represent predicted entropy for the compounds listed.

Table II

Incremental values δS*(E, E') (in J mol⁻¹ K⁻¹) between neighboring elements E and E'. Data based on predicted entropies are in parentheses

Element	δS*(H,F) H	δS*(F,Cl) F	δS*(Cl,Br) Cl	δS*(Br,Cl) Br	δS*(I,Br) I	δS*(Na,Li) Li	δS*(K,Na) Na	δS*(Rb,K) K	δS*(Cs,Rb) Rb	δS*(B,Cs) Cs	δS*(Al,B) B	Al
H	37.3	34.6	31.0	30.3	29.5	29.4	29.2	28.6	28.7	28.0	28.6 16.0	27.3
δS*(F,H)	37.3	9.5	11.0	11.0	17.5	17.3	9.0	10.5	6.1	−42.7	14.7	27.3
F	34.6	9.5	11.0	7.1	12.6	17.3	9.0	12.5	12.5	12.9	12.7 14.7	12.8
δS*(Cl,F)	13.1	11.0	11.1	7.6	16.9	16.9	9.3	10.5	6.4	−42.9	12.7	12.8
Cl	31.0	11.0	11.1	11.3	12.6	16.9	9.3	10.5	6.4	12.9	11.8 14.8	11.6
δS*(Br,Cl)	11.8	11.1	11.4	7.7	16.7	16.4	9.3	10.5	6.4	−42.4	11.8	11.6
Br	30.3	11.0	11.3	11.4	16.9	16.4	9.3	10.5	6.4	11.4	11.8 14.6	11.6
δS*(I,Br)	8.1	7.1	7.6	7.5	8.0	16.8	9.7	8.7	5.7	−42.4	7.6	8.2
I	29.5	11.5	11.4	11.4	8.0	16.8	9.7	10.5	6.5	7.9	7.6 15.2	8.2
δS*(Li,I)	−35.9	−35.8	−34.7	−34.7	−34.2	16.4	−29.8	−29.9	−31.1	−31.8	(−31.0)	(−30.9)
Li	29.4	12.6	11.4	11.3	16.7	8.0	9.2	9.3	5.8	5.8	(15.3)	(16.9)
δS*(Na,Li)	17.5	17.3	16.9	16.9	16.7	16.4	9.7	9.3	5.4	16.3	(16.9)	(16.9)
Na	29.2	9.0	9.3	9.3	9.3	16.4	9.7	9.8	5.4	10.1	(15.3)	(9.2)
δS*(K,Na)	9.6	9.0	9.3	9.3	9.3	9.2	9.8	8.7	5.7	10.1	(9.2)	(9.2)
K	28.6	12.5	10.5	10.5	10.5	9.3	9.8	8.7	5.7	13.4	(15.3)	(10.5)
δS*(Rb,K)	10.4	10.5	10.5	10.5	10.5	9.3	9.8	8.7	12.7	13.4	(10.5)	(10.5)
Rb	28.7	12.5	11.4	11.3	16.7	9.3	9.8	12.7	12.7	13.4	(10.5)	(10.5)
δS*(Cs,Rb)	6.8	6.1	6.4	6.4	6.5	5.8	5.4	5.7	6.4	7.2	(6.7)	(6.7)
Cs	28.0	12.9	11.3	11.4	16.7	9.2	10.1	9.8	13.4	7.2	(15.3)	(6.7)
δS*(B,Cs)	−43.3	−42.7	−42.9	−42.4	−42.7	−41.9	−41.3	−42.2	−45.1	−45.6	(−45.6)	(−43.9)
B	28.6	12.7	11.8	11.8	15.2	16.9	9.2	10.5	6.7	7.2	(15.3)	(15.3)
δS*(Al,B)	16.0	14.7	14.8	14.6	15.2	(16.9)	(9.2)	(10.5)	(6.7)	(15.3)	(15.3)	(15.3)
Al	27.3	12.8	11.6	11.6	15.3	(16.9)	(9.2)	(10.5)	(6.7)	(15.3)	(15.3)	(15.3)

numerically equaling 17.1. Since NaLi and LiNa are identically the same, let us thus assume the above equality – or equivalently,

$$S^*(\text{NaLi}) = 1/2[S^*(\text{Li}_2) + S^*(\text{Na}_2)] \ . \tag{3}$$

From the literature values for the homonuclear diatomics, we derive $S^*(\text{NaLi})$ equals 219.4 from which a value of $\delta S^*(\text{Na, Li}) = 16.6$ for the difference of sodium and lithium would be obtained. The average of the difference of all ten NaY and LiY species is 16.9. The difference between the three methods spans 0.5 which corresponds to less than 0.2 kJ mol^{-1} when used in $T\Delta S$ and hence ΔG. Encouraged, let us consider other values of the difference quantity $\delta S^*(\text{M, M}')$. For $\delta S^*(\text{K, Na})$ the difference flutters around 9.3. Again assuming the heteronuclear species has the average value of the two homonuclear species, we would derive a value of 245.8 corresponding to a value of 9.8 for the difference quantity. For the value of $\delta S^*(\text{K, Li})$, we have three ways of obtaining the value. The first makes use of the identity

$$\delta S^*(\text{Y, Y}'') = \delta S^*(\text{Y, Y}') + \delta S^*(\text{Y}', \text{Y}'') \ . \tag{4}$$

From this $\delta S^*(\text{K, Li})$ would be expected to equal $17.1 + 9.3 = 26.4$ J mol^{-1} K^{-1}. The average difference of the two sets of values for $S^*(\text{KY})$ and $S^*(\text{LiY}) = 26.3$ and this is also the value found assuming $S^*(\text{KLi})$ is the average of $S^*(\text{K}_2)$ and $S^*(\text{Li}_2)$. Relatedly, a general value of ca 10.7 is found for $\delta S^*(\text{Rb, K})$ and of ca 6.5 is found for $\delta S^*(\text{Cs, Rb})$.

Halides give us a related set of S^* differences. For fluorine and chlorine, the difference quantity, $\delta S^*(\text{Cl, F})$, equals 11.8 J mol^{-1} K^{-1}. There is a wider range of values than for the above pairs of elements, and as will be seen, wider than for other pairs discussed below. For example, the HCl/HF difference is surprisingly large, 13.1 and the ClF/F$_2$ difference is likewise small, 9.5. It is tempting to ascribe this to an example of the anomalous properties of fluorine[11]. The seemingly large range of ca ±2 J mol^{-1} K^{-1}, however, results in but a range less than 1 kJ mol^{-1} when used in $T\Delta S$ and hence ΔG. This quantity is smaller than errors in many of the corresponding enthalpy measurements and so will be ignored here. Nonetheless that fluorine, well precedented for surprises, is involved giving us reason for pause and so, this range of values is worthy of looking at more closely at a later time.

The corresponding $\delta S^*(\text{Br, Cl})$ equals 11.5 J mol^{-1} K^{-1} while $\delta S^*(\text{I, Br})$ equals 7.7, again with narrow ranges of values. That all of the differences were accompanied by a narrow range means that the transitive property expressed as Eq. (4) is well obeyed, or equivalently $\delta S^*(\text{Y, Z})$ is also some constant

with a narrow range when Y and Z are both halogens. In turn, following from the analysis of the lithium-sodium case above, we deduce the general reliability of the average entropy equation

$$S^*(YZ) = 1/2[S^*(Y_2) + S^*(Z_2)] \ . \tag{5}$$

Admittedly, our various inter-element comparisons generally involved atoms of the same type (alkali metals, halogens) in the adjacent rows in the Periodic Table. Let us now compare the heavy alkali metal Cs and the light halogen F by examining the difference quantity $\delta S^*(\text{Cs, F})$. The range is large, going from 34.8 for the case of affixed F to 47.3 for Cs. The average is 41.4 with a range of 12.5 corresponding to a violation of Eq. (*5*) of 6.3 J mol^{-1} K^{-1}. Without affixed F, the average is now 42.2 with a range of 9.1. This corresponds to an error of *ca* 2 kJ mol^{-1} in Gibbs energy at 300 K. This is larger than we have seen before, larger than we would like, but "we can live with it".

The astute reader may have noted that we almost completely ignored species containing hydrogen in our analysis. Hydrogen is an even more of an outlier than fluorine in the current context with $\delta S^*(\text{F, H})$ ranging from 37.3 for the case where the other element in the diatomic was H to 27.3 for Al. Perhaps, we should not even consider fluorine in the current context, and instead consider iodine, a large, heavy atom of comparable electronegativity to the light, small hydrogen. The range now for $\delta S^*(\text{I, H})$ is 69.9 to 59.9 for the all hydrogen case (H_2) and HI, to the aluminum-containing species AlH and AlI. However, much as it was shown that the discrepancy with fluorine was of relatively minor consequence, so it is with hydrogen. More precisely, if we ignore H_2, then the revised range is from 62.3 to 59.7 and the average is 60.5 J mol^{-1} K^{-1}, an altogether numerically acceptable value and range, and again we recover the validity of the average entropy Eq. (*5*) found for so many of our diatomic YZ species of interest.

Let us now return to our earlier assumption that alkali halides should have low absolute entropies. We recognize that the halogen of row r in the Periodic Table has a very similar mass to the alkali metal of the subsequent row r+1: after all, the two elements differ only by two protons and "a few" neutrons. Let us for now avoid the case of $\delta S^*(\text{Na, F})$ so as not to involve the potentially anomalous fluorine. Whether we are talking about the alkali halides, interhalogens and alkali metal dimers, $\delta S^*(\text{K, Cl})$ averages as 12.8 with a large range of 8.9 to 15.9. However, it is hard to ascribe this to bond polarity and resulting tightness. All of the differences congregate towards 10 when comparing the ionic potassium halides to the electronegative halogen-containing, but essentially covalent di- or interhalogens, and con-

gregate towards 15 when comparing the ionic potassium halides to the electropositive alkali metal-containing, but essentially covalent metal dimers. Interestingly, the value of $\delta S^*(Cs, F)$ is but 41.4 with a corresponding large range of values, these two elements having very dissimilar masses. The situations for $\delta S^*(Rb, Br)$ and $\delta S^*(Rb, I)$ are reminiscent of their lighter counterparts $\delta S^*(K, Cl)$ and $\delta S^*(K, Br)$. In turn, $\delta S^*(Na, F)$ and $\delta S^*(Na, Cl)$ show the comparative entropic dissimilarity of diatomic species containing Na and F, and the admittedly still surprising similarity of those with Na and Cl.

Numerical Summary, Anticommutativity and Transitivity Relations

By arithmetic, it is seen that the difference quantity $\delta S^*(E, E')$ is anticommutative for all pairs of elements E and E':

$$\delta S^*(E, E') = -\delta S^*(E', E) \ . \tag{6}$$

In the particular, we have found the following numerically rather reliable difference quantities $\delta S^*(Na, Li) = 16.9$ J mol^{-1} K^{-1}; $\delta S^*(K, Na) = 9.3$; $\delta S^*(Rb, K) = 10.7$; $\delta S^*(Cs, Rb) = 6.5$; $\delta S^*(Cl, F) = 11.8$; $\delta S^*(Br, Cl) = 11.5$; $\delta S^*(I, Br) = 7.7$; $\delta S^*(K, Cl) = 12.8$; $\delta S^*(Cs, F) = 41.4$. The difference quantity is also transitive for any three elements E, E' and E''

$$\delta S^*(E, E') + \delta S^*(E', E'') = \delta S^*(E, E'') \tag{7}$$

as long as the "data base" is the same for all three elements and/or the above difference quantities were exactly constant. From Eqs (6) and (7) we derive

$$\delta S^*(E, E') - \delta S^*(E'', E') = \delta S^*(E, E'') \ . \tag{8}$$

For example, consider $\delta S^*(Cs, K)$. From the interalkali difference quantities for Rb and K, and Cs and Rb, we proffer

$$\delta S^*(Rb, K) + \delta S^*(Cs, Rb) = \delta S^*(Cs, K) \ , \tag{9}$$

which numerically equals 18.2 J mol^{-1} K^{-1}. However, from interhalogen and alkali halide difference quantities, we suggest

$$\delta S^*(Cs, F) - \delta S^*(Cl, F) - \delta S^*(K, Cl) = \delta S^*(Cs, K) \tag{10}$$

that numerically equals 16.8 J mol^{-1} K^{-1}. Agreement is good suggesting consistency of our data sets and our equations.

Least-Squares Analytical Procedure

The above observations suggest that (i) we can, and perhaps, should be more rigorous in our analysis, (ii) there may be some basis for additivity in the data, (iii) elemental contributions to the entropy might be assignable and (iv) these gaseous elemental values could be used to predict further data, including the missing data for trellides in Table I.

To examine this question we proceed as follows. We consider a subset of the data (that for the alkali metal halides) and apply an approach, originally used by Waddington[12], which we have previously used[13] to derive single-ion components of thermodynamic data for hydration enthalpies, Gibbs energies and entropies of hydration and viscosity *B*-coefficients from combined data. Here the problem is similar. We need to separate the elemental contributions from the overall molecular ones. The difference here is that we do have dimers (*e.g.* Cl_2, Na_2, B_2) which can be used to solve the problem of assigning absolute parameters. The approach adopted would offer a way forward when this was not a possibility by parametrizing the single elemental data in terms of a constant an undetermined parameter, Θ_S. The data for the 20 alkali metal halides, symmetry number-corrected entropies, $S^*(MX)$, in the lower left-hand quartile of Table I is taken as the starting point[14] for our analysis for which the theory is summarized in Appendix. Following the partial differentiation minimization procedure (Appendix, refs[12,13]) through, we obtain the results given in Table III.

The question now arises: to what extent can we use these results (derived exclusively from the data for the alkali metal halides) to predict symmetry number-corrected entropies for the remaining dihalogens, hydrides, alkali metal dimers and trellides appearing in Table I? We also ask the question –

TABLE III
Individual elemental contributions, $S^*(M_i)$ (M_i = Li, Na, K, Rb, Cs) and $S^*(X_j)$ (X_j = F, Cl, Br, I) to the symmetry number-corrected entropy, $S^*(MX)$ for the alkali halides, MX (all values in J mol^{-1} K^{-1})

Element M_i	Li	Na	K	Rb	Cs
$S^*(M_i)$	$217.5 - \Theta_S$	$234.4 - \Theta_S$	$243.6 - \Theta_S$	$254.1 - \Theta_S$	$260.5 - \Theta_S$
Element X_j	F	Cl	Br	I	
$S^*(X_j)$	$-17.1 + \Theta_S$	$-4.5 + \Theta_S$	$6.9 + \Theta_S$	$14.7 + \Theta_S$	

can we also predict values for the missing trellide combinations in Table I? Recombination of the pairs of elemental values in Table III regenerates the data in the lower left-hand (and upper right-hand) quartile of Table I successfully. As an example: $S^*(NaBr) = S^*(Na) + S^*(Br) = 234.4 - \Theta_S + 6.9 + \Theta_S = 241.3$ J mol^{-1} K^{-1}, which can be compared to the archival experimental value 241.2 J mol^{-1} K^{-1}.

Prediction of $S^*(M_2)$ and $S^*(MM')$ for Alkali Metal Dimers and $S^*(X_2)$ and $S^*(XX')$ for Di- and Interhalogen Compounds

The symmetry number-corrected entropy for Na$_2$, $S^*(Na_2)$, listed in Table I, is found to be 236.0 J mol^{-1} K^{-1}. Arbitrarily selecting this one result enables us to evaluate the undetermined parameter Θ_S in Table III and hence assign absolute values for the elemental contributions, $S^*(M)$ and $S^*(X)$ for all the elements listed in Table III. These can then be further used to predict $S^*(M_2)$ and $S^*(MM')$ for alkali metal dimers and $S^*(X_2)$ and $S^*(XX')$ for dihalogen compounds. Tables IV and V display the results and compare the experimental data. Accordingly, for Na$_2$ we can write:

$$S^*(Na_2) = 2(234.4 - \Theta_S) = 468.8 - 2\,\Theta_S = 236.0 , \qquad (11)$$

from which we can derive that

TABLE IV
Absolute values for the element symmetry number-corrected entropy contributions, $S^*(M_i)$ (M_i = Li, Na, K, Rb, Cs) and $S^*(X_j)$ (X_j = F, Cl, Br, I) adopting the value $\Theta_S = 116.4$ (all values in J mol^{-1} K^{-1})

Element M_i	Li	Na	K	Rb	Cs
$S^*(M_i)$	101.1	118.0[a]	127.2	137.7	144.1
Element X_j	F	Cl	Br	I	
$S^*(X_j)$	99.3	111.9	123.3	131.1	

[a] It is important to note that this value could be obtained directly by halving the $S^*(Na_2)$ value in Table I and the other values were inferred from the individual MX data. The procedure adopted in this paper generates least-squares minimized values for all the parameters and has the effect of overall averaging. Furthermore the procedure presented in this paper would be especially appropriate if no data for the homonuclear diatomics (M$_2$, X$_2$ or Tr$_2$) was available.

Predictions for the entropies (in J mol^{-1} K^{-1}) of the alkali metal dimers, $S^*(M_2)$, $S^*(MM')$ and the di- and interhalogens $S^*(X_2)$ and $S^*(XX')$. The first rows are the predicted S^*, the second rows experimental values and the third rows errors (in %)

Element	Li	Na	K	Rb	Cs
Li	202.2	219.1	228.3	238.8	245.2
	202.8	219.2	228.4	237.7	243.5
	0.3	0.0	0.0	0.5	0.7
Na	219.1	236.0	245.2	255.7	262.1
	219.2	^{a}	245.7	254.4	259.8
	0.0	–	0.2	0.5	0.9
K	228.3	245.2	254.4	264.9	271.3
	228.4	245.7	255.5	264.2	269.9
	0.0	0.2	0.4	0.3	0.5
Rb	238.8	255.7	264.9	275.4	281.8
	237.7	254.4	264.2	276.9	283.3
	0.5	0.5	0.3	0.5	0.5
Cs	245.2	262.1	271.3	281.8	288.2
	243.5	259.8	269.9	283.3	290.5
	0.7	0.9	0.5	0.5	0.8

Element	F	Cl	Br	I
F	198.6	211.2	222.6	230.4
	208.4	217.9	229.0	236.1
	4.7	3.1	2.8	2.4
Cl	211.2	223.8	235.2	243.0
	217.9	228.9	240.0	247.6
	3.1	2.2	2.0	1.9
Br	222.6	235.2	246.6	253.4
	229.0	240.0	251.3	259.0
	2.8	2.0	1.9	2.2
I	230.4	243.0	253.4	262.2
	236.1	247.6	259.0	266.5
	2.4	1.9	2.2	1.6

^{a} Used to derive Θ_S.

$$\Theta_S = 116.4 \text{ J mol}^{-1} \text{ K}^{-1} , \tag{12}$$

which leads to the absolute values for the elements listed in Table IV and the predictions (Table V) for the alkali metal dimers and dihalogen compounds for which the errors lie in the range $0.3 \leq \varepsilon_{ij}\% \leq 4.7$. Using the absolute values generated in Table IV we can now predict the symmetry number-corrected entropies for the homonuclear, M_2, and mixed, MM', alkali metal dimers, and the dihalogen, X_2, and interhalogen diatomics, XX', as shown in Table V.

Prediction of $S^*(MH)$, $S^*(HX)$ and $S(H_2)$ for the Hydrides

From a knowledge of one hydride entropy value, we are able to establish $S^*(H)$, an element not yet encountered in our analysis. This example illustrates the procedure for other elements in general (see below for B and Al) and in this case enables prediction of values for all other hydrides in Table I. We arbitrarily choose one hydride, say HCl for which $S^*(\text{HCl}) = 186.9$ J mol^{-1} K^{-1}. Proceeding from here we can use the undetermined parameter values and write

$$186.9 = S_{Hi} - \Theta_S + S_{Clj} + \Theta_S = S_{Hi} - 4.5 . \tag{13}$$

Accordingly we derive

$$S^*(H) = S_{Hi} - \Theta_S = 191.4 - \Theta_S \tag{14}$$

and taking the value of Θ_S in Eq. (*12*) establish that

$$S^*(H) = 75 \text{ J mol}^{-1} \text{ K}^{-1} . \tag{15}$$

Alternatively we can subtract our absolute value for $S^*(\text{Cl}) = 111.9$ J mol^{-1} K^{-1} from the value for $S^*(\text{HCl})$ to give the same result.

Combining $S^*(H)$ with the elemental data in Table IV leads to the predictions in Table VI for diatomic hydrides.

Prediction of Missing Data for $S(Tr_2)$ and $S^*(MTr)$

We now ask whether our approach can supply the missing data in Table I and whether, once predicted, this new data is compatible with the $\delta S^*(E, E')$ differences already observed in Table II. Selecting two trellide diatomics, BE

and AlE paired with element E for which we have established the $S^*(E)$ absolute value enables us to quantify $S^*(B)$ and $S^*(Al)$ as shown in Table VII. These values lead to the following predictions for the entropies of the compounds missing from Table I (Table VIII) and the bracketed entries in Table II show the various $\delta S^*(E, Tr)$ differences observed which are broadly consistent with those already established. Our conclusion is that the as-

TABLE VI
Predictions for the entropies of the diatomic alkali metal and halogen hydride, $S^*(MH)$ and $S^*(HX)$ (all values in J mol^{-1} K^{-1})

$S^*(MH)$	LiH	NaH	KH	RbH	CsH
Predicted entropy	176.1	193.0	202.2	212.7	219.1
Experimental value (Table I)	170.9	188.4	198.0	208.4	215.2
Error, %	3.0	2.4	2.1	2.1	1.8
$S^*(HX)$	HF	HCl	HBr	HI	H_2[a]
Predicted entropy	174.3	[b]	198.3	206.1	150.0
Experimental value (Table I)	173.8	186.9	198.7	206.8	136.5
Error, %	0.3	–	0.2	0.3	9.9[a]

[a] Prediction for H_2 is by far the worst of the set of diatomics we have considered. [b] Used to assign $S^*(H)$.

TABLE VII
Values for $S^*(B)$ and $S^*(Al)$ (in J mol^{-1} K^{-1})

Trellide diatomic choice to assign $S^*(Tr)$	$S^*(Tr)$	Trellide diatomic choice to assign $S^*(Tr)$	$S^*(Tr)$
BH	96.9	AlH	112.9
BF	101.2	AlF	115.9
BCl	101.3	AlCl	116.1
BBr	101.7	AlBr	116.3
BI	101.5	AlI	116.7
Average $S^*(B)$	100.5 ± 3.6	Average $S^*(Al)$	115.8 ± 2.9

sumption of elemental additivity is able to predict already established entropy data quite satisfactorily (apart from that for H_2) and has likely provided reasonable estimates for data currently unavailable.

Shortcut Procedure

Because additivity applies well to the experimental data in Table I, a shortcut procedure which would give reasonable estimates for diatomic S^* values would define $S^*(E) = 1/2S^*(E_2)$ across the diagonal of Table I. This leads to $S^*(E)$ values equal to 104.2 J mol^{-1} K^{-1} (E = F); 114.4 (Cl); 125.6 (Br); 133.3 (I); 101.4 (Li); 118.0 (Na); 127.8 (K); 138.5 (Rb); 145.2 (Cs) close to the values obtained from our least-squares analysis and listed in Table IV.

REMAINING QUESTIONS AND CONCLUSIONS

Some questions still remain and so are topics for future investigation. Why is H_2 different from all other diatomics? Is H_2 an outlier because of its exceptionally small mass, because of the presumed pronounced importance of its natural ortho-para admixture, or have we been too covetous in assuming rules like Eq. (*5*) should be valid for any pair of molecules. For species with seemingly low-lying excited states such as the alkali metal trellides, how dependent is the entropy on the choice of electronic state chosen? How does our additivity regularity relate to Latimer's rules for solids[15]? We pass over these questions for now.

APPENDIX

Considering a data set for the symmetry number-corrected entropies, $S^*(AB)_{ij}$ for a total of mn diatomics, AB, which contain m different elements A_i (i = 1, 2, ... m) and n different elements B_j (j = 1, 2, ... n), the aim is to assign a single elemental contribution to each of the elements A, $S^*(A_i)$ and a similar property to each of the elements B, $S^*(B_j)$ in terms of an undeter-

TABLE VIII
Predicted entropies, $S^*(TrE)$ (in J mol^{-1} K^{-1}), for trellides absent from Table I

$S^*(TrE)$	LiTr	NaTr	KTr	RbTr	CsTr	Tr$_2$	BAl
Tr = B	201.6 ± 3.6	218.5 ± 3.6	227.7 ± 3.6	238.2 ± 3.6	244.9 ± 3.6	201.0 ± 3.6	216.3 ± 4.6
Tr = Al	216.9 ± 2.9	233.8 ± 2.9	243.0 ± 2.9	253.5 ± 2.9	260.2 ± 2.9	231.6 ± 2.9	216.3 ± 4.6

mined parameter, Θ_S. In practice, however, since $S^*(AB)_{ij}$ is obtained from experimental or, in some cases, theoretical data, the entropies for the elements may not be exactly additive and if ε_{ij} is the deviation of the pair, *ij*, from additivity, a more usual situation will be that

$$S^*(A_i) + S^*(B_j) + \varepsilon_{ij} = S^*(AB)_{ij} . \tag{A1}$$

The most efficacious choice of $S^*(A_i)$ and $S^*(B_j)$ will be such that

$$\sum_{i=1}^{m} \sum_{j=1}^{n} \varepsilon_{ij}^2 \to \min \tag{A2}$$

which leads[12,13] to the result that

$$S^*(A_1) = \frac{1}{n} \sum_{j=1}^{n} S^*(AB)_{ij} - \Theta_S = S_{Ai} - \Theta_S \tag{A3}$$

and

$$S^*(B_j) = \frac{1}{m} \sum_{i=1}^{m} S^*(AB)_{ij} - [S^*(AB)_{ij}]_{av} + \Theta_S = S_{Bj} + \Theta_S , \tag{A4}$$

where

$$[S^*(AB)_{ij}]_{av} = \frac{1}{mn} \sum_{i=1}^{m} \sum_{j=1}^{n} S^*(AB)_{ij} \tag{A5}$$

and Θ_S represents an undetermined parameter. Note that on recombination of the separate elemental entropy contribution, $S^*(A_i)$ and $S^*(B_j)$, to give the entropy for the molecule ($S^*(AB)_{ij}$), the parameter Θ_S vanishes by cancellation, thus

$$S^*(A_i) + S^*(B_j) = S_{Ai} - \Theta_S + S_{Bj} + \Theta_S = S_{Ai} + S_{Bj} = S^*(AB)_{ij} . \tag{A6}$$

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14. Our analysis could equally well be applied to the following areas of Table I. The upper left-hand quartile for the 16 di- or interhalogens, XX'. In this case our analysis would give two parametrizations of elemental entropy contributions for the halogen atoms. When X is the first atom, the parametric form would be: $S^\star(X) = S_{Xi} - \Phi_S$ and when X is the second listed halogen atom in the form: $S^\star(X) = S_{Xj} - \Phi_S$ in terms of an undetermined parameter Φ (Note: $\Phi \neq \Theta$ because we might be choosing a different data set for the analysis, *e.g.* the homonuclear diatomics, and so want to distinguish between the resulting parameters.) This approach would give two values for the same element, which could be equated and Φ evaluated directly. The result would be absolute individual elemental contributions, $S^\star(X)$ which would additively sum to generate the original data.

Applied to "the lower right-hand quartile" of Table I, for the 25 alkali metal dimers, MM′ a similar analysis would provide immediately evaluation of the (different) undetermined parameter in this case also. Finally, applied to the whole Table I, an analysis would produce the overall most efficacious parameters to use outside the table of compounds but could not provide any basis for testing the predictivity of this approach. Hence we make use of the choice of subset used in this paper.

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