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On Additivity Rules in Molecular Thermodynamics

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Abstract: Benson and Buss have shown that molecular heat capacities and entropies can be moderately well estimated as sums of empirical atomic contributions. This additivity approximation is examined from the standpoint of statistical thermodynamics and the atomic parameters are semiquantitatively accounted for. The dominant role of atomic ligancy on the translational part of the entropy is explained. On the level of atomic additivity, molecular vibrations can be likened to the modes of a heteroatomic Einstein crystal. Possibilities for more elaborate atomic parametrization schemes are discussed.

1. Introduction

Heat capacities and entropies of molecular substances in the ideal gaseous state can be estimated to moderate accuracy on the basis of atomic additivity rules. Benson and Buss,[1] in their detailed study of thermodynamic additivity principles, assigned a set of empirical values, reproduced in Table I, for atomic contributions to molar heat capacity $\bar{C}_p°$ and entropy $\bar{S}°$ at 298°K. Within the group of 75 compounds they considered, the atomic additivity assumption for $\bar{C}_p°$ and $\bar{S}°$ was generally good to within ±2 cal/(°K mol). (For symmetrical molecules, $R \ln \sigma$ is subtracted from the sum of atomic entropies.)

In Table I, l stands for the ligancy of an atom: the number of other atoms directly bonded to it. For example, C has a ligancy of 4 in CH_4, 3 in C_2H_4, 2 in C_2H_2, and 1 in CO. It is striking that atomic entropies are predominantly dependent on ligancy whereas heat capacities appear relatively insensitive.

In the scheme developed by Benson and Buss, additivity of atomic properties plays the role of a zeroth-order approximation. The corresponding first- and second-order approximations involve additivity of bond contributions and of group contributions, respectively.[2] Our concern in this paper will, however, be limited to atomic additivity.

It is perhaps remarkable that such additivity principles work at all. The theoretical calculation of thermodynamic properties from molecular parameters and spectroscopic data by the methods of statistical mechanics is, of course, well established.[3] To a high level of approximation, the relevant parameters are just molecular weight, moments of inertia, fundamental vibrational frequencies, and symmetry number (plus, in special situations, electronic contributions, internal rotational barriers, etc.). The molecular weight enters, of course, *via* its logarithm and none of the other parameters is, at first glance, anything with an additive atomic structure. It will be our purpose to account semiquantitatively for the nature of atomic contributions to heat capacity and entropy and to show why additivity approximations work even as well as they do.

2. Heat Capacity

For an n-atomic molecule in the ideal-gas limit

$$\bar{C}_p° = \begin{cases} 4R + \sum_{i=1}^{3n-6} C(\nu_i) & \text{(non-linear)} \\ {}^7\!/_2R + \sum_{i=1}^{3n-5} C(\nu_i) & \text{(linear)} \end{cases} \tag{1}$$

where the ν_i are fundamental vibrational frequencies. Electronic contributions are assumed to be negligible at the temperature considered. In the harmonic approximation, $C(\nu_i)$ is the Einstein heat-capacity function.

$$C(\nu_i) = \frac{R x_i^2 e^{x_i}}{(e^{x_i} - 1)^2}, \quad x_i = \frac{hc}{kT}\,\nu_i(\text{cm}^{-1}) \tag{2}$$

Table I. Benson and Buss Values for Atomic Contributions to $\bar{C}_p°$ and $\bar{S}°$ at 298°K (cal/°K mol)

		$S^{(i)}$			
		l			
Atom	$C_p^{(i)}$	1	2	3	4
H	0.85	21.0			
D	1.20	21.7			
C	3.75	22.0	5.3	−13.5	−32.6
N	3.40	22.9	5.8	−12.1	
O	3.40	25.5	8.8		
F	2.40	25.5			
Cl	3.70	28.4	10.5		
Br	4.20	31.3			
I	4.60	33.3			
Si	5.90				−29.3
P				−9.5	
S	4.70	27.0	12.8	−11.0	−33.5

Since $0 \leq C(\nu) < R$, one can represent the translational, rotational, and PV contributions to C_p as five or six fictitious vibrational modes of appropriate frequency, such as to put eq 1 in the more symmetrical form

$$\bar{C}_p° = \sum_{i=1}^{3n} C(\nu_i) \tag{3}$$

Now the heat capacity is also approximately represented as a sum of atomic contributions, i.e.,

$$\bar{C}_p° \approx \sum_{\substack{i=1\\ \text{atoms}}}^{n} C_p^{(i)} \tag{4}$$

This suggests that each atomic term corresponds approximately to a set of three modes. Assuming, for simplicity, that the three normal frequencies associated with a given atom are equal, we can write

$$C_p^{(i)} \approx \frac{3Rx_i^2 e^{x_i}}{(e^{x_i} - 1)^2} \tag{5}$$

Indeed the values of $C_p^{(i)}$ in Table I lie in the appropriate range 0 to $3R$. We have, in effect, treated a molecule as a miniature Einstein crystal. The additivity implied by eq 4 is, moreover, equivalent to Kopp's rule for crystalline compounds. By using the empirical $C_p^{(i)}$ values in eq 5, we obtain the set of frequencies ν_i listed in Table II.

These atomic frequencies, with the exception of the one for Si, seem physically reasonable in that each lies in the range between typical stretching and bending frequencies involving that atom.[4] For example, the value 508 cm^{-1} for Cl lies between the bend in CCl_4, 319 cm^{-1}, and the C-Cl stretch, 570 cm^{-1}. For S, 354 cm^{-1} lies between the R-S-H bend in mercaptans, 332 cm^{-1}, and the S-S stretch, in the range 430-490 cm^{-1}.

3. Translational Entropy

The atomic entropies given in Table I depend primarily on ligancy, only secondarily on atomic mass. For a given element, $S^{(i)}$ decreases in regular steps averaging about 18 eu as the ligancy is increased. A qualitative explanation of this trend was given by Benson and Buss, as follows. The molar entropies of the gaseous compounds considered are all of roughly the same magnitude, around 65 eu/mol. Thus putting additional atoms on to a given central atom will not change the total entropy very much. But since these terminal atoms carry with them fixed atomic entropy values, that of the central atom must be decreased in compensation as its ligancy is increased. We shall put this argument on a more quantitative basis in this section.

Table II. Effective Atomic Frequencies at 298°K

Atom	x_i	ν_i, cm^{-1}
H	5.29	1096
D	4.73	980
C	2.41	499
N	2.67	553
O	2.67	553
F	3.45	715
Cl	2.45	508
Br	2.09	433
I	1.79	371
Si	.35	73
S	1.71	354

The molar translational entropy of an ideal gas is given by the Sakur-Tetrode equation.

$$\bar{S}_{tr}° = R \ln \left[\frac{(2\pi mkT)^{3/2}\bar{V}° e^{5/2}}{h^3 N_0}\right] \tag{6}$$

Setting $T = 298°$K, this can be reduced to a simple numerical relationship involving only the molecular weight.

$$\bar{S}_{tr}° = 25.9915 + 2.9807 \ln M \text{ eu/mol} \tag{7}$$

Molecular weight is, of course, an additive parameter *par excellence*, but not so its logarithm. Nonetheless, an approximate additivity relation can be established if the molecular weights M are predominantly clustered about some mean value M_0. For then

$$\ln M = \ln M_0 + \ln (M/M_0) \tag{8}$$

and assuming $M/M_0 \sim 1$

$$\ln (M/M_0) \approx (M/M_0) - 1 \tag{9}$$

One can do a bit better than this truncated expansion by seeking the optimal least-squares linear fit $\ln x \approx \alpha x - \beta$ in the range, say, $1 \leq x \leq 2$. Minimizing the integral $\int_1^2(\ln x - \alpha x + \beta)^2\,dx$ with respect to α and β gives the values $\alpha = 0.6821$ and $\beta = 0.6368$. Thus

$$\ln (M/M_0) \approx 0.6821\,(M/M_0) - 0.6368 \tag{10}$$

in the range $M_0 \leq M \leq 2M_0$. Now the average molecular weight of the 75 compounds considered by Benson and Buss is approximately 80. By equating this value to the geometric mean of M_0 and $2M_0$ we get, to the nearest integer, $M_0 = 56$. Thus eq 7 can be approximated by the linear relationship

$$\bar{S}_{tr}° \approx 36.09 + 0.03631M \text{ eu/mol} \tag{11}$$

This lies within ±0.2 eu of the exact value in the molecular weight range $M = 53$-121 and within ±1 eu in the range $M = 31$-172.

The question now arises as to how one could formulate eq 11 as a sum over atoms. Most of its magnitude is in the constant term and this cannot be simply divided among the constituent atoms since each atom has no way of "knowing" how many other atoms the molecule has. One can, however, invoke an elementary summation principle involving atomic ligancies. In a simply-connected n-atomic molecule (no rings) the sum of the ligancies equals twice the total number of bonds (single and multiple bonds counted equally). The number of bonds is, in turn, $n - 1$, so that

$$\sum_{i=1}^{n} l_i = 2n - 2 \tag{12}$$

(This corresponds, in graph theory, to a famous theorem of Euler.) We can alternatively write

Table III. Atomic Translational Entropies at 298°K

	$S_{tr}^{(i)}$, eu/mol			
	l			
Atom	1	2	3	4
H	18.08			
D	18.12			
C	18.48	0.44	−17.61	−35.66
N	18.55	0.51	−17.54	
O	18.63	0.58		
F	18.76			
Cl	19.33	1.29		
Br	20.54			
I	21.23			
Si				−35.08
P			−16.92	
S	19.21	1.16	−16.88	−34.93

$$\sum_{i=1}^{n}(1 - (\tfrac{1}{2}l_i)) = 1 \qquad (13)$$

By inserting this representation of unity into the first term of eq 11, we arrive at the approximate atomic additivity formula

$$\bar{S}_{tr}^{0} \approx \sum_{i=1}^{n} S_{tr}^{(i)}$$
$$S_{tr}^{(i)} = 36.09\,(1 - (\tfrac{1}{2}l_i)) + 0.03631 M_i \qquad (14)$$

in which l_i and M_i are respectively the ligancy and atomic weight of atom i. Note that the argument leading from eq 11 to 14 is exact. The only approximation in this representation of atomic translational entropy comes from manipulation of the logarithm. Calculated values of $S_{tr}^{(i)}$ are given in Table III. For the heavy atoms Br and I, we have used the alternative values M_0 = 124 and 190, respectively, to reflect the higher average molecular weights of molecules containing these atoms.

Remarkably, we have accounted almost precisely for the average increment of 18 eu. We have shown, moreover, that l = 1 and 2 is associated with positive $S^{(i)}$, l = 3 and 4 (or greater) with negative $S^{(i)}$. Included in the above scheme, incidentally, is also the case l = 0, which represents the monatomic entropy to the same level of accuracy.

4. Vibrational and Rotational Entropy

The differences between the empirical entropy values in Table I and the corresponding calculated translational entropies in Table III do *not* show any systematic variation with ligancy (except possibly for sulfur). We shall conclude therefore that the residual vibrational and rotational contributions to entropy are, at least approximately, independent of ligancy.

The vibrational entropy can be treated by adaptation of the Einstein model, in analogous fashion with the heat capacity. Accordingly we assume

$$S_{vib}^{(i)} \approx 3R\left[\frac{x_i}{e^{x_i} - 1} - \ln(1 - e^{-x_i})\right] \qquad (15)$$

The atomic frequencies determined in section 2 imply the atomic vibrational entropies listed in Table IV. We are, of course, overcounting by the five or six fictitious modes introduced into eq 3. However, molecular vibrations contribute much less proportionately to entropy than to heat capacity, so that the associated error is not serious. Comparison for several molecules of accurately calculated vibrational entropies with those obtained using eq 15 shows agreement well within ±1 eu/mol.

Table IV. Atomic Vibrational Entropies at 298°K

Atom	$S_{vib}^{(i)}$, eu/mol	Atom	$S_{vib}^{(i)}$, eu/mol
H	0.19	Cl	1.92
D	0.30	Br	2.55
C	1.98	I	3.23
N	1.61	Si	4.08
O	1.61	S	3.44
F	0.87		

The rotational contribution to entropy appears to be the most difficult to characterize from the standpoint of atomic additivity. This is because the contribution of an atom to a principal moment of inertia is most sensitive to its location relative to the molecular center of mass. There is, moreover, a different formula for rotational entropy in linear and nonlinear molecules (although about 90% of the compounds considered are nonlinear).

Lacking as we do any *a priori* approach to atomic rotational entropies, we shall merely tabulate their approximate empirical values based on subtraction of translational and vibrational contributions (Tables III and IV) from total atomic entropies (Table I). We again assume negligible electronic contributions. The results are shown in Table V. Interestingly, there is a fairly good correlation between the atomic rotational entropy of atom X and half the rotational entropy of the X_2 molecule, calculated with σ = 1 (rather than 2). These latter quantities are also shown in Table V. The correlation is, in fact, poor only for C, N, Si, and S.

As an illustrative example, let us cite the molecule CF_3CN. From spectropscopic parameters, Janz[5] calculates the following values at 298°K: S_{tr} = 39.57, S_{rot} = 24.09, S_{vib} = 7.57, $\bar{S}°_{298}$ = 71.22, $\bar{C}_p°$ = 18.61. The additivity rules of Benson and Buss predict $\bar{S}°_{298}$ = 69.9, $\bar{C}_p°$ = 18.1 while the methods developed above give S_{tr} = 39.61, S_{vib} = 8.18.

5. Further Elaborations

The molar heat capacity given by eq 1 contains a constant term $4R$ or $\tfrac{7}{2}R$ which amounts, on the average, to something like 50%. One could certainly exploit this fact in utilizing ligancy-dependent atomic heat capacities appropriately weighted by factors $(1 - \tfrac{1}{2}l_i)$. Introduction of more parameters should, in any event, result in a better fit of experimental data. The necessity of introducing ligancy is somewhat more compelling in the case of translational entropy since the constant term in eq 11 usually contributes over 90%. Still, this same constant is more like 60% of the total entropy, a fraction not dramatically greater than that for the heat capacity.

Since much more extensive and accurate heat-capacity data are now available, it might be worthwhile to work out a more elaborate atomic-additivity scheme, introducing ligancy to take account of the translational, rotational, and PV contributions. We might, in addition, put forward the following suggestion with regard to the vibrational contributions. For a nonlinear, noncyclic molecule, one can roughly characterize the $3n - 6$ vibrations as $n - 1$ stretching modes plus $2n - 5$ "softer" deformation modes, such as bending, twisting, wagging, rocking, etc. By virtue of the ligancy summation formula, eq 12, we have the identities

$$\sum_{i=1}^{n} \tfrac{1}{2}l_i = n - 1$$

and (16)

$$\sum_{i=1}^{n} (\tfrac{5}{2}l_i - 3) = 2n - 5$$

Table V. Atomic Rotational Entropies at 298°K

Atom	$S_{\text{rot}}^{(i)\,a}$	$\frac{1}{2}S_{\text{rot}}\,(X_2)^b$
H	2.7	2.21
D	3.3	2.90
C	1.5, 2.9, 2.1, 1.1	5.81
N	2.7, 3.7, 3.8	5.60
O	5.3, 6.6	5.93
F	5.9	6.44
Cl	7.1, 7.3	7.70
Br	8.2	8.79
I	8.8	9.56
Si	1.7	7.78
P		7.48
S	4.4, 8.2, 2.2, −2.0	7.50

[a] Calculated by difference. [b] Calculated from rotational constants tabulated in Herzberg, "Spectra of Diatomic Molecules," Van Nostrand, Princeton, N.J., 1950, but using $\sigma = 1$. Si value calculated using Si–Si distance of 2.32 Å in silane.

This suggests the following representation for atomic heat capacity

$$C_p^{(i)} \approx 4R(1 - (\tfrac{1}{2}l_i)) + \tfrac{1}{2}l_iC(\nu_i') + (\tfrac{5}{2}l_i - 3)C(\nu_i'') \qquad (17)$$

in which ν_i' and ν_i'' are empirically determined "hard" and "soft" atomic frequencies. Analogously, for linear molecules

$$C_p^{(i)} \approx \tfrac{7}{2}R(1 - \tfrac{1}{2}l_i) + \tfrac{1}{2}l_iC(\nu_i') + (2l_i - 2)C(\nu_i'') \qquad (18)$$

A suitable average of (17) and (18) might pertain to a mixed group of linear and nonlinear molecules.

A very similar analysis would pertain to the vibrational entropy except that the constant term would be missing and the Einstein entropy function used in place of $C(\nu)$.

The additivity of vibrational contributions to thermodynamic functions could also be based on the concept of atomic force constants recently developed by King.[6] Such an approach could certainly be worked into our scheme should a more accurate accounting for vibrations become necessary.

Finally, we shall suggest an elaboration for the rotational entropy. Rigorously, in terms of spectroscopic rotational constants

$$\bar{S}_{\text{not}} = \begin{cases} R \ln \left[\dfrac{1}{\sigma}\,\dfrac{\pi^{1/2}}{(ABC)^{1/2}}\left(\dfrac{ekT}{hc}\right)^{3/2}\right] & \text{(nonlinear)} \\ R \ln\left(\dfrac{ekT}{\sigma hcB}\right) & \text{(linear)} \end{cases} \qquad (19)$$

These two cases might be combined formally as follows

$$\bar{S}_{\text{not}} = \eta R \ln\,(\gamma/B') - R \ln \sigma \qquad (20)$$

wherein

$$\gamma \equiv ekT/hc$$

$$\eta = \begin{cases} 1 & \text{linear} \\ \tfrac{3}{2} & \text{nonlinear} \end{cases}$$

$$B' = \begin{cases} B & \text{linear} \\ (ABC/\pi)^{1/3} & \text{nonlinear} \end{cases}$$

For a mixed group of molecules, η in eq 20 could be interpreted as a suitable average.

Moments of inertia have the structure $I = \sum_i m_i\rho_i^2$ in which ρ_i represents a plane projection of the distance of atom i from the center of mass. In some average sense one might write $I \approx \sum_i I_i$ with $I_i = m_i(\rho_i^2)_{\text{av}}$. Since rotational constants are inversely proportional to moments of inertia, it is suggested that

$$1/B' \approx \sum_i 1/B_i \qquad (21)$$

If now B_0 represents the mean value of B' for some group of molecules, we can approximate the logarithm as done in section 3. Since rotational constants can vary over several orders of magnitude, however, it is probably just as well to use simply $\ln x \approx x - 1$. The result is

$$\bar{S}_{\text{not}} \approx \eta R \ln \frac{\gamma}{eB_0} + \eta RB_0\sum_i \frac{1}{B_i} - R \ln \sigma \qquad (22)$$

corresponding to atomic contributions

$$S_{\text{not}}^{(i)} \approx \eta R \ln \frac{\gamma}{eB_0}\left(1 - \frac{l_i}{2}\right) + \frac{\eta RB_0}{B_i} \qquad (23)$$

The sequence of rotational entropy contributions for sulfur in Table V might conceivably be exhibiting this behavior. By our estimates, $S_{\text{rot}}^{(i)} \approx 4.4$, 8.2, 2.2, and −2.0 eu for $l = 1$ to 4. Now, the $l = 2$, 3, and 4 values conform approximately to $10(1 - \tfrac{1}{2}l) + 8$ eu, but the $l = 1$ value of $S_{\text{rot}}^{(i)}$ would then has to be about 13 eu. Clearly, better empirical data will be required before this line of development can be pursued further.

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