

Entropy Explained: The Origin of Some Simple Trends

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Motivation

With the widespread availability and application of commercial software (1) to approximate the solution of the Schrödinger equation, this capability has moved rapidly into the undergraduate curriculum as a way to introduce students to the practical computation of a wide variety of molecular properties. Students learn that wave functions, generated by density functional methods for example, are the basis not only for the geometric parameters of a given molecule, but for the energetics of molecules and their reactions as well.

While unimolecular reactions (isomerizations) have the free energy (ΔG°) approaching the enthalpy (ΔH°), entropy becomes increasingly important when the number of molecules, n , in a reaction changes: $\Delta n = n_{\text{products}} - n_{\text{reactants}} \neq 0$. Indeed, it is a favorite textbook problem to show examples where ΔS° opposes ΔH° , and a temperature range where the sign of ΔG° is dominated by entropy, not enthalpy. While the fact that $\Delta n > 0$ predicts $\Delta S^\circ > 0$, knowing the *magnitude* of ΔS° is generally “beyond the scope of this course”.

In the past, chemists using computational methods to evaluate reaction energetics have avoided examining ΔS° (and by extension ΔG°), concentrating instead on the electronic energies obtained for the converged geometry (which are directly related to ΔH° by the addition of a factor of RT to the sum of electronic and thermal energies and including a correction for the zero point energy of the molecule). After highlighting the accuracy of density functional theory (DFT) methods for calculating the entropy of single molecules, we hope to show that reaction entropy obeys some simple trends whose origin can be easily understood. Students and practicing chemists alike can then expect and understand when contributions due to entropy need to be taken into account. The results stand as a useful applied example for teaching entropy in an elementary physical chemistry course, and show how the use of computational packages can be combined with the student “discovering” trends for chemically relevant systems for himself or herself. Thanks to the presence of analytical (instead of numeric) calculation of vibrational frequencies, this is not even a time-consuming task.

Accuracy of DFT Methods in Calculating Entropies

Density functional theory is increasingly used as a relatively time-inexpensive computational method for finding optimized geometries of compounds of chemical interest, including most elements of the periodic table (2). Evaluating the accuracy of the computed properties against the current, accepted experimental values provides a measure of confidence that the conclusions drawn in a computational “experiment” are not merely artifacts of the method used. This

approach gives the beginning user or physical chemistry class situations where the “right” answer is known. While computational methods do not easily approach the accuracy and precision of spectroscopic measurements, they do provide in most cases accurate qualitative models. Here we are interested in emphasizing that DFT methods compute the total entropy of simple organic molecules very well. We are also interested in understanding the limits of commercial programs that calculate entropy by looking at any observed correlation with the molecular weight of the subject compound and any dependence on basis set or molecular symmetry chosen. We will provide some simple guidelines as to whether entropy must be taken into account when looking at a particular chemical reaction.

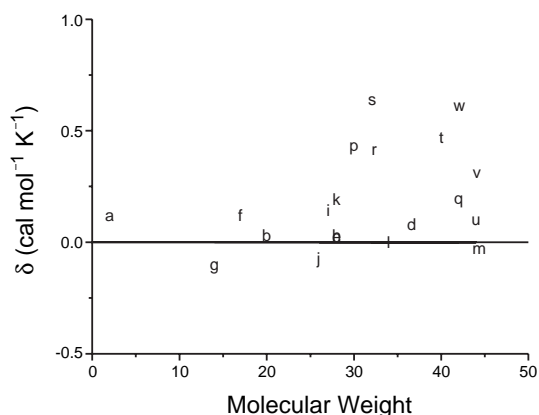
A list of entropies calculated¹ with Gaussian 98 (1) for a variety of gas phase organic compounds can be found in Table 1, along with the corresponding measured experimental values for the standard entropy of these compounds (3). These particular compounds were chosen to give a good range of degree of unsaturation (alkyne vs alkene vs alkane), steric strain (cyclopropane vs propene), electronic unsaturation (vinylidene vs acetylene), amount of internal rotation around single bonds, and the role of heteroatoms (hydrazine vs ethylene), as well as to provide a logical set of molecules from which a number of chemically sensible disproportionation reactions could be written.

From Table 1, and the corresponding plot of the difference of the calculated entropy from the experimental entropy values against the molecular weight (Figure 1), one can immediately observe that DFT reproduces the experimental values remarkably well. The average deviation of $0.3 \text{ cal mol}^{-1} \text{ K}^{-1}$ (0.09 kcal/mol at 298.15 K) of the calculated from the measured standard entropy values is well within accepted error limits for calculated energies (current levels of calculation and use of simplified models give an error bar of around 3 kcal/mol for E , thus small errors in S play a negligible role).

A useful comparison to make is the correlation between molecular weight and the deviation of the calculated entropic parameters from the experimentally measured ones (Figure 1). If it were found that with a larger molecular weight the computation of entropy produced a poorer value, particular care would have to be taken to ensure values calculated for large structures could be trusted. However, no correlation between molecular weight and deviation from experimentally measured entropy values was observed, so larger systems should be computed with some degree of confidence in the reliability of the numbers obtained. Molecules with a larger number of low energy internal vibrations (methyl group rotation or out-of-plane bending, for example) had a slightly higher calculated error.

Table 1. A Comparison of Calculated and Experimental Entropy Values

Molecule	$S^\circ/\text{cal mol}^{-1} \text{K}^{-1} (3)$		Label
	Calculated	Experimental	
H ₂	31.1	31.2	a
HF	41.5	41.5	b
CH ₄	44.5	44.5	c
HCl	44.6	44.7	d
N ₂	45.8	45.8	e
NH ₃	46.0	46.1	f
:CH ₂ (triplet)	46.7	46.6	g
CO	47.2	47.3	h
HCN	48.1	48.2	i
HC≡CH	48.1	48.0	i
F ₂	48.3	48.5	k
CNH	49.1	—	—
PH ₃	50.3	50.2	l
CO ₂	51.1	51.1	m
HN=NH	52.2	—	—
O=CH ₂	52.2	52.3	n
H ₂ C=CH ₂	52.3	52.4	o
:C=CH ₂ (singlet)	53.1	—	—
H ₃ C-CH ₃	54.4	54.8	p
cyclopropane	56.6	56.8	q
H ₂ N-NH ₂	56.6	57.0	r
HOCH ₃	56.7	57.3	s
O=C=CH ₂	57.7	—	—
CH ₂ =C=CH ₂	57.8	58.3	t
ethylene oxide	57.9	58.0	u
cyclopropene	58.0	—	—
O=CH(CH ₃)	62.8	63.0	v
H ₂ C=CH(CH ₃)	63.2	63.8	w

Figure 1. ΔS° (experimental) – ΔS° (calculated) (δ) as a function of molecular weight.

Dependence of Calculated Entropy on Basis Set

Another question to ask in defining the reliability of calculated entropies is their dependence on basis set. While with small organic molecules an increase in basis set size does not appreciably increase the time needed for the computation, with larger molecules this can become a problem (time scales as n^3 to n^4 for the number of basis functions, n); smaller basis sets, then, allow the student or practicing chemist to get a “feel” of what the entropy of a system is without investing a lot of computational resources. A small sample of molecules (which again represent different degrees of saturation) including ethane, ethylene, acetylene, methylene, methane, and hydrogen, were calculated with three common basis sets differing in the number and kind of polarization functions placed on the atoms (namely 6-31G, 6-31G*, and 6-31G**).

No significant difference in entropy (or enthalpy of reactions involving these molecules at different basis sets) was found between these molecules computed with different basis sets; less than $0.04 \text{ cal mol}^{-1} \text{K}^{-1}$ difference in total entropy was observed in all cases. This independence can be rationalized by the observation that s orbitals on hydrogen, and s and p orbitals on carbon (or the heteroatoms) should be sufficient in these cases to adequately model the bonding interactions and, consequently, calculate the frequencies on which some of the entropic contributions depend (although these values cannot be used for the assignment of spectroscopic data). Here, all vibrational entropies are small as there are few soft vibrational modes (like rotation) present; a change in basis set, which would influence most directly the value of the calculated frequencies, is thus not determining in the total entropy value. Systems that have a larger vibrational entropy are likely to be more basis-set dependent.

Dependence of Calculated Entropy on Molecular Symmetry

Within the Gaussian set of programs, the point group of the molecule is determined from the symmetry of the input structure. The geometry optimization and subsequent calculations are carried out in this symmetry (a step in the optimization that would involve lowering the symmetry of the molecule causes the optimization to abort). Larger molecular calculations are most often carried out in C_1 symmetry, either because there are no other symmetry elements present or because the user wishes not to constrain the path of the optimization to that allowed by the initial point group. Often, as in the case of $(\text{PH}_3)_2\text{Ir}(\text{H})_2(\text{H}_2)\text{Cl}$ discussed later in this paper, optimizations with a symmetry plane present (C_s in this example) result in a converged structure with one or more imaginary frequencies that correspond to motions that would break the symmetry plane. To converge a structure to an energy *minimum* (no imaginary frequencies), the computation must be carried out again in a lower symmetry group (here C_1).

Nevertheless, because of numerical convergence (i.e., the change in energy or force displacements are below the standard cutoffs) some molecules can be converged to energy *minima* in more than one point group. While the geometric parameters and overall energy are nearly identical, parameters dependent on the rigorous molecular symmetry of the molecule (rotational entropy) are incorrectly calculated when the

molecule converges in the “wrong” point group. CH_4 , for example, can be converged to nearly identical geometry and energy in two point groups, T_d (the rigorously correct one) and C_{3v} , which give different entropy values, an artifact of the software application. Such errors in calculated entropy are especially pronounced in linear molecules ($D_{\infty h}$ vs C_s in acetylene result in a $6.7 \text{ cal mol}^{-1} \text{ K}^{-1}$ difference in total entropy) because of the incorrect introduction of additional moments of inertia.

Two problems are at issue here: first, the symmetry number, σ , is different (and incorrectly computed) for molecules in different point groups, causing the value obtained for the entropy to be incorrect by a factor of $R \ln(1/\sigma)$. Secondly, as a nonlinear molecule approaches linearity, there is a question of which frequency to remove; this confusion, combined with a formula for a nonlinear molecule being applied to a molecule that is basically linear, results in a failure of the program to calculate a “correct” entropy with an “incorrect” geometry. This dependence on correct assessment of point group and correct input of the initial structure is especially relevant to the increasing number of undergraduate physical chemistry courses incorporating computational chemistry into the curriculum. Several other examples are listed in Table 2.

Some Simple Trends in Reaction Entropy in One-to-Two Particle Systems

Many reactions in chemistry that are not simply isomerizations ($\Delta S^\circ \approx 0$) involve two molecules coming together to form one, or the reverse. For example, consider the dehydrogenation of alkanes to form alkenes, or dihydrogen (H_2) binding to a transition metal. In such cases, the entropy contribution to the overall free energy (ΔG°) cannot be ignored.

Two recent papers in calorimetric studies, which rely on model organic reactions that may “simulate” more complex processes such as those involving organometallic species, have noted that ΔS° is relatively constant for a range of reactions where $\Delta n = 1$ (and constant at *twice* the value for $\Delta n = 2$) (4). While this is exceptionally useful for connecting ΔH° to an approximate ΔG° value, it is surprising that molecular identity has so little apparent influence on the magnitude of ΔS° ($\Delta n = 1$). Do molecules behave like nondescript hard spheres in their contribution to S° ? In order to computationally understand the magnitude of ΔS° (found experimentally to be $8 \pm 2 \text{ kcal/mol}$ at 298.15 K) and to develop some simple trends that explain which entropic components contribute most to this value, a sample of reactions (Table 3) were analyzed. Because we are not concerned with the overall value of ΔH° , we can take advantage of simple chemical transformations that include important classes of molecules but may not be experimentally feasible. These reactions represent cases in which different numbers of linear or nonlinear molecules are produced, along with cases that differ by the amount of steric strain, unsaturation, etc. The average $T\Delta S$ for all of these reactions is 9.38 kcal/mol , with values ranging from 7.38 to 12.66 kcal/mol . A simple set of trends in entropy becomes obvious upon examination; this can assist in understanding the sources and amounts of entropy in chemical systems.

Table 2. Symmetry Dependence of Calculated Entropies for Selected Molecules

Molecule	Calculated S° /cal mol ⁻¹ K ⁻¹	Point Group
CH ₄	44.48	T_d
	47.23	C_{3v}
:C=CH ₂ (triplet)	53.14	C_{2v}
	54.52	C_s
O=CH ₂	52.23	C_{2v}
	53.61	C_s
HOCH ₃	56.71	C_s
	56.72	C_1
CH ₂ =C=CH ₂	57.84	D_{2h}
	59.26	C_2
cyclopropene	57.97	C_{2v}
	59.35	C_1
cyclopropane	56.57	D_{3h}
	58.76	C_{2v}
	60.14	C_1
O=C=CH ₂	57.72	C_{2v}
	59.09	C_s
ethylene oxide	57.87	C_{2v}
	59.25	C_1

Reactions That Produce H₂ Have $T\Delta S = 8 \pm 1 \text{ kcal/mol}$ at 298 K

One of the first observable conclusions is that reactions that produce H_2 as one of the two particles have an average overall entropy change of 8.40 kcal/mol (ranging from 7.38 to 9.70 kcal/mol). This is largely independent of the degree of unsaturation or the presence of heteroatoms (molecular identity in general). In each case, the major component of the reaction entropy results from translational entropy. (The classic illustration here is of one billiard ball moving to strike another so that two billiard balls are moving.) The nature of the second component matters very little; the translational entropy with dihydrogen (of particularly small mass) as one of the “billiard balls” is nearly a constant 8.31 kcal/mol .

Increases in Rotational Entropy Account for the Larger Reaction Entropy in Reactions That Produce No Linear Molecules

The last five reactions in Table 3 are distinguished by the production of two non-dihydrogen products. Additionally, in all but one of these reactions, no linear molecules are produced. What is it about these reactions that cause a higher total entropy? Which component is changing?

Let us first consider the increase in translational entropy among these reactions. For an ideal gas, the translational contribution of entropy for independent particles as a function

Table 3. Reaction Entropies and Component Analysis of Two-Particle Producing Reactions at 298.15 K

Reaction ^a	$T\Delta S^\circ$ /(kcal/mol)				
	Calculated	Electronic	Translational	Rotational	Vibrational
$\text{N}_2\text{H}_2 \rightarrow \text{N}_2 + \text{H}_2$	7.38	0.00	8.31	-0.91	-0.02
$\text{CH}_2=\text{C}(\text{H})\text{CH}_3 \rightarrow \text{H}_2 + \text{CH}_2\text{CCH}_2$	7.68	0.00	8.33	-0.25	-0.40
$\text{OC}(\text{H})\text{CH}_3 \rightarrow \text{H}_2 + \text{OCCH}_2$	7.78	0.00	8.33	0.00	-0.55
$\text{OCH}_2 \rightarrow \text{CO} + \text{H}_2$	7.79	0.00	8.31	-0.49	-0.02
$\text{CH}_3\text{OH} \rightarrow \text{H}_2 + \text{OCH}_2$	7.95	0.00	8.31	0.03	-0.39
$\text{N}_2\text{H}_4 \rightarrow \text{H}_2 + \text{N}_2\text{H}_2$	7.96	0.00	8.31	0.43	-0.78
$\text{C}_2\text{H}_4 \rightarrow \text{H}_2 + \text{HCCH}$	8.02	0.00	8.31	-0.57	0.29
$\text{OC}(\text{H})\text{CH}_3 \rightarrow \text{CO} + \text{CH}_4$	8.64	0.00	9.81	-0.06	-1.12
$\text{C}_2\text{H}_6 \rightarrow \text{H}_2 + \text{C}_2\text{H}_4$	8.68	0.00	8.31	0.79	-0.42
$\text{CH}_4 \rightarrow \text{H}_2 + \text{:CH}_2$ (T)	9.94	0.65	8.25	1.04	0.00
$\text{C}_2\text{H}_4 \rightarrow \text{H}_2 + \text{:CCH}_2$ (S)	9.54	0.00	8.31	0.95	0.27
cyclopropane $\rightarrow \text{H}_2 + \text{cyclopropene}$	9.70	0.00	8.33	1.39	-0.02
$\text{H}_2\text{C}=\text{C}(\text{H})\text{CH}_3 \rightarrow \text{CH}_4 + \text{:CCH}_2$ (S)	10.26	0.00	9.79	1.22	-0.75
$\text{OCCH}_2 \rightarrow \text{CO} + \text{:CH}_2$ (T)	10.80	0.65	9.73	0.99	-0.57
$\text{H}_2\text{CCH}_2 \rightarrow 2 \text{:CH}_2$ (T)	12.25	1.30	9.48	1.59	-0.12
$\text{CH}_2\text{CCH}_2 \rightarrow \text{:CH}_2$ (T) + :CCH_2 (S)	12.52	0.65	9.71	2.51	-0.35
cyclopropane $\rightarrow \text{C}_2\text{H}_4 + \text{:CH}_2$ (T)	12.66	0.65	9.73	2.49	-0.21

^aS and T are singlet and triplet, respectively.

of pressure can be written (5a) as:

$$S_i^\circ = Nk \left\{ \ln \left[\left(\frac{2\pi mkT}{h^2} \right)^{3/2} \frac{kT}{P^\circ} \right] + \frac{5}{2} \right\} \quad (1)$$

Going from H_2 to CO will increase the translational entropy by $R[\ln(14)^{3/2}]$ or $7.9 \text{ cal mol}^{-1} \text{ K}^{-1}$ (2.3 kcal/mol at 298.15 K) as the molecular weight has increased by a factor of 14. The increase in translational entropy, then, can be explained as the large increase in the mass of one of the two particles that are produced. This dependence on mass can be easily seen by graphing the change in entropy in a reaction at 298.15 K as a function of the two masses of the daughter particles ($M \rightarrow M_1 + M_2$, where here M_1 and M_2 are x and y respectively) (Figure 2).² Expressing the translational component to reaction entropy in kcal mol^{-1} in terms of the masses (in amu) of the daughter particles (x and y) gives a formula (eq 2) for any reaction where one particle goes to two particles:

$$T\Delta S_i^\circ = \left(\frac{RT}{4.184(1000)} \right) \times \left\{ \frac{5}{2} + \ln \left[\left(\frac{2\pi m_u kT}{h^2} \right)^{3/2} \frac{kT}{P^\circ} \right] + \ln \left[\frac{x^{3/2} y^{3/2}}{(x+y)^{3/2}} \right] \right\} \quad (2)$$

Evaluating all constants gives the numerical expression at

298.15 K:

$$T\Delta S_i^\circ = (0.5925) \left\{ 13.09 + \ln \left[\frac{x^{3/2} y^{3/2}}{(x+y)^{3/2}} \right] \right\} \quad (3)$$

By taking a "slice" of this three dimensional graph when $x = 2$ (one of the particles is hydrogen) one can see that the mass of the second particle is of little importance in the range of most typical hydrocarbons (masses 16 or greater); the change in entropy is approximately $8.3 \text{ kcal mol}^{-1}$ (Figure 3). The value of $8.3 \text{ kcal mol}^{-1}$ originates from equation 3; if the heavier daughter particle, y , has approximately the same mass as the parent particle, $x + y$, then the masses cancel each other. The term that remains, $\ln(x^{3/2})$, gives a value of 1.03 for hydrogen, which when combined with the terms for all the other constants, gives a reaction entropy of $8.3 \text{ kcal mol}^{-1}$.

The main reason for the difference in the entropy values for the reactions in Table 3, however, is not in the translational entropy, though that does indeed still largely control the value of the calculated $T\Delta S^\circ$ for the reaction. The rotational entropy (5b), which had been near zero for nearly all of the first reactions that liberated H_2 , is now increasing. This can be understood if we look at the shape of the molecules produced in the latter reactions; in these cases, none of the molecules are linear. For polyatomic, nonlinear molecules the calculation of rotational contributions to entropy must take into account the possibility of three different moments of inertia; linear molecules with smaller moments of inertia have small rotational partition functions and small contributions to S° compared with nonlinear molecules with larger, multiple

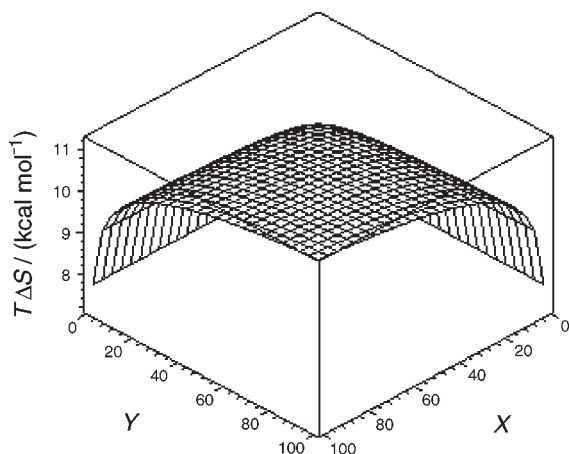


Figure 2. Graph of translational entropy contributions (at 298.15 K) to a reaction system with daughter particles of masses x and y (in atomic mass units).

moments of inertia and correspondingly larger contributions to S° . The larger rotational entropy of the products in these reactions, then, is in large part responsible for the increase in overall calculated $T\Delta S^\circ$ (an average of 11.70 kcal/mol for reactions that produce no linear molecules). We can see this dependence of the molecular shape of the product molecules reflected also in unusually small $T\Delta S^\circ$ values for reactions that produce two linear molecules, though less dramatically. The average for reactions that release two linear molecules is 7.73 kcal/mol (compared to 8.40 kcal/mol for all H_2 releasing reactions evaluated).

Vibrational Entropy Only Plays a Significant Role in the Overall Reaction Entropy If the Number of Low Frequency Vibrations Changes Significantly from Reactant to Product

Changes in vibrational entropy in the organic reactions studied play a relatively small role in the overall calculated $T\Delta S^\circ$. The vibrations that play the largest role in the calculated S_{vib} values must be low-energy (low-frequency) vibrations, such as rotation of a CH_3 group. In most of the reactions, the change in vibrational entropy from reactants to products is near zero, reflective of the small change in rigidity of the molecules in question.

In a few instances, however, larger than average $T\Delta S_{\text{vib}}$ contributions are observed. For example, the change in rotational entropy from reactants to products is -1.12 kcal/mol for the disproportionation of acetaldehyde, $OC(H)CH_3$, to carbon monoxide and methane. This negative change (reflective of the greater vibrational entropy of the reactant) can be understood by observing that there are no low-energy vibrations in the product molecules; the rotation around the $C-CH_3$ bond has been lost in the products. The vibrations that remain, $C-H$ stretches for example, are higher in energy and contribute less to the vibrational entropy. Similar trends can be observed in other listed reactions that lose low-energy vibrations (propylene with easy rotation and hydrazine with rotation and inversion at nitrogen, for example). However, even in these cases of larger-than-average changes in

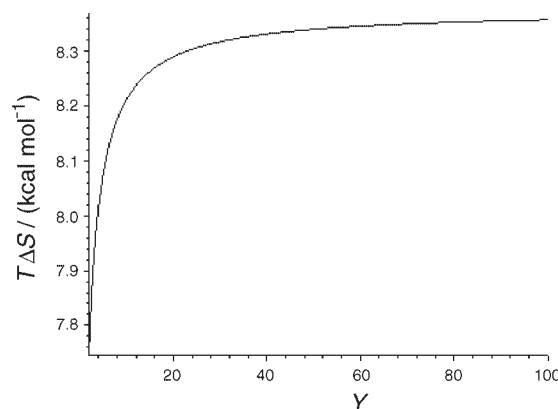


Figure 3. Graph of translational entropy contributions (at 298.15 K) to a reaction system with daughter particles of mass $x = 2$ and y (in atomic mass units).

vibrational entropy, contributions to the total entropy from translation, and even rotation, are much larger; changes in entropy thus should not depend strongly (<2 kcal/mol) on bonds *within* the molecules. In other words, molecules lose their unique differences and become, nearly, billiard balls.

There Is an Entropy Gain on Going from a Singlet to a Triplet Electronic State

Nearly all the molecules calculated are ground state singlets; however, methylene, $:CH_2$, is a ground state triplet. The entropy contribution from the electronic state is a constant $R \ln(g)$, where $R = 1.99 \text{ cal mol}^{-1} \text{ K}^{-1}$ and g is the degeneracy for the spin multiplicity ($g = 2S + 1$). $:CH_2$ then, has an electronic contribution to entropy of $2.19 \text{ cal mol}^{-1} \text{ K}^{-1}$, or 0.65 kcal/mol at 298.15 K. This electronic entropy is reflected in reactions that involve these triplet species.

Application to One-to-Three Particle Systems

Similar trends can be observed (Table 4) for reactions that produce three particles from one. Ideally, reactions that liberate hydrogen would have on average an overall reaction entropy of 2(8.4) or 16.8 kcal/mol; we see here for the reactions that liberate two equivalents of hydrogen an average of 15.54 kcal/mol, symptomatic of the other product also being a linear molecule. Once again, we see that by far the largest contributor to the calculated $T\Delta S^\circ$ is the translational entropy of the products. We can extrapolate the results of the two-particle calculations here and say that similar one-to-three particle reactions (i.e. that liberate two equivalents of hydrogen and either a linear or nonlinear third product) should have overall reaction entropies of approximately 15–17 kcal/mol.

The last two reactions in Table 4 also follow the trends observed earlier for two-particle producing reactions. In both cases, the total entropy is higher than that observed for the reactions that produced H_2 ; this is particularly reflected in the increase in the translational contribution to the reaction entropy. The rotational contribution also increases

dramatically, owing to the production of nonlinear molecules with higher, multiple moments of inertia. Consistent with the production of more nonlinear molecules giving a higher entropy, the reaction producing three equivalents of methylene has a higher rotational entropy than the reaction producing two nonlinear molecules and dihydrogen. Somewhat larger negative vibrational entropies are observed here, also consistent with the loss of easy rotation around C–C single bonds.

Entropy Calculations for Transition Metal Systems

In general, while experimental entropy values have been measured for small organic compounds, comparatively few inorganic compounds have been experimentally determined. Computations, particularly DFT calculations, can thus provide an especially helpful way to determine the entropy of systems that result in a change in the overall number of particles. As previously mentioned, such entropic contributions to the overall reaction free energy can make a difference, even in the overall sign (whether the reaction will be thermodynamically favored or not) of ΔG° . For example, in the reaction at 298.15 K,

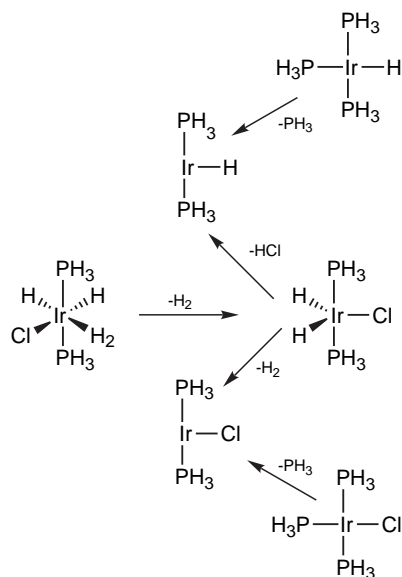


$\Delta H^\circ = -7.3$ kcal/mol and $T\Delta S = -7.6$ kcal/mol, leading to $\Delta G^\circ = 0.3$ kcal/mol (6).

We wanted, then, to look computationally at a simple organometallic system, to see if the trends observed for organic systems held also here. The molecules discussed here were calculated in C_1 symmetry; calculation in higher symmetry groups resulted in imaginary frequencies being observed (no energy *minima*).

Trends in Reaction Entropy in Organometallic Systems Mirror Those of the Organic Systems

$(\text{PH}_3)_2\text{Ir}(\text{H}_2)(\text{H})_2\text{Cl}$, containing one dihydrogen and two hydride ligands, can provide the basis for writing several one-to-two particle reactions (Scheme I, Table 5) (7).



Scheme I

Here, we again see that for many of the reactions that liberate H_2 , the overall reaction entropy is near the 8 kcal/mol values seen earlier for the organic reactions. The value is somewhat higher when HCl, a linear molecule but one of higher

Table 4. Reaction Entropies and Component Analysis of Three-Particle Producing Reactions at 298.15 K

Reaction ^a	$T\Delta S/(\text{kcal/mol})$				
	Calculated	Electronic	Translational	Rotational	Vibrational
$\text{N}_2\text{H}_4 \rightarrow 2\text{H}_2 + \text{N}_2$	15.34	0.00	16.62	-0.48	-0.80
$\text{CH}_3\text{OH} \rightarrow 2\text{H}_2 + \text{CO}$	15.74	0.00	16.62	-0.47	-0.42
$\text{CH}_2=\text{C}(\text{H})\text{CH}_3 \rightarrow \text{H}_2 + \text{:CH}_2(\text{T}) + \text{:CCH}_2(\text{S})$	20.21	0.65	18.04	2.27	-0.75
$\text{CH}_2=\text{C}(\text{H})\text{CH}_3 \rightarrow 3 \text{:CH}_2(\text{S})$	22.93	1.95	19.21	2.90	-1.14

^aS and T are singlet and triplet, respectively.

Table 5. Reaction Entropies and Component Analysis of Two-Particle Producing Reactions for a Transition Metal System at 298.15 K

Reaction	$T\Delta S/(\text{kcal/mol})$			
	Calculated	Translational	Rotational	Vibrational
$(\text{PH}_3)_2\text{Ir}(\text{H}_2)(\text{H})_2\text{Cl} \rightarrow \text{H}_2 + (\text{PH}_3)_2\text{Ir}(\text{H})_2\text{Cl}$	10.28	8.37	0.87	1.05
$(\text{PH}_3)_2\text{Ir}(\text{H}_2)\text{Cl} \rightarrow \text{H}_2 + (\text{PH}_3)_2\text{IrCl}$	7.16	8.37	0.85	-2.06
$(\text{PH}_3)_2\text{Ir}(\text{H})_2\text{Cl} \rightarrow \text{HCl} + (\text{PH}_3)_2\text{IrH}$	8.51	10.82	1.40	-3.72
$(\text{PH}_3)_3\text{IrH} \rightarrow (\text{PH}_3)_2\text{IrH} + \text{PH}_3$	10.42	10.77	3.10	-3.45
$(\text{PH}_3)_3\text{IrCl} \rightarrow (\text{PH}_3)_2\text{IrCl} + \text{PH}_3$	10.62	10.78	3.70	-3.86

mass, is liberated. The difference from the organic reactions here is not one of translational or rotational entropy, but rather of an increase in the vibrational entropy of the reactant molecules due to the inclusion of *many* more low-frequency vibrations (the free rotation around the Ir–PH₃ bond, easy rotation of coordinated H₂, and the low-frequency stretches of Ir–H and Ir–Cl bonds) in the reactant molecule (and the subsequent loss of some of these in the products).

This increase in vibrational entropy reflects the “softer” nature of metal-to-ligand bonding in transition metal compounds. Transition metal compounds are often fluxional, with two or more geometries being isoenergetic or the intramolecular exchange of ligands (i.e., in a trigonal-bipyramidal five-coordinate molecule) having a low energetic barrier. In the transition metal compounds employed in this study, for example, (PH₃)₂IrH₂Cl is calculated to have a vibrational entropy 3.5 cal mol⁻¹ K⁻¹ higher than (PH₃)₂Ir(H₂)(H₂)Cl, even though the latter has a coordinated dihydrogen molecule with a low vibrational frequency of rotation. This can be explained in this case by the extremely flat potential energy surface for change in the H–Ir–Cl angle; the “Y-shaped” geometry calculated here is nearly isoenergetic with the “T-shaped” geometry of the meridional ligands (8). This higher vibrational entropy in the unsaturated (fewer than 18 electrons at the metal center) Ir complex accounts for the higher than usual reaction entropy in the formation of (PH₃)₂IrH₂Cl and H₂ from (PH₃)₂Ir(H₂)(H₂)Cl (Table 5). It is important to note here, however, that while the vibrational contribution approaches or surpasses the contribution to $T\Delta S$ from rotational entropy, even with “soft” vibrations in transition metal compounds the overall reaction entropy is still *near* 8 kcal/mol.

Similar to the trends observed in those organic reactions producing no linear molecules, among the organometallic systems calculated here reactions that liberate no linear molecules (producing an Ir species and PH₃, for example) have noticeably higher total reaction entropy. One can see several con-

tributors to this. First, the translational entropy once again is seen to increase when particles heavier than H₂ are produced. Secondly, the rotational entropy of the products increases as there are no linear molecules with small moments of inertia. Working against those two increases, however, is a decrease in the products’ vibrational entropy, due here in large part to the loss of a low energy Ir–P bond rotation of the PH₃ group. Overall, however, the reaction entropy increases to an average of 10.52 kcal/mol. Corresponding trends are observed in one-to-three particle systems (Table 6). Again, we see that the release of molecules beside H₂ increases the overall entropy, in part due to an increase in the translation entropy of the molecules.

Trends Found in Organic and Transition Metal Systems Extend to Non-First Row Main Group Compounds

In order to expand our understanding of the role of vibrational contributions to entropy, we chose to calculate non-hydrocarbon main group compounds (or their heteroatom-substituted derivatives). Second, third, and fourth row main group compounds should have lower vibrational frequencies associated with them (corresponding to “softer” vibrational modes) and should, therefore, show a contribution to the vibrational entropy larger than their first row counterparts but smaller than transition metal species (Table 7).

The silicon, germanium, and tin analogs of ethane and ethylene were calculated to give a comparable series of main group reactions. We see here little difference between the purely hydrocarbon organic reactions where two particles are produced from one and these heavier analogs; the calculated $T\Delta S$ is still around 8 kcal/mol when one linear molecule of H₂ is released, and is dominated by translational contributions to entropy, with a smaller contribution from the rotational term. In these reactions, the rotational contribution from entropy is somewhat higher, due to their non-planarity (the Si, Ge, and Sn analogs of ethylene are in the point group C_{2v}) (9).

Table 6. Reaction Entropies and Component Analysis of Three-Particle Producing Reactions for a Transition Metal System at 298.15 K

Reaction	$T\Delta S$ /(kcal/mol)			
	Calculated	Translational	Rotational	Vibrational
(PH ₃) ₂ Ir(H ₂)(H ₂)Cl → 2H ₂ + (PH ₃) ₂ IrCl	17.44	16.73	1.72	-1.02
(PH ₃) ₂ Ir(H ₂)(H ₂)Cl → H ₂ + HCl + (PH ₃) ₂ IrH	18.79	19.19	2.28	-2.67

Table 7. Reaction Entropies and Component Analysis of Two-Particle Producing Reactions for Main Group Systems at 298.15 K

Reaction	$T\Delta S$ /(kcal/mol)			
	Calculated	Translational	Rotational	Vibrational
C ₂ H ₆ → H ₂ + H ₂ C=CH ₂	8.68	8.31	0.79	-0.42
Si ₂ H ₆ → H ₂ + H ₂ Si=SiH ₂	9.34	8.35	1.26	-0.26
Ge ₂ H ₆ → H ₂ + H ₂ Ge=GeH ₂	8.84	8.36	1.34	-0.86
Sn ₂ H ₆ → H ₂ + H ₂ Sn=SnH ₂	8.75	8.37	1.38	-1.00

Surprisingly, even though there exist in the second row cases lower vibrational frequencies for out-of-plane bending, etc., these frequencies must not differ by enough to begin to affect the vibrational entropy to a large degree. It may be, therefore, that fluxional transition metal compounds represent a limiting case of the vibrational entropy contribution.

Pedagogical Use

Much of chemical research, and indeed science in general, lies in the ability to observe and then explain trends in recorded measurements; use of the trends here discussed for entropy as a basis for a student project (either within the context of a physical chemistry laboratory or as an extended homework assignment in a physical chemistry lecture) allows students to observe trends in a physical property for themselves and gain practice in explaining them, taking into account what they have already learned in other chemistry courses about the structure of molecules and observed vibrational frequencies. Students gain a valuable introduction to an increasingly useful and important area of physical chemistry (computational chemistry) that complements existing discussions of thermodynamics (when is a reaction favored?), statistical mechanics (what molecular properties influence the observed measurement?), and quantum mechanics (can an “approximate” wave function generate useful and relevant predictions of molecular properties?). Thinking about where entropy “comes from” and its effect on chemical reactivity helps to develop a student’s chemical intuition about what molecular property (mass? chemical identity? spin state? vibrational frequencies? etc.) is most important in a given situation.

The ease of use of many computational packages for electronic structure calculations, especially those that involve a graphical user interface where the initial geometry can be input easily as a chemical drawing and whose basic manipulations and format are already familiar to students who have used menu-driven software, lends itself to use in the undergraduate curriculum. Since the focus of a student project of this type would be to discover and explain trends in a thermodynamic property (entropy) whose background is already typically given in a physical chemistry course and not simply the calculation of a number, assistance to the student on how to do the calculation could be provided to whatever degree necessary (10). A short introduction to computational chemistry and density function theory in general could be given in one to two lecture periods, with the remaining time (or a recitation period) given to a short demonstration of how to use the software.

Summary

Here we have investigated the DFT calculated entropies of a variety of organic and organometallic reactions. We have highlighted that the computed entropies correlate closely with measured entropy values in organic systems, with no significant dependence on molecular weight or basis set. Of particular note is the need to correctly evaluate the symmetry of the molecular species and input the geometry accordingly for accurate entropic values to be obtained.

For organic systems with small contributions to vibrational entropy, an average of 8.4 kcal/mol for the reaction

entropy (one particle to two) was observed when one of the particles was H₂; this value is largely determined by the translational entropy of the system. The average is slightly lower for reactions that produce two linear molecules and up to 4 kcal/mol higher when no linear molecules are produced due to differences in rotational entropy of the reactants and products. Little dependence on molecular identity results in a near constant $T\Delta S^\circ$ because the vibrational entropy that more closely depends on the identity of the molecules plays a minor role. For a one-to-two particle reaction where neither product is a linear molecule, an average reaction entropy of 11.7 kcal/mol is obtained. Reactions that produce three particles mirror the above trends, with the overall reaction entropy being considerably smaller when linear molecules are produced.

The entropy of inorganic reactions can also be calculated by DFT methods; the values obtained correlate well with organic reactions that produce identical numbers and kinds of linear products. The difference here lies mainly in the increased contribution of vibrational entropy in the inorganic molecules with “softer” vibrations; the total reaction entropy, then, is more dependent on the vibrational frequency value of the systems (and, as such, is likely more dependent on basis set choice). However, the identity of the system plays a still small, if less negligible, role. We see much less effect of vibrational entropy in second, third, and fourth row main group compounds.

This work has given evidence of a standard correction to add to the calculated ΔH° values (often approximated by ΔE) to evaluate ΔG . The direction of a reaction with a large positive value of ΔH° is unlikely to be influenced by an added entropic factor of 8–10 kcal/mol; however, inclusion of entropy in reactions with a $\Delta H^\circ < 10$ kcal/mol will differentiate between isomerization and disproportionation reactions. It is also good to keep in mind that there is a different entropy correction for the release of H₂ versus a nonlinear molecule; this could also allow one to distinguish between two otherwise feasible processes. With at least an 8 kcal/mol entropic deficit, metal systems where an incoming ligand is bound with energy (ΔH) less than 10 kcal/mol must be considered nonbonding (ΔG). At the transition state of an associative or disassociative reaction, the two particles are interacting; thus, the entropy of the system is closer to that of one particle than two because of translational entropy. Variation of the entropy is expected to occur between the transition state and the two particle system. Here, we have considered only the *overall* reaction entropy (and its effect on the free energy, ΔG°); we do not propose these entropy values as applicable to transition states.

The trends discussed in this paper can serve as a basis for understanding the contributions of different sources of entropy to the overall reaction $T\Delta S^\circ$ for students and practicing chemists alike; the method employed (i.e., using a commercial program to “discover” trends in a thermodynamic property through investigating various reactions) can serve as an example of discovery-based learning in the curriculum. The work here could be easily adapted for an extended homework assignment, group project, or exam that would incorporate practice in experimental design (which reactions will be calculated and why), modern computational methods (what factors—method, basis set, input symmetry, etc.—will

affect the result), and writing about chemistry (what trends are expected? observed? why?).

Computational Methods

All calculations were performed with the Gaussian 98 package (1), using the B3PW91 functional (11). Selected organic molecules were calculated with internal 6-31G, 6-31G*, and 6-31G** basis sets as discussed in the text (12). All entropy values of organic molecules reported in the tables are taken from calculations using the 6-31G* basis set. For the transition metal examples, internal basis sets used included LANL2DZ for Ir and P and 6-31G* for H and Cl; this choice of basis set resulted in geometric parameters similar to those previously reported (7). The basis set LANL2DZ is the Los Alamos National Laboratory ECP plus a double zeta valence on Ir and P (13); additional d polarization functions were added to phosphorus in all DFT calculations (14). Internal LANL2DZ was also used as the basis set for Si, Ge, and Sn. Organic compounds were calculated in the highest symmetry group to which they belong; all optimizations of transition metal compounds were performed with C_1 symmetry. In each case, minima were confirmed by analytical calculation of frequencies, which were also used to calculate the given thermochemical parameters. In the case of the organic molecules, complete geometry optimization and frequency calculation took less than five minutes of computer time on a desktop PC (time from submission to output availability).

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^uSupplemental Material

Supplemental material for this article including sample Gaussian input files and additional graphs and equations used for plotting (in Maple format) is available in this issue of *JCE Online*.

Notes

1. See the appendix to this article, available in *JCE Online*, for additional technical details including sample input files.
2. See the appendix to this article, available in *JCE Online*, for additional graphs and equations used for plotting (in Maple format).

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