

## Thermodynamic Data Bases and Optical Isomerism

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The article points out that the common sources of thermodynamic data do not respect optical isomerism though the substantial feature is not recognized. This fact implies widespread imprecisions involved in applications of the sources. The point is illustrated on difluorodisulfane. It is also pointed out that the chirality partition function plays a substantial role in the relative stabilities of fullerene isomers.

*Key words:* optical isomerism, chirality partition function, thermodynamic data bases, fullerenes, calculations of thermodynamic functions.

### INTRODUCTION

All molecules can be classified<sup>1</sup> with respect to reflection symmetry, *i.e.* presence or absence of a rotation-reflection axis  $S_n$  (called also alternating, improper, or mirror axis). Let us recall that the notion of an  $n$ -fold alternating axis of symmetry  $S_n$  involves<sup>2</sup> two special cases, a plane of symmetry  $\sigma = S_1$

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and a center of symmetry  $i = S_2$ . Objects with no reflection symmetry are called<sup>3</sup> dissymmetric, the others nondissymmetric. The dissymmetric (in contrast to nondissymmetric) objects are not superimposable upon their mirror images. Hence, in order to exist in two enantiomeric forms it is necessary for a molecule to be dissymmetric. However, presence of feasible intra-molecular motions (like a nearly free internal rotation which can be present in quite simple systems – *e.g.* dimethylacetylene) can prevent an experimental distinction at least under some observation conditions. Otherwise, the terms dissymmetric and nondissymmetric can be identified with chiral (optically active) and achiral (optically inactive), respectively. If one checks the point-symmetry groups<sup>4,5</sup> it can be found that only the  $C_n$ ,  $D_n$ ,  $T$ ,  $O$ , and  $I$  groups are free of a rotation-reflection axis  $S_n$ . A very particular but most important case of the dissymmetric species is represented by molecules with just one asymmetric atom, especially carbon; they exhibit  $C_1$  symmetry, *i.e.*, they are asymmetric.

## COMMON THERMODYNAMIC DATA BASES

Let us consider a molecule possessing one of the  $C_n$ ,  $D_n$ ,  $T$ ,  $O$ , and  $I$  symmetries critical for the dissymmetry property. There are two limiting situations: (*i*) a pure optical isomer (either  $l$  or  $d$ ), or (*ii*) an equimolar mixture of the two optical isomers, *i.e.* a racemate. The equilibrium constant for isomerization of the  $l$  and  $d$  isomers equals 1 and thus, the situation (*ii*) is reached in the infinite time limit. Molar entropy terms (and related quantities),  $S_T^\circ(i)$  and  $S_T^\circ(ii)$ , in cases (*i*) and (*ii*), respectively, are different. Their difference is equal<sup>6</sup> to  $R \ln 2$  where  $R$  stands for the ideal gas constant:

$$S_T^\circ(ii) = S_T^\circ(i) + R \ln 2 \quad (1)$$

This formula can be interpreted in terms of the entropy of mixing – the racemic mixture is less ordered state than the separate enantiomers and therefore has higher entropy. In microscopic terms, we deal with two sets of states,  $l$  and  $d$ , with the same energies which produces a degeneracy factor of 2.

Let us now move from the domain of textbooks to the real research life and open the most commonly used JANAF Tables.<sup>7a</sup> There is no word on optical isomerism in its introductory part. Still, there are in fact numerous molecules belonging to the critical point groups of symmetry and covered by the thermodynamic data source. Let us take difluorodisulfane FSSF(g) as an example (Figure 1). We could also take some organic compound with an asymmetric carbon atom like CHFClBr(g), however, the former case actu-

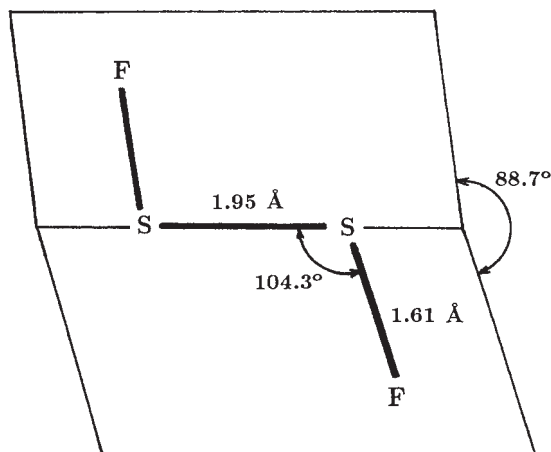


Figure 1. The minimum-energy structure of  $F_2S_2$  of  $C_2$  symmetry found in the RHF/6-31G\* calculations.

ally stresses the more general nature of the concept of optical isomerism. Difluorodisulfane belongs to the  $C_2$  point group of symmetry; hence, one can distinguish its two optical isomers. Nevertheless, it is not stated in Ref. 7a if the presented values of the standard entropy  $S_T^\circ$  and thermodynamic potential  $-[(G_T^\circ - H_{298.15}^\circ) / T]$  (also known as the Giauque function  $\Phi_T^\circ$ ) refer to one of the isomers or to their equimolar mixture. There is no other way to answer the question than to take all the molecular parameters and to repeat the computation in the partition-function terms (Table I – note that a standard-state choice of 1 atm = 101325 Pa, a bit different from the original choice

TABLE I

The Standard<sup>a</sup> Molar Entropy of Difluorodisulfane FSSF(g) at Room Temperature from Different Sources

Source	Isomeric Composition	$S_{298.15}^\circ / \text{J K}^{-1} \text{mol}^{-1}$
JANAF <sup>7</sup>	<i>l</i> or <i>d</i> <sup>b</sup>	293.97
This work	<i>l</i> & <i>d</i>	299.73
RHF/6-31G* <sup>8</sup>	<i>l</i> or <i>d</i> <sup>b</sup>	292.19
This work	<i>l</i> & <i>d</i>	297.94
MP2/6-31G* <sup>8</sup>	<i>l</i> or <i>d</i> <sup>b</sup>	294.33
This work	<i>l</i> & <i>d</i>	300.09

<sup>a</sup> The standard state - an ideal gas at 1 atm = 101325 Pa pressure.

<sup>b</sup> Deduced recursively in this work.

of 0.1 MPa,<sup>7a</sup> is employed; this can be easily recalculated back and forth, however, the 101325 Pa choice is still more common). Then, we can conclude that the JANAF values<sup>7</sup> refer to a one-component case (the conclusion was verified in discussions with the authors).<sup>7b</sup> The choice may have some historical roots<sup>7b</sup>— the JANAF Tables primarily deal with inorganic compounds and inorganic optical isomers are not as important as they are in organic chemistry. The point is expected<sup>7b</sup> to be addressed in a future edition.

### AN ILLUSTRATIVE COMPUTATIONAL EXAMPLE

The ideal gas-phase thermodynamic functions can be computed not only from spectroscopic but also from quantum-chemical data. Therefore, molecular-orbital packages supply computation of minimum-energy structures with thermodynamic quantities. Let us take an advanced software,<sup>8</sup> Gaussin 90, and apply it to the FSSF case, for example at the restricted Hartree-Fock level in the standard 6-31G\* basis set, RHF/6-31G\* (for recent theoretical treatments of the F<sub>2</sub>S<sub>2</sub> system, see Refs. 9–12). A local energy minimum of C<sub>2</sub> symmetry is indeed found. However again, neither in the manual nor in the computer output, a reference to the optical isomerism and its handling can be found. Thus, we also have to repeat all the partition-function treatment, now with the molecular parameters of quantum-chemical origin. Only after this extra step we can conclude that the thermodynamic quantities refer to a one-component case and not to the equimolar mixture of two optical isomers.

The quantum-chemical calculations of FSSF allow a deeper insight into its intra-molecular motions. One could simply expect two structures, a minimum and a saddle point on the FSSF internal-rotational potential curve, one planar *cis* and the other planar *trans*. However, both experiment<sup>7a</sup> and computations agree that the minimum is in fact a nonplanar C<sub>2</sub> structure. There is indeed an activated *cis* complex (C<sub>2v</sub> symmetry). For the other configuration the computation indicates a slightly more complex situation (Figure 2). There is a stationary point of C<sub>2h</sub> symmetry, *i.e.* planar *trans*, but it has two imaginary vibrational frequencies, not one. If we relax its symmetry from C<sub>2h</sub> to C<sub>s</sub> we can find the required activated complex (Figure 2). It still has *trans* configuration but two different SF bond lengths and two different values of the SSF bond angle. Table II surveys the computed RHF/6-31G\* harmonic vibrational frequencies and relative energies for the four stationary points on the FSSF potential hypersurface. It should be realized that for the all reported stationary points their vibrational analysis was performed in Cartesian coordinates, *i.e.* the stationarity with respect to all geometrical degrees of freedom was checked.

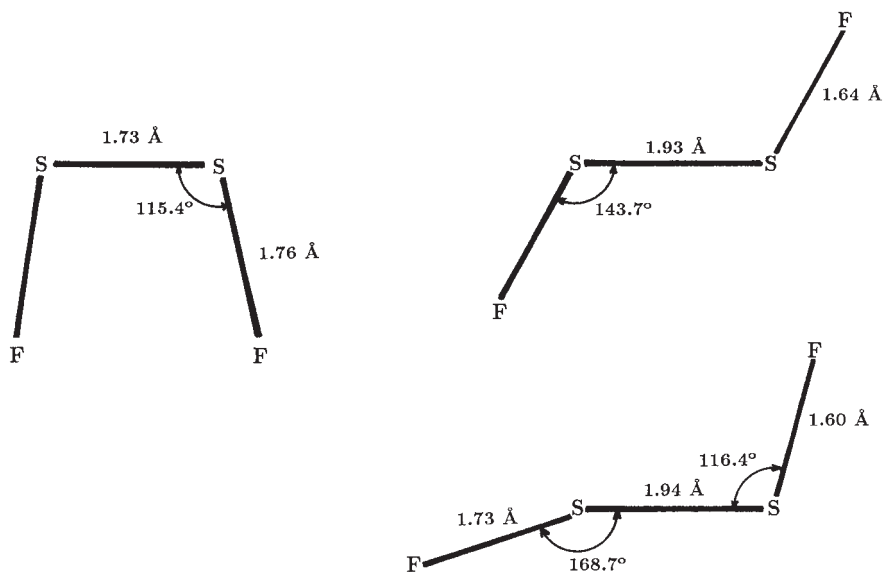


Figure 2. Saddle points found on the RHF/6-31G\* potential energy hypersurface of  $F_2S_2$ : left – the internal-rotational activated complex of  $C_{2v}$  symmetry (*cis*), upper right – stationary point with two imaginary frequencies and  $C_{2h}$  symmetry, lower right – the internal-rotational activated complex with  $C_s$  symmetry.

TABLE II

Characterization of the Stationary Points Found on the RHF/6-31G\* Potential Energy Hypersurface<sup>a</sup> of Difluorodisulfane FSSF

Symmetry	$(\Delta E/\text{kJ mol}^{-1})^b$	$(\omega_i/\text{cm}^{-1})^c$		
$C_2$	0	185	293	348
		611	859	884
		(185)	(279)	(315)
		(607)	(746)	(773)
$C_s$	353	563 <i>i</i>	97	363
		540	560	882
$C_{2h}$	359	445 <i>i</i>	79 <i>i</i>	260
		622	719	729
$C_{2v}$	510	219 <i>i</i>	158	271
		596	920	1076

<sup>a</sup> For the local minimum ( $C_2$ ) the MP2/6-31G\* values are given in parentheses.

<sup>b</sup> Potential energy with respect to the local minimum  $C_2$ .

<sup>c</sup> Harmonic vibrational frequencies;  $i = \sqrt{-1}$ .

In the FSSF illustrative example, the potential barriers are high enough to prevent an easy interconversion of both optical isomers. However, even if there is a fast motion, reducing a possibility of separation or experimental distinction of two optical isomers, it does not automatically mean that one cannot compute, at least formally, thermodynamic quantities of both one-component case or two-component mixture (Eq. (1)). The wide-spread approximation of the rigid rotor and harmonic oscillator would however be rather rough, at least for some degrees of freedom. In fact, a contradiction is met - for relatively high potential barriers (more precisely, one should rather work with a ratio of the barrier height and the product of the Boltzmann constant and temperature) the simple partition-function approximation works well but the inter-isomer equilibrium may be difficult to achieve. For relatively low barriers the equilibrium is easily established but there may be a need for a higher approximation of the partition functions<sup>13</sup> (especially in the limiting case of a stereochemical non-rigidity). There is a similar need for a more advanced partition function with, say, a nearly planar pyramidal molecule when approaching achiral planar form.

Finally, it is interesting to note that the  $S_{298.15}^{\circ}$  terms computed from spectroscopic and quantum-chemical parameters are quite close. Their difference is only about one third of the term  $R \ln 2$  we are primarily dealing with here. This good agreement between both sources justifies the use of the RHF/6-31G\* computational level here though we could use still a higher approximation, for example Møller-Plesset second order perturbation theory<sup>14</sup> MP2/6-31G\* (this article is not focussed on a discussion of quantum-chemical methods and their applicability - for an account on quantum-chemical theories and basis sets, the interested reader should consult, *e.g.*, references 15, they document generally a very good quality of geometries from this type of calculations). As can be seen in Table I, the MP2/6-31G\* entropy agrees still better with the spectroscopic value. Moreover, we did not scale the calculated frequencies though they are usually overestimated. Scaling factors of 0.89<sup>16</sup> and 0.93<sup>17</sup> were suggested for the RHF/6-31G\* and MP2/6-31G\* level, respectively. Such scaling should in fact somewhat increase the computed entropy values. This good agreement between both sources of the entropy term is just a particular consequence of the well known fact that the quantum-chemical approximations work relatively very well for molecular geometries and vibrational frequencies (though they are generally not sufficient, *e.g.*, for dissociation energies).

## WIDER IMPLICATIONS

Clearly enough, both JANAF and Gaussian 90 values themselves are correct, but they are not described sufficiently to eliminate misreadings. Similarly, in a comprehensive chapter on polyatomic molecules in another widespread compendium,<sup>18</sup> the question of optical isomerism is again not mentioned. Anyhow, our discussion of the missing  $R\ln 2$  term is not at all an academic problem. We live in the time of data bases and electronically handled information. Let us consider an engineer or astrophysicist interested in composition of a gas-phase chemical reaction mixture. The scholar, most probably, takes the standard enthalpies and entropies of the relevant species from a data base, being hardly interested what are the related point-groups of symmetry. Then, instead of a proper equilibrium constant, a value differing from it by a factor of 2 may be taken into consideration. It may have considerable effects on the computed equilibrium concentrations.

It is well known that the standard thermodynamic terms without a standard-state specification lack meaning (though, for an ideal gas-phase species the standard state could be deduced backwards by a repetition of the computational treatment). Both JANAF Tables<sup>7a</sup> and Gaussian 90 (Ref. 8) contain a proper standard state specification, indeed (though they in fact deal with different choices, 1 bar and 1 atm, respectively). In this sense, however, the thermodynamic terms of a species, belonging to one of the  $C_n$ ,  $D_n$ ,  $T$ ,  $O$ , and  $I$  symmetries, also lack meaning if the kind of mixture under study is not specified. Although there may be an *ad hoc* explanation that the sources deal with pure substances, not mixtures, it does not really prevent the mentioned erroneous application in practice. Therefore, thermodynamic data bases should be completed with such kind of information. As an alternative, they could supply side-by-side data for both limiting situations.

A topical illustrative example may be served with fullerenes. Chirality has been recognized for some of the species and thermodynamic consequences treated for example for  $C_{20}$  and  $C_{50}$  (Ref. 19), or  $C_{78}$  (Ref. 20), through a concept of the chirality partition function.<sup>19</sup> Depending on kinetic factors, either one or both optical isomers can be formed in fullerene synthesis. A pertinent instructive example is supplied<sup>21-26</sup> by the  $C_{84}$  system. An NMR analysis<sup>21</sup> concluded that  $C_{84}$  had two major isomers of  $D_2$  and  $D_{2d}$  symmetry in a ratio of 2:1. Computations indeed found<sup>22-24</sup> two low-lying, nearly isoenergetic structures of the respective symmetries. In order to an agreement in the 2:1 concentration ratio is achieved between theory and experiment, the chirality of the  $D_2$  species is to be taken into account accordingly<sup>25,26</sup> otherwise computations would yield a value close to 1:1 (and quantum chemistry might be suspected of a failure). This finding should also suggest that thermodynamic equilibrium between both  $D_2$  enantiomers was indeed reached in the experiment.<sup>21</sup>

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## SAŽETAK

### Baze termodinamičkih podataka i optička izomerija

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Vrlo često se u bazama termodinamičkih podataka nalaze i podaci koji ne uzimaju u obzir optičku izomeriju. Upotreba takvih podataka uzrokuje nedovoljnu točnost kao što je pokazano na primjeru difluorosulfana. Također je utvrđeno da partijska funkcija kiralnosti znatno utječe na relativne stabilnosti izomera fullerena.