

A computational study of entropy rules for charged fullerenes

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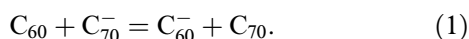
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Thermochemical data for fullerenes are relatively very rare, however, some thermochemical information can be derived from gas-phase experiments using the Knudsen cell mass spectrometry method. The third-law treatment can be carried out on the observed data, though one crucial presumption is needed, viz. that the change in the thermodynamic potential $\Delta\Phi_T^o$ in the course of the considered reactions is negligible: $\Delta\Phi_T^o = 0$. It would be difficult to check the presumption directly in experiment, but it can be done by computations. Model reactions are selected like $C_{60} + C_{70}^- = C_{60}^- + C_{70}$. The change in the thermodynamic potential $\Delta\Phi_T^o$ and the change in the standard entropy ΔS_T^o are computed. For example, at a temperature of $T = 1000$ K, the standard changes for the reaction evaluated by the SAM1 method are $\Delta\Phi_T^o = 1.513$ cal/(mol · K) and $\Delta S_T^o = -0.054$ cal/(mol · K). In overall, the computations support a reasonable applicability of the critical thermodynamic presumption.

The reported research has been supported by the National Science Council, Taiwan, Republic of China.

Charged fullerenes have frequently been computed, in particular charged C_{60} owing to interesting Jahn-Teller distortions [1–10]. In this paper, charged fullerenes are computed with a special attention to their gas-phase thermodynamic functions. Thermochemical data for fullerenes are still rare – only the heats of formation for C_{60} , C_{70} , and two C_{60} derivatives are available [11–17]. Some thermochemical information can however be derived from gas-phase experiments [18] using mass spectrometry. In the method, equilibrium constants for electron transfer reactions between fullerenes were measured [18] and the related standard Gibbs free-energy changes derived. A typical charging reaction under consideration is of the following type:



However, the second law treatment of the data could not produce [18] accurate enthalpy terms. The third law treatment represents another option:

$$\Delta H_0^o = T\Delta\Phi_T^o - RT \ln K_p. \quad (2)$$

In Eq. (2), K_p denotes the measured equilibrium constant for electron transfer reactions of the type described by Eq. (1) and $\Delta\Phi_T^o$ refers to the change in the standard thermodynamic potential (also known as the Giauque function):

$$\Phi_T^o = -\frac{G_T^o - H_0^o}{T}. \quad (3)$$

A key presumption for the thermodynamic potentials has been introduced [18]

$$\Delta\Phi_T^o \approx 0. \quad (4)$$

Then, the standard enthalpy changes ΔH_0^o and electron affinities for higher fullerenes can be derived [18]. In this paper, presumption (4) and the related entropy conjecture

$$\Delta S_T^o \approx 0 \quad (5)$$

are studied for fullerene electron-exchange reactions (1).

1. Computations

The computations reported here have been performed with the SAM1 (Semi-Ab-Initio Model 1) semiempirical quantum-chemical method [19], in particular with its implementation in the AMPAC package [20]. The complete geometry optimizations are based on the analytical energy gradient in Cartesian coordinates. The harmonic vibrational analysis is carried out with the numerical second derivatives of energy. No scaling of the computed harmonic vibrational frequencies is however applied as such scaling factors are not yet known for fullerenes. While the computations for closed shell species are relatively straightforward, open shell systems are numerically quite difficult. The results reported in this paper are based on unrestricted Hartree-Fock treatment of open shell systems. Special attention has been paid to evaluation [21] of the symmetries of the relaxed structures. From the computed rotational, vibrational, and symmetry parameters, the rigid rotor and harmonic oscillator partition functions are constructed and the thermodynamic functions of interest are derived.

2. Results and discussion

Charging high-symmetry fullerenes can frequently impose Jahn-Teller effects. A change in the point group of symmetry can change the symmetry number σ . Chirality is another issue pertinent to fullerene cages [22,23], though only the C_n , D_n , T , O , and I groups allow for chirality. For an enantiomeric pair its partition function has to be doubled. It can formally be done by means of the chirality partition function or chirality factor χ (assuming just two possible values, 1 or 2). Hence, in

Table 1. SAM1 computed thermodynamic data for charged C₆₀ and C₇₀

Precies	S_{1000}^o , cal/(mol · K)	$\Delta H_{f,298}^o$, kcal/mol	Point group of symmetry	$\frac{\sigma}{\chi}$	$H_{1000}^o - H_0^o$, cal/mol
C ₆₀ ⁰	382.37	775.26	<i>I_h</i>	60	173 386
C ₆₀ ¹⁻	404.19	694.77	<i>C₂</i>	1	178 240
C ₆₀ ¹⁺	402.06	934.14	<i>C₂</i>	1	177 974
C ₆₀ ²⁻	392.14	744.16	<i>D_{5d}</i>	10	175 079
C ₆₀ ²⁺	390.25	1220.77	<i>D_{5d}</i>	10	174 908
C ₇₀ ⁰	442.90	829.65	<i>D_{5h}</i>	10	203 024
C ₇₀ ¹⁻	464.78	721.33	<i>C_s</i>	1	209 445
C ₇₀ ¹⁺	462.30	960.45	<i>C_s</i>	1	208 478
C ₇₀ ²⁻	451.14	774.07	<i>C_{2v}</i>	2	204 536
C ₇₀ ²⁺	447.55	1242.50	<i>C_{2v}</i>	2	203 621

Gas phase species throughout; the standard state — ideal gas phase at 1 atm = 101 325 Pa pressure. S_{1000}^o — the standard entropy at $T = 1000$ K; $\Delta H_{f,298}^o$ — the heat of formation at room temperature; σ/χ — ratio of the symmetry number σ and chirality factor χ ; $H_{1000}^o - H_0^o$ — the change in the standard enthalpy between 1000 and 0 K.

Table 2. SAM1 standard thermodynamic-potential and entropy changes

Process	$\Delta \Phi_{1000}^o$, cal/(mol · K)	ΔS_{1000}^o , cal/mol · K
C ₆₀ ⁰ + C ₇₀ ¹⁻ = C ₆₀ ¹⁻ + C ₇₀ ⁰	1.513	-0.054
C ₆₀ ⁰ + C ₇₀ ¹⁺ = C ₆₀ ¹⁺ + C ₇₀ ⁰	1.152	0.286
C ₆₀ ⁰ + C ₇₀ ²⁻ = C ₆₀ ²⁻ + C ₇₀ ⁰	1.348	1.530
C ₆₀ ⁰ + C ₇₀ ²⁺ = C ₆₀ ²⁺ + C ₇₀ ⁰	2.308	3.232

Gas-phase species throughout.

evaluations of thermodynamic terms the ratio

$$\frac{\sigma}{\chi} \quad (6)$$

is important. As seen in Table 1, this ratio can change dramatically upon charging.

Quotient (6) reflects only a part of the changes induced by charging. There are other changes in structural and vibrational patterns and in rotational-vibrational partition functions. Only after taking all the changes into account, one can evaluate the changes in thermodynamic functions upon charging.

Table 1 presents a survey of the SAM1 computed data for neutral and charged fullerene cages under consideration. The presented heats of formation are not directly important for our purpose. In fact, the $\Delta H_{f,298}^o$ terms computed by SAM1 are overestimated compared to the observed values [11–15]. The standard entropy S_T^o and heat-content function $H_T^o - H_0^o$ are computed for a representative [18] temperature of 1000 K.

The standard reaction changes of the thermodynamic potential and entropy are given in Table 2. The presented values are quite close to zero. Hence, the SAM1 results in Table 2 indeed support the conjectures formulated by Eqs. (4) and (5). In particular, if we write the entropy

conjecture for reaction from Eq. (1), we get

$$S_T^o(C_{60}^-) - S_T^o(C_{60}) \approx S_T^o(C_{70}^-) - S_T^o(C_{70}), \quad (7)$$

which in other words says that adding one electron to the C₆₀ or C₇₀ cage brings about the same entropy change. Given the number of various factors involved, the results formulated by Eqs. (4), (5) or (7) are rather surprising. The results also suggest that possible inaccuracy introduced by the presumption into the terms derived from observed data is comparable with the primary experimental errors [18] themselves.

The authors thank the National Center for High-Performance Computing in Hsinchu, Taiwan, Republic of China, for computer time.

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