

Computing the relative gas-phase populations of C₆₀ and C₇₀: Beyond the traditional $\Delta H_{f,298}^\circ$ scale

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Computations and experiments have shown that the relative heat of formation (i.e., the heat of formation per carbon atom) of C₇₀ is lower than of C₆₀. Moreover, various computations suggest that this is actually a general trend among fullerene cages. The relationship is particularly important for gas-phase fullerenes. Experiments have shown that C₆₀ is typically more populated than C₇₀ when produced in high-temperature gas-phase synthesis. It is not immediately obvious how to reconcile those two terms, or whether the relative heats of formation and the relative populations are in conflict or in agreement. This article deals with this problem, treating it as a general task of relative stabilities of gas-phase clusters of different dimensions (i.e., nonisomeric clusters) under different types of thermodynamic equilibria. The results are then applied to C₆₀ and C₇₀ and point out that the conventional standard pressure of 1 atm is considerably different from actual fullerene-synthesis conditions. Apparently, we should expect considerably lower cluster pressures in carbon-arc synthesis. At 1 atm, C₇₀ is more populated than C₆₀, but at the conditions of a saturated carbon vapor the stability order is reversed in favor of C₆₀ so that an agreement with experiment is obtained already within the thermodynamic treatment. The pressure effects are modeled using the MNDO, AM1, PM3, and SAM1 quantum-chemical semi-empirical methods as well as the

available experimental data. The computations consistently show that, if the pressure effects are considered, C₆₀ becomes more populated than C₇₀. Relationships of the thermodynamic treatment to more sophisticated but impractical kinetic analysis are also discussed. © 2001 by Elsevier Science Inc.

Keywords: relative populations of fullerenes, relative heats of formation, stability measures, Gibbs function, semiempirical methods

INTRODUCTION

It has been well known^{1,2} from the very early days of fullerene science that C₆₀ is formed in higher concentrations than C₇₀, although the ratio strongly depends on production conditions. For example, C₆₀ was much more prominent² when the time for the clustering process was increased. As soon as the electric-arc synthetic technique was discovered,³ the strong dependency of fullerene yield on helium gas pressure had been established. Moreover, the C₇₀/C₆₀ ratio varies⁴ in a relatively wide interval in graphite vaporization methods (0.02–0.18), and also in combustion methods where the ratio can in fact be even reversed (0.26–5.7). Apparently, we are dealing with an especially complex thermodynamic and kinetic scheme. On the other hand, computations in fullerene science^{5–8} primarily deal with thermodynamic stabilities rather than with kinetics, usually just at the level of heats of formation at room temperature.

We have been computing^{9,10} equilibrium compositions of isomeric fullerene mixtures and our computations have agreed with available experiments. The computations are carried out¹¹

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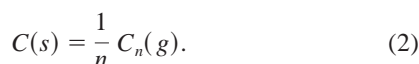
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entirely within an equilibrium thermodynamic scheme. The agreement between computations and observations can suggest that the supposed¹¹ interisomeric thermodynamic equilibrium does exist in experiments. There may also be other interpretations, such as that although the interisomeric equilibrium is not yet reached, the relative nonequilibrium and equilibrium isomeric concentrations do not differ significantly. The computational treatment of isomeric mixtures has several interesting features. The results depend on temperature but not on pressure; only the relative and not the absolute values of the heats of formation are needed; the form of the master equation allows for ample cancellation of terms in the partition functions (in particular, the cluster mass is canceled out exactly, or the vibrational-frequency scaling factors are cancelled out almost exactly.¹²) This success of thermodynamic-equilibrium approach for fullerene isomers has suggested a similar treatment of nonisomeric fullerenes.

Traditionally, heats of formation at room temperature $\Delta H_{f,298}^\circ$ have been the key quantity for stability reasoning. For gas-phase carbon clusters it is defined by the following formal chemical reaction:



However, it has been common to consider the standard reaction enthalpy change for a normalized process with a unified left side:



The enthalpy change for reaction 2 (Equation 2) is obviously equal to $\frac{1}{n} \Delta H_{f,298}^\circ$ (i.e., heat of formation per carbon atom) and allows for a straightforward comparison between clusters of different dimensions. It is true that ab initio methods produce¹³ the total energy; however, it can be converted to the heats of formation or related to some common reference standard (although the basis set superposition error can be a factor.¹⁴) The reduced term $\frac{1}{n} \Delta H_{f,298}^\circ$ was computed^{15,16} for small carbon clusters already at the MINDO/2 level (Figure 1), one of the very first methods that could produce reasonable heats of formation. The MINDO/2 computations of one-, two-, and three-dimensional small carbon clusters C_n pointed out^{15,16} a simple, smooth dependency of the relative heats of formation $\Delta H_{f,298}^\circ/n$ on the number of carbons n . Of course, at that time virtually nothing was known beyond n of about 8, the computational upper limit of semi-empirical quantum chemistry of those days. After two decades and after fullerene synthesis,³ the curve was extended into the fullerene domain, for example, with the MNDO method^{17,18} and ab initio HF/STO-3G computations^{19,20} (Figure 2) or with simple semi-empirical tight-binding computations.²¹ The qualitative picture is always the same. Although a shallow minimum could possibly be seen in some of the curves for C_{60} , basically, they are still smooth decreasing dependencies. Hence, it has been difficult to see the very special stability of C_{60} , or to readily demonstrate the known higher populations of C_{60} over C_{70} from such smoothly decreasing curves. As an alternative, one could consider HOMO–LUMO gaps. Figure 3 shows the MNDO computed HOMO–LUMO gaps^{17,18} for selected fullerenes. There is a better

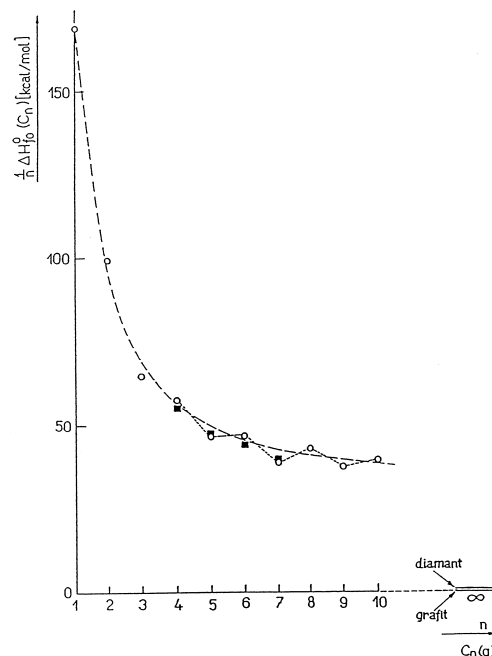


Figure 1. The MINDO/2 computed^{15,16} heats of formation per atom at room temperature for a few first gas-phase carbon clusters (linear, cyclic, polyhedral; the words grafit and diamant denote graphite and diamond, respectively).

relationship to the observed reality; however, the differences are not particularly pronounced.

The previous paragraph actually indicates a need for a more general but still feasible evaluation of the relative stabilities of fullerenes of different dimensions, i.e., nonisomeric fullerenes. In its most general form, the problem could be treated as a complex kinetic scheme described by a huge number of kinetic differential equations. The scheme can be solved if the values of the rate constants for all reaction channels are known. The equilibrium composition comes as the limiting case of infinite time. If we treat the problem from a thermodynamic point of view, we should realize that the conventional standard pressure of 1 atm is considerably different from actual fullerene-synthesis conditions. Here, we do not refer to helium gas pressure, but to carbon vapor pressure. Apparently, we should expect lower cluster pressures in the carbon-arc synthesis than the conventional 1 atm. The gas-phase reaction entropy and Gibbs free energy change considerably with pressure, as can be demonstrated for the $C_{60}(g)$ and $C_{70}(g)$ cases based on quantum-chemical calculations.²² For example, the equilibrium constant $K_{60/70}$ for an interconversion between the two clusters, expressed in their partial pressures p_i , indeed indicates²² a pressure dependency of the composition:

$$K_{60/70} = \frac{p_{70}^{6/7}}{p_{60}} = \frac{(1 - x_{60})^{6/7}}{x_{60}} P^{-1/7}, \quad (3)$$

where P stands for the total pressure of the two clusters and x_{60} is the mole fraction of buckminsterfullerene.

This type of problem was studied²² in the 1980s, although exclusively based on the AM1 method (and even before application to carbon clusters, the treatment was originally applied to steam).^{23–25} However, experimental heats of formation

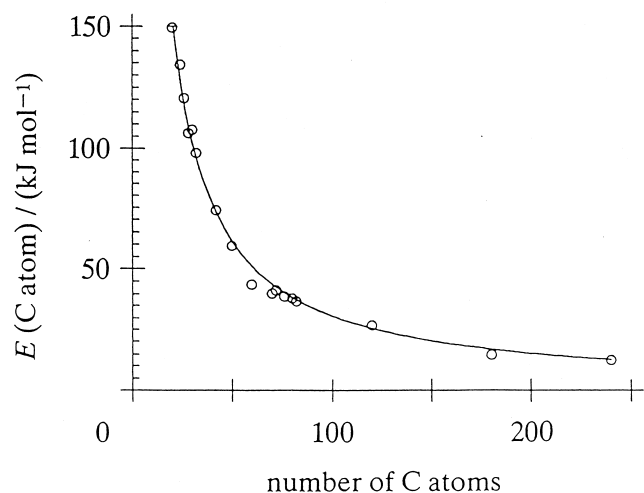
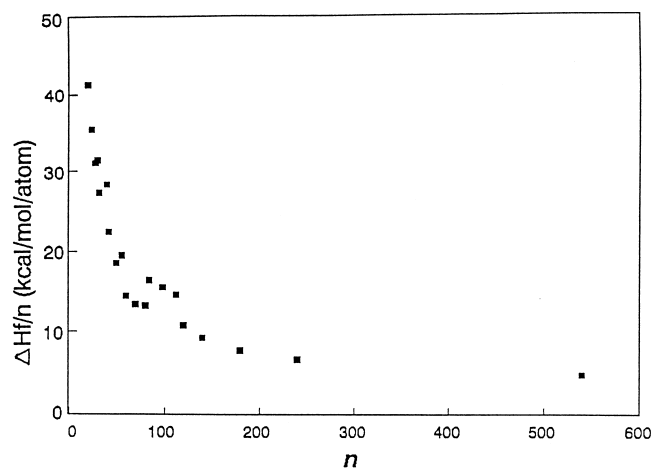


Figure 2. The MNDO heats of formation per atom^{17,18} (top) and ab initio HF/STO-3G relative energies^{19,20} (bottom) for selected fullerenes.

show^{26–32} now that the AM1 method was²² actually the worst choice as it gives the most overestimated values for fullerenes.

The general qualitative picture^{22,33–37} is as follows. At 1 atm pressure, C₇₀ is more populated than C₆₀, but at the conditions of a saturated carbon vapor (presently simulated simply as a mixture of seven clusters) the stability order is reversed in favor of C₆₀, which agrees with experimental results. In other words, we are evaluating the species considering their Gibbs functions, and pressure effects, in particular. This article examines the pressure effects using the AM1 method as well as the MNDO, PM3, and SAM1 methods and the available experimental data and is a part of the effort toward a general pressure-dependent stability scheme for all higher fullerenes.

FORMULAE AND COMPUTATIONS

The quantum-chemical calculations used in this contribution are of MNDO, AM1, PM3, and SAM1 quality, i.e., the four semi-empirical methods most frequently applied at present.^{38–44} Geometry optimization was performed with the MOPAC and AMPAC program packages.^{45,46} The entropy data were derived from the AM1 computations.²² The heats of

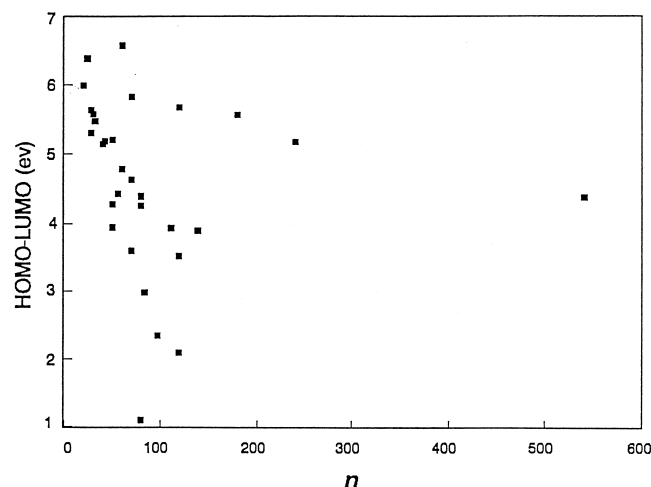


Figure 3. The MNDO computed HOMO–LUMO gaps^{17,18} for selected fullerenes.

formation could also be derived by ab initio methods after some adjustments. One technique^{47,48} employs a theoretical equivalent of the heat of formation as energy for conversion from a planar “idealized” graphitic sheet to the fullerene. This requires an optimization of different sizes of monolayer graphite and extrapolation of the (cohesion) energy term per atom toward graphite. Another approach^{26,49} deals with an additional fitted parameter for carbon atoms. The description of thermochemistry of fullerenes from ab initio methods is still under development.⁵⁰

Let us now consider all the clusters C_n, i.e., all the values for *n*, and for each *n* value all the possible isomers. At present we have been considering^{34–37} just seven clusters: *n* = 1, 2, 3, 4, 5, 60, and 70. Clearly enough, expansion to any larger set of clusters is just a technical, not a conceptual problem. Let us suppose that the thermodynamic equilibrium between the carbon gas phase and graphite is established, i.e., the partial chemical equilibria introduced by reaction 1 (Equation 1) indeed satisfy the related equilibrium constants:

$$K_{p,n} = p_n \quad (4)$$

where *p_n* denotes the partial pressure of C_n (it is actually expressed in atm; 1 atm = 101325 Pa). If all the partial equilibria (2) are established, we reach the state of the saturated carbon vapor with a unique total saturated pressure *p*^{*} (for a given temperature *T*). In our model truncated set of carbon aggregates it means:

$$p^* = p_1 + p_2 + p_3 + p_4 + p_5 + p_{60} + p_{70}. \quad (5)$$

There is also an alternative and more general formulation of the problem. The alternative formulation is related to the gas-phase mono-atomic carbon cluster C₁(g), i.e., free carbon atom:

$$nC(g) = C_n(g) \quad (6)$$

and is described by another set of equilibrium constants, *K*_{*p,n*}[′]:

$$K'_{p,n} = \frac{p_n}{p_1^n}. \quad (7)$$

The equilibrium constants $K'_{p,n}$ are related to the starting equilibrium constants $K_{p,n}$ by:

$$K'_{p,n} = \frac{K_{p,n}}{K_{p,1}^n}. \quad (8)$$

Now, we can consider any total pressure p , not just the saturated p^* but also any undersaturated or supersaturated pressure. However, it remains true that:

$$p = p_1 + p_2 + p_3 + p_4 + p_5 + p_{60} + p_{70}. \quad (9)$$

To simplify the scheme, we can introduce an auxiliary variable x_1 with a meaning of the mole fraction of the mono-atomic cluster $C_n(g)$. This substitution converts Equation 9 into the following algebraic equation of the 70th order:

$$1 = x_1 + \sum_{i=2}^{70} K'_{p,i} x_1^i p^{i-1}, \quad (i = 2 - 5, 60, 70). \quad (10)$$

We can solve^{34–37} Equation 10 for a selected temperature T and pressure p numerically with any required precision. Once the term x_1 is known, other mole fractions are simply given:

$$x_n = K'_{p,n} x_1^n p^{n-1}. \quad (11)$$

The equilibrium constant $K'_{p,n}$ is derived here from quantum-chemical and statistical mechanical calculations, the constant $K_{p,1}$ has been derived from experiment.⁵¹

RESULTS AND DISCUSSION

Table 1 surveys the computed and observed^{29,32} heats of formation at room temperature for $C_{60}(g)$ and $C_{70}(g)$. All the computed values are overestimated compared with the observed terms. Even the results of the best method, SAM1 are rather high. All the values from Table 1 have been used in the computations of the $C_{60}(g)$ and $C_{70}(g)$ relative populations.

Table 2 presents results for the saturated carbon vapor. At such very low pressures the scheme always gives the correct order of the relative populations of C_{60} and C_{70} . We do not know the real carbon vapor pressure in the electric-arc chamber. The carbon-vapor pressure itself is never measured—it is always covered by helium gas pressure. We do not know if there is a uniform carbon-vapor pressure in the chamber. As there is a big temperature gradient in the apparatus for fullerene synthesis, one can expect strong mechanical flows of the hot gases. However, it seems likely that for lower temperatures we shall actually deal with supersaturated carbon vapor.

Table 1. Survey of the $C_{60}(g)$ and $C_{70}(g)$ heats of formation at room temperature (kcal/mol) from selected sources

Source	$C_{60}(g)$	$C_{70}(g)$
AM1	973.3	1071.9
MNDO	869.3	945.0
PM3	811.7	884.2
SAM1	775.3	829.7
Observed ^a	599.2	627.7

^a Adjusted³² experimental values.²⁹

Table 2. Computed populations of $C_{60}(g)$ and $C_{70}(g)$ (mole fractions in %) in the model saturated carbon vapor for two selected temperatures

Source of $\Delta H_{f,298}^\circ$	$C_{60}(g)$	$C_{70}(g)$
$T = 2000 \text{ K}$		
AM1	0.208×10^{-91}	0.189×10^{-102}
MNDO	0.490×10^{-80}	0.138×10^{-88}
PM3	0.956×10^{-74}	0.613×10^{-82}
SAM1	0.916×10^{-70}	0.560×10^{-76}
Observed	0.159×10^{-50}	0.654×10^{-54}
$T = 5000 \text{ K}$		
AM1	0.294×10^{-43}	0.254×10^{-48}
MNDO	0.104×10^{-38}	0.891×10^{-43}
PM3	0.341×10^{-36}	0.406×10^{-40}
SAM1	0.134×10^{-34}	0.984×10^{-38}
Observed	0.663×10^{-27}	0.661×10^{-29}

We can model such supersaturated carbon vapor through a choice of the general total pressure p (different than the saturated pressure p^* in Equation 9). If we increase the pressure to very high, unrealistic values we can reverse^{34–37} the C_{60}/C_{70} relative stability order. For example, at 2000 K and 1 atm pressure, C_{70} represents³⁴ almost 100% of the model seven-membered carbon vapor. Clearly enough, at a given temperature, we can compute a particular pressure that produces a required C_{60}/C_{70} ratio. We know only this relative ratio from experiment but not some absolute concentrations in the gas phase. The computed³⁴ partial pressures of C_{60} and C_{70} under the saturation regime are considerably low. They can be enhanced by increased pressure (into the supersaturated region).

There may also be some preferential condensation on the walls based on relatively high sublimation temperatures that could actually enhance the fullerene fraction in the solid material. The condensation/sublimation processes are still to be implemented into our thermodynamic scheme. Only after this additional step should one move toward construction of a general kinetic scheme of fullerene formation. The kinetic scheme, if supplied with reliable computed rate constants, should be able to reproduce known observed facts. Moreover, it has to have the thermodynamic scheme as its own limit for infinite time.

The thermodynamic scheme is quite sensitive to the input heats of formation. Thus, before the scheme itself is applied in a large scale to other higher fullerenes, we have to be able to produce accurate values of the total heats of formation (i.e., not only the relative energetics such as for the isomeric problem). Hence, some scaling of the directly computed values is to be designed. Moreover, we have to be able to select rationally some representative values of temperatures and pressures for fullerene synthesis.

In conclusion, let us return once again to the computed smooth dependencies for $\frac{1}{n} \Delta H_{f,298}^\circ$ in Figure 2. In fact, there is a simple way to predict these dependencies without actually

computing them. Let us limit our reasoning to the isolated pentagon rule (IPR) fullerenes.⁵² Qualitatively speaking, we deal with two types of bonds, frequently called 5/6 bonds (between pentagons and hexagons) and 6/6 bonds (shared by two hexagons). Let us suppose that those two types of bonds can be represented³² by some uniform dissociation energies, $H_{5/6}$ and $H_{6/6}$. In a general IPR fullerene C_n we always have sixty 5/6 bonds, while the number of the 6/6 bonds is variable, $\frac{3n}{2} - 60$. Now, we can readily write for the atomization heat of the considered C_n :

$$\Delta H_{at} = 60 \times H_{5/6} + \left(\frac{3n}{2} - 60 \right) \times H_{6/6}. \quad (12)$$

The atomization and formation heats for carbon aggregates are linked by the heat of vaporization of carbon, ΔH_{vap}^o :

$$\frac{\Delta H_f^o}{n} = - \frac{\Delta H_{at}}{n} + \Delta H_{vap}^o \quad (13)$$

or simply in terms of the bond energies:

$$\frac{\Delta H_f^o}{n} = - \frac{3}{2} H_{6/6} + \Delta H_{vap}^o + \frac{60}{n} \times (H_{6/6} - H_{5/6}). \quad (14)$$

This functional dependency can formally be expressed by:

$$\frac{\Delta H_f^o}{n} = A + \frac{B}{n}, \quad (15)$$

where B is a positive constant and A is a relatively small number. Hence, Equation 15 is indeed a smoothly decreasing curve of the type shown in Figure 2. The shape could have been predicted even before any computations. However, it could have been counterproductive as an indication that there had been nothing special before the diamond/graphite stability domain. One has to interpret the outcome from a modelling in just the right way.^{53–55}

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