

C₆₀(g), C₇₀(g), SATURATED CARBON VAPOUR AND INCREASE OF CLUSTER POPULATIONS WITH TEMPERATURE: A COMBINED AM1 QUANTUM-CHEMICAL AND STATISTICAL-MECHANICAL STUDY

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Saturated vapour above graphite and the content of C_n(g) aggregates therein have been studied at various temperatures. The equilibrium constants of C(g) into C_n(g) association have been obtained for: (i) $n = 1-5$ from the available tabulated thermodynamical data, (ii) C₆₀ and C₇₀ from a quantum-chemical description in terms of the AM1 method as a source of molecular parameters for the construction of partition functions, and (iii) the other aggregates by linear inter- or extrapolation of the data sub (i) and (ii). The content of clusters with $n \geq 2$ in the saturated vapour has been shown to increase steeply with temperature. This increase is due to small clusters ($n \approx 2-5$), whereas the recently proved particular structures C₆₀ and C₇₀ are — according to these calculations — negligibly populated in the saturated vapour at all temperatures studied. At the conditions of saturated vapour the population of C₆₀ always exceeds that of C₇₀ by several orders of magnitude. The relations of these calculations to the recent observations of distinct populations of C₆₀ and C₇₀ are discussed.

In the last years the interest has been rapidly increasing — both experimental and theoretical — in gas-phase atomic and molecular clusters, the bond types in these aggregates ranging from very weak van der Waals complexes up to the common chemical bond. The theoretical treatments gradually change from a mere description in the terms of structure and energy to a more complete description in the terms of thermodynamic functions, which enables evaluation of the cluster populations, too. Water clusters, (H₂O)_n(g), were treated in this way recently, and a paradoxical temperature increase of the cluster populations at the conditions of saturated vapour was pointed out¹⁻³.

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One interesting group among these clusters is formed by the class of structures exclusively composed of one type of atoms, *e.g.* Li_n (*e.g.*^{4,5}), C_n (*e.g.*^{6,7}), S_n (*e.g.*^{8,9}), and others (*e.g.*¹⁰⁻¹²). Out of this class the C_n aggregate system has attracted attention quite recently. Although these formations have already been studied earlier^{6,7,13-22}, a quite new impulse was given by Kroto *et al.*²³ who found two distinct peaks in the mass spectrum of the vapours produced by a laser evaporation of graphite. The more intensive of the two peaks was found at $n = 60$ and the other at $n = 70$. This finding initiated a chain of experimental²⁴⁻²⁸ and theoretical studies²⁹⁻³⁹.

The above-mentioned results indicated — in connection with the interpretation of the observation²³ — a necessity of a theoretical evaluation of thermodynamics of formation of the C_{60} and C_{70} aggregates in the context of evaluation of their

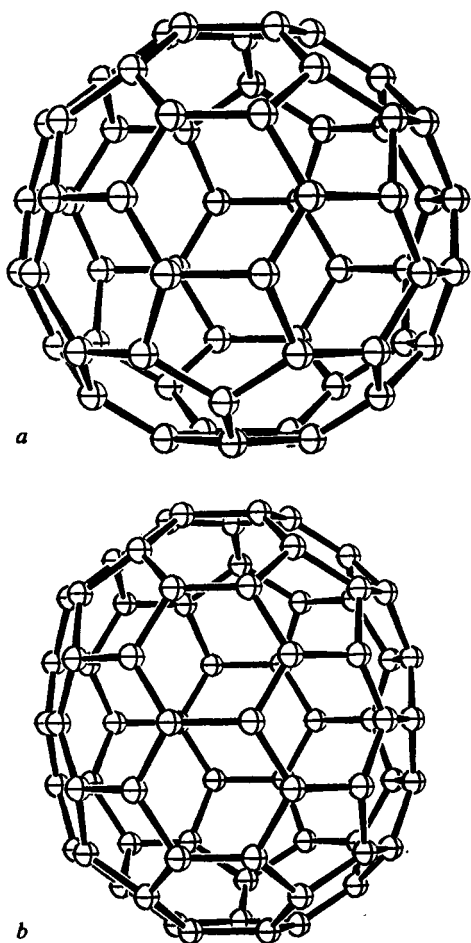


FIG. 1

The structure schemes *a* of the C_{60} aggregates with the point group of symmetry I_h and *b* of the C_{70} aggregates with the point group of symmetry D_{5h} (at the bottom) found³⁸ in the terms of the quantum-chemical AM1 method

populations in the equilibrium carbon vapour above graphite. With respect to the previous favourable results⁴⁰ of application of semi-empirical quantum-chemical methods, the AM1 method⁴¹ representing a new parametrization of the MNDO method has been chosen for this purpose.

CALCULATIONS

The AM1 optimizations of geometry parameters of the C₆₀ and C₇₀ aggregates led³⁸ to local energy minima with the *I_h* and *D_{5h}* symmetries (Fig. 1). Table I presents a survey of basic energy and vibration characteristics (wavenumbers of harmonic normal vibrational modes) of these systems in the terms of the AM1 method. These characteristics were used for a construction of the equilibrium constants of the reactions:



for $n = 60$ and 70 within the approximation of the partition functions of rigid rotor and harmonic oscillator⁴⁰. The thermodynamic functions of the C(*g*) monomers were taken from tabulated data¹⁷. These data¹⁷, based on experimental information, include also those for $n = 2-5$. In all, it is thus possible to describe the thermodynamics of the reactions (A) for six cases and, hence, treat the carbon vapour as a mixture of seven clusters ($n = 1-5, 60, \text{ and } 70$) – for a survey, see Table II.

For the equilibrium constants of reactions (A) in the terms of partial pressures:

$$K'_{p,n} = p_n/p_1^n, \quad (I)$$

TABLE I

The basic AM1 information about energetics and harmonic vibrations of the C₆₀(*g*) and C₇₀(*g*) aggregates

Species	The point group of symmetry	$\Delta H_{f,0}^\circ$ ^a	$\Delta H_{f,298}^\circ$ ^b	Histogram of the vibration frequencies ^c																	
				2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	
C ₆₀ (<i>g</i>)	<i>I_h</i>	4.0870	4.0725	5	7	10	12	11	16	16	15	1	4	7	13	24	3	9	16	5	
C ₇₀ (<i>g</i>)	<i>D_{5h}</i>	4.5009	4.4848	5	10	12	17	11	16	21	15	1	7	6	16	20	13	9	15	10	

^a The heat of formation at 0 K in MJ/mol; ^b the heat of formation at room temperature in MJ/mol; ^c the interval of vibration wavenumbers is divided into subintervals of 100 cm⁻¹, and numbers of vibrational frequencies in the individual intervals are given. The code *z* denotes the following interval of frequencies in cm⁻¹: 100*z* ≤ ω < 100(*z* + 1).

it can be seen (Fig. 2) that their decadic logarithm exhibits a good linear correlation with the n index:

$$\log K'_{p,n} = \log K'_{p,2} + (n - 2) \delta, \quad (n > 2). \quad (2)$$

TABLE II

The equilibrium constants^a $K'_{p,n}$ of the associations of $C(g)$ to $C_n(g)$ at selected temperatures and the centered linear increment δ of the change of $\log K'_{p,n}$ for n changing by one

T K	log $K'_{p,n}$						δ
	$n = 2$	3	4	5	60	70	
500	55.765	125.88	176.10	242.33	3 582.6	4 206.6	60.945
1 000	24.757	56.198	76.994	106.22	1 544.6	1 815.2	26.278
2 000	9.159	21.044	27.330	38.062	524.76	618.48	8.932
3 000	3.928	9.213	10.772	15.364	185.94	220.93	3.170
4 000	1.302	3.248	2.490	4.024	17.162	22.911	0.300
5 000	-0.279	-0.362	-2.488	-2.782	-83.799	-95.542	-1.416

^a $K'_{p,n} = p_n/p_1^n$ belongs to the reaction $n C(g) \rightleftharpoons C_n(g)$; the standard state is represented by the ideal gas at 1 atm = 101 325 Pa; when using the convention of the dimensioned equilibrium constants, the dimension of $K'_{p,n}$ is $[\text{atm}^{-(n-1)}]$.

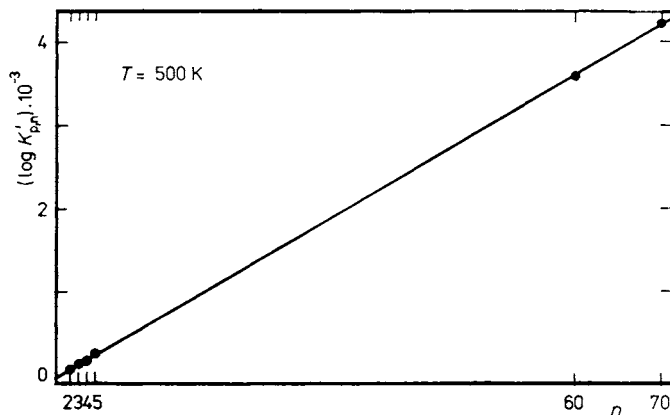


FIG. 2

An example of the linear correlation between the decadic logarithm of the association equilibrium constant ($n C(g) \rightleftharpoons C_n(g)$), $\log K'_{p,n}$, and the value of the carbon content n at the temperature $T = 500$ K

This enables an evaluation of the equilibrium constants $K'_{p,n}$ also for those values of the n index which lie outside the basic seven-membered set. Table II gives a survey of the values of the δ increment at various temperatures.

If the equilibrium carbon vapour above graphite is considered, it is useful to adopt the equilibrium constants $K_{p,n}$ of the reactions (B) described by Eq. (3) (the reliable values of $K_{p,1} = p_1$ being available in ref.¹⁷):



$$K_{p,n} = K'_{p,n} K_{p,1}^n \quad (3)$$

In the equilibrium above graphite the partial pressures p_n fulfil the condition:

$$p^* = \sum_n p_n, \quad (4)$$

where p^* means the pressure of the saturated vapour. In our context two models were considered: (i) A seven-membered model of carbon vapours for $n = 1-5, 60$, and 70 (based on the AM1 and tabulated¹⁷ data), and (ii) a model without limitation of magnitude of the clusters based on the linear correlation (2) of the data sub (i).

Although the (ii) model is less useful for the $\text{C}_{60}/\text{C}_{70}$ problem itself (because it wipes off the specificity of these two aggregates), it enables inclusion of all the clusters, which is substantial in our context. Due to the condition (2), the cluster populations ($n > 2$) in the (ii) model form a geometric series, which makes it possible (somewhat surprisingly) to express the pressure p^* in the closed form:

$$p^*(\infty) = p_1 + p_1^2 K'_{p,2} / (1 - p_1 10^\delta). \quad (5)$$

Finally, the composition of equilibrium vapour above graphite is advantageously expressed in the terms of molar fractions x_n :

$$x_n = p_n / p^*. \quad (6)$$

DISCUSSION AND CONCLUSIONS

Table III presents a survey of the populations of the clusters in the terms of molar fractions in saturated carbon vapour at various temperatures for the two models considered (i, ii). In analogy to the recently reported results about the water vapour¹⁻³, the saturated carbon vapours also show a distinct increase of the clusters with $n \geq 2$ with increasing temperature. This paradoxical result, however, does not contradict the temperature decrease in the equilibrium constants $K'_{p,n}$ but represents a consequence of a competition between this decrease in the association equilibrium con-

TABLE III

The molar fractions of the $C_n(g)$ aggregates in equilibrium ideal gas mixture above graphite which were obtained within the seven-cluster model (7) and the model with unlimited cluster magnitude (∞)

T, K	Model	$P^*{}^a$ atm	$x_n, \%$							x_{ass} %
			n = 1	2	3	4	5	60	70	
500	7	$2.11 \cdot 10^{-67}$	100.0	$1.23 \cdot 10^{-9}$	$3.41 \cdot 10^{-6}$	$1.19 \cdot 10^{-22}$	$4.26 \cdot 10^{-23}$	$5.56 \cdot 10^{-350}$	$1.11 \cdot 10^{-392}$	$3.41 \cdot 10^{-6}$
	∞	$2.11 \cdot 10^{-67}$	100.0	$1.23 \cdot 10^{-9}$	$2.29 \cdot 10^{-15}$	$4.27 \cdot 10^{-21}$	$7.95 \cdot 10^{-27}$	$5.76 \cdot 10^{-342}$	$2.90 \cdot 10^{-399}$	$1.23 \cdot 10^{-9}$
1 000	7	$6.35 \cdot 10^{-30}$	99.4	$3.58 \cdot 10^{-3}$	$6.24 \cdot 10^{-1}$	$2.46 \cdot 10^{-9}$	$2.61 \cdot 10^{-9}$	$6.42 \cdot 10^{-177}$	$2.33 \cdot 10^{-198}$	$6.28 \cdot 10^{-1}$
	∞	$6.31 \cdot 10^{-30}$	100.0	$3.61 \cdot 10^{-3}$	$4.32 \cdot 10^{-6}$	$5.17 \cdot 10^{-9}$	$6.20 \cdot 10^{-12}$	$1.27 \cdot 10^{-172}$	$7.75 \cdot 10^{-202}$	$3.61 \cdot 10^{-3}$
2 000	7	$7.63 \cdot 10^{-11}$	43.8	2.11	54.1	$3.49 \cdot 10^{-3}$	$6.30 \cdot 10^{-3}$	$2.08 \cdot 10^{-92}$	$1.89 \cdot 10^{-103}$	56.2
	∞	$3.51 \cdot 10^{-11}$	95.3	4.59	$1.31 \cdot 10^{-1}$	$3.75 \cdot 10^{-3}$	$1.07 \cdot 10^{-4}$	$1.28 \cdot 10^{-89}$	$4.65 \cdot 10^{-105}$	47.3
3 000	7	$3.43 \cdot 10^{-4}$	15.8	7.29	76.4	$1.50 \cdot 10^{-1}$	$3.19 \cdot 10^{-1}$	$3.16 \cdot 10^{-65}$	$7.03 \cdot 10^{-73}$	84.2
	∞	$8.15 \cdot 10^{-5}$	66.6	30.7	2.46	$1.98 \cdot 10^{-1}$	$1.59 \cdot 10^{-2}$	$9.42 \cdot 10^{-63}$	$1.06 \cdot 10^{-73}$	33.4
4 000	7	0.701	9.52	12.7	74.9	$8.72 \cdot 10^{-1}$	1.99	$5.71 \cdot 10^{-52}$	$5.57 \cdot 10^{-58}$	90.5
	∞	0.169	39.3	52.6	7.00	$9.31 \cdot 10^{-1}$	$1.24 \cdot 10^{-1}$	$8.34 \cdot 10^{-50}$	$1.46 \cdot 10^{-58}$	60.7
5 000	7	65.1	7.16	17.5	67.4	2.35	5.56	$2.94 \cdot 10^{-44}$	$2.54 \cdot 10^{-49}$	92.8
	∞	18.5	25.1	61.5	11.0	1.96	$3.50 \cdot 10^{-1}$	$2.41 \cdot 10^{-42}$	$7.90 \cdot 10^{-50}$	74.9

^a The pressure of saturated carbon vapour; 1 atm = 101 325 Pa, ^b the molar fraction of components of the carbon vapour in the associated form ($x_{\text{ass}}(T) = x_2 + x_3 + x_4 + x_5 + x_6 + x_7 + x_{\infty}$; $x_{\text{ass}}(\infty) = \sum_{n=2}^{\infty} x_n$).

stants and increase in the pressure of the saturated vapour with temperature. The temperature increase of the cluster populations in the saturated vapour is exhibited by both the models, although the values of model (ii) are systematically lower (cf. the term x_{ass} in Table III). This lowering is connected with the systematically lower value of the pressure p^* which is – in the model (ii) – due, *inter alia*, to the decrease of the value of term $K'_{p,3}$ as a consequence of the correlation (2). This result, which has been obtained only for the water and carbon vapours so far, could focus attention on the cluster observations in the region of relatively high temperatures and pressures which have not been used yet.

With regard to the particular aggregates C_{60} and C_{70} , both the models show that these aggregates form a negligible component in the saturated vapour, since the predominant components are the smallest aggregates. Nevertheless, at all the temperatures studied the C_{60} aggregate appears to be substantially more distinctly populated than the C_{70} aggregate.

The present study exclusively deals with the problems of thermodynamic equilibrium and stability and says nothing about the kinetic factors leading to this equilibrium. The already reported observations^{23,26} of non-reactivity of the two large aggregates in fact mean relatively very low values of the corresponding rate constants, hence equilibria are only established with difficulties, too. The same can be applied also to the inter-cluster equilibria and the equilibrium above graphite. The populations of these clusters once formed within a suitable reaction regime can be stabilized – in spite of the requirements of the thermodynamic equilibrium – at relatively high values due just to these kinetic factors (*i.e.*, a similar situation to that which can be quite currently encountered, *e.g.*, with optical isomers).

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