FULLERENE SYNTHESIS CONDITIONS AND MECHANISM

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Physical aspects are considered for synthesizing fullerenes from carbon vapor. A simple model is proposed for the formation of fullerenes from insular graphite nuclei, which enables one to describe the process in relation to the activation energies of the main stages. The synthesis area for regular fullerenes in the temperature-concentration plane is bounded by the carbon condensation isotherm, on which the rate of fullerene synthesis is equal to the range of capture of free atoms and the line on which the rate of the process becomes small. To avoid the fullerene being captured by graphite traps, the carbon vapor should be completely utilized in fullerene synthesis in this area.

A fairly extensive literature was accumulated on the structure and properties of shell carbon clusters (fullerenes) and the corresponding solid phase (fullerite). However, the synthesis conditions for the new material have been dealt with briefly only in the first descriptions of the physical experiments [1-3], and there are no technological papers. Here I discuss some major physical aspects that must be incorporated in technological developments.

Fullerene synthesis begins with the formation of insular nuclei of basal-plane graphite of monatomic thickness. When such a planar nucleus attains a sufficiently large size, it becomes unstable and begins to be transformed to a fullerene. The synthesis of fullerenes is improbable or in general impossible under the same conditions when ordinary graphite nuclei are formed (more than one atom thick).

This is confirmed by the following arguments. The literature mentions several possible synthesis mechanisms:

1) in the first state, small fragments of the graphite basal plane are formed, which then merge, and if the shapes and orientations of the colliding fragments are favorable, the defects heal gradually during thermally activated sintering;

2) in the first stage, the fragments include a large number of $C_{30}$ clusters, which collide in pairs in favorable orientations and join up into spherical shells more effectively than the arbitrary fragments in the first mechanism; and

3) in the first stage, numerous $C_{20}$ fragments are synthesized amongst others. These fragments have a special shape and are joined together in such a way that their centers form five-cornered cells, and they then trap individual carbon atoms and grow into closed shells.

The first two hypotheses are based on the realization of very rare events and can hardly explain why the condensation products under certain conditions contain over 10% fullerenes by mass. The third hypothesis is a particular case of the one proposed below.

At a low vapor concentration and sufficiently high temperature, the carbon atoms incident on an insular fragment will have time to diffuse over it and occupy the most favorable positions and enable the nucleus to maintain its monatomic thickness and approximate to circular shape. The carbon atoms in a circular island occupy two positions differing in energy: ones with the lower binding energy $E_1$ at the edge and ones with the higher energy $E_2$ within the island. Energy also favors shape change in the growing nucleus, in which the perimeter is reduced with unchanged area and some of the atoms pass from the edge to better positions within the island. Consequently, the nucleus will become curved and tend to acquire a segmented shape. On the other hand, the curvature is accompanied by the occurrence of five-cornered cells, and thus energy loss, which is the greater the more substantial the curvature. The conflict between these factors gives rise to a certain equilibrium curvature, and the further growth should terminate with the formation of a sphere having a certain radius.
Fullerene Synthesis is a Thermally Activated Process. We give a simplified description based on an extremely idealized mechanical model for a nucleus, which is justified by the qualitative character of the description and the clarity it provides.

We assume that the growing nucleus retains the form of a segment of a sphere with variable radius \( R \). The current value of the radius for the equivalent planar circular island is denoted by \( r \), and the current value of the radius at the base of the segment by \( a \). We assume that the distance between atoms at the edge of the island is \( b \), while within the island each atom has an area \( b^2 \). The island can bend in two directions, and its planar state corresponds to a minimum in the potential energy, which is considered as a function of the segment height. The bottom of the potential well is almost parabolic, so the binding energy is given approximately by

\[
E_1 = E_{10} (1 - mb^2/R^2), \quad E_2 = E_{20} (1 - mb^2/R^2),
\]

in which \( m \) is a dimensionless coefficient (the values for the external and internal atoms are taken as identical for simplicity), while \( E_{10} \) and \( E_{20} \) are the binding energies for a planar nucleus and

\[
a = r \sqrt{1 - \frac{r^2}{4R^2}},
\]

while the total binding energy of the shell is

\[
E = \frac{\pi}{b} \left( 1 - \frac{mb^2}{R^2} \right) \left[ \frac{r^2}{b} E_{20} - 2 (E_{20} - E_{10}) r \sqrt{1 - \frac{r^2}{4R^2}} \right].
\]

The condition for a maximum in the total binding energy is found by differentiating (3) with respect to \( R \) and equating the derivative to zero, which gives an equation for the equilibrium \( R(r) \):

\[
2mbE_{20} \sqrt{1 - \frac{r^2}{4R^2}} - (E_{20} - E_{10}) \times \left[ 4 \frac{mb^2}{4R^2} \left( 1 - \frac{r^2}{4R^2} \right) + \frac{r^2}{2} \left( 1 - \frac{mb^2}{R^2} \right) \right] = 0.
\]

We restrict consideration to the behavior at the start of stability loss and simplify (4) by neglecting \( r^2/R^2 \):

\[
r^2 - \frac{4mbE_{20}}{E_{20} - E_{10}} + 8mb^3 = 0.
\]

Quadratic equation (5) has two roots \((r/b)_{1,2}\), but one of them is unphysically small. The island retains absolute stability in the interval between the roots, i.e., when its size is less than the critical value, but when the critical size is reached, which corresponds to the second root, it loses stability and begins to be transformed to a sphere.

In the first stage (up to loss of stability in the planar island), the growth condition for the insular form is that the time between successive collisions of the island with carbon atoms \( t_1 \) should not be less than \( t_2 \), the time for the diffusion of an atom from the center to the edge, \( t_1 \geq t_2 \).

General concepts in molecular gas physics give

\[
t_1 = \frac{1}{n \pi r^2 v_0 \sqrt{T/2T_0}},
\]

where \( r \) is the radius of the island, \( n \) the volume concentration of carbon atoms, and \( v_0 \) their average velocity at temperature \( T_0 \) (the factor 2 incorporates the arbitrary orientation of the island relative to the incident atom).

The diffusion to the edge is thermally activated, and the relation is

\[
t_2 = \left( \frac{r}{b} \right)^2 \tau_0 \exp \frac{u}{kT},
\]

in which \( \tau_0 \) is the period of the thermal vibrations for an atom diffusing along the surface, \( u \) the diffusion activation energy, and \( k \) is Boltzmann’s constant. The island growth condition can thus take the form