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FULLERENES OF THE ΔN=2 SERIES

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Abstract. Fusion reactions of triangle C_3 and square C_4 carbon molecule with each other create elementary fullerenes C_6 and C_8. In its turn surface reactions of the fullerenes formed with square C_4 carbon molecule produce other prism fullerenes C_{10}, C_{12} and C_{14}. The surface reactions $C_6 + C_4 \to (C_6C_4) \to C_{10}$, $C_{10} + C_4 \to (C_{10}C_4) \to C_{14}$, $C_8 + C_4 \to (C_8C_4) \to C_{12}$ are modeled on the basis of Arrhenius's postulate. All the fullerenes obtained constitute the Δn= 2 series fullerenes of the periodic system of basic perfect fullerenes. Together with the Δn= 4 series this series finishes designing the periodic system from above.

Keywords: carbon molecule, energy, fullerene, fusion reaction, modeling, periodic system

1. Introduction

The periodic system of fullerenes [1, 2] consists of horizontal series and vertical columns (groups). The horizontal series form the Δn periodicities, where the fullerene structure changes from threefold symmetry to sixfold through four and fivefold ones. They contain the following series: Δn= 6, 8, 10, 12, 14, 16, 18 and include fullerenes from C_{14} to C_{108}. In addition to these series, fullerenes of the Δn=4 series, C_8, C_{12}, C_{16}, C_{20}, C_{24} and C_{28}, are incorporated into the system. It is suggested that they are created by fusion of the elementary fullerenes C_4, C_6, C_8, C_{10}, C_{12} and C_{14}. By this is meant a tetrahedron, triangular, tetra, penta, hexa and heptangular prisms. In its turn the elementary fullerenes form the Δn=2 series. To complete the system, it is necessary to add these fullerenes to the periodic system. However, it is not enough to include one or another series into the system, but it is necessary to suggest the mechanism of creating the members of such series from the more simple parts. In this contribution we present possible formation mechanisms of the Δn=2 series fullerenes.

2. Structure, energy and formation

As pointed out above, the Δn=2 series contains the perfect species: C_4, C_6, C_8, C_{10}, C_{12} and C_{14}. Their optimized structures and energies are obtained through the use of Avogadro package [3]; a modified color graphic being developed because the package graphics is incomprehensible. The elementary fullerenes are shown in Fig. 1. However the issue remains open about their formation mechanism.

There are suggested several mechanisms of fullerene formation [4]. It seems reasonable to choose one of them which is more universal and proved to have success. To our mind it is 'the fusion reaction' of lesser fullerenes or cupola half-fullerenes. However for the elementary fullerenes these structures are discussed only briefly. "We are compelled to returning to ancient Greeks, because in the diverse forms of Greek philosophy there are already in the bud all the posterior types of Weltanschauung" (Friedrich Engels). Following this advice, let us

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return to Plato (427-347 BC). Here we find five regular polyhedrons: tetrahedron, octahedron, cube, icosahedron and dodecahedron [5]. Plato considered the first four of them as productive elements (*τετρα − γεννημα*): fire, air, earth and water. Their faces are regular triangles and squares. Plato accepted them as the letters of entity language (*στοιχειον*); the dodecahedron was compared to ether.

Following Plato, take for the 'letters' a triangle and a square. The question arises how they can be produced. Seek help from chemistry where carbon cyclic molecules such as cyclopropane C_3H_6, cyclobutane C_4H_8, cyclopentane C_5H_{10}, and cyclohexane C_6H_{12} are known. Removing hydrogen atoms from them, we obtain the necessary letters (Fig. 2).

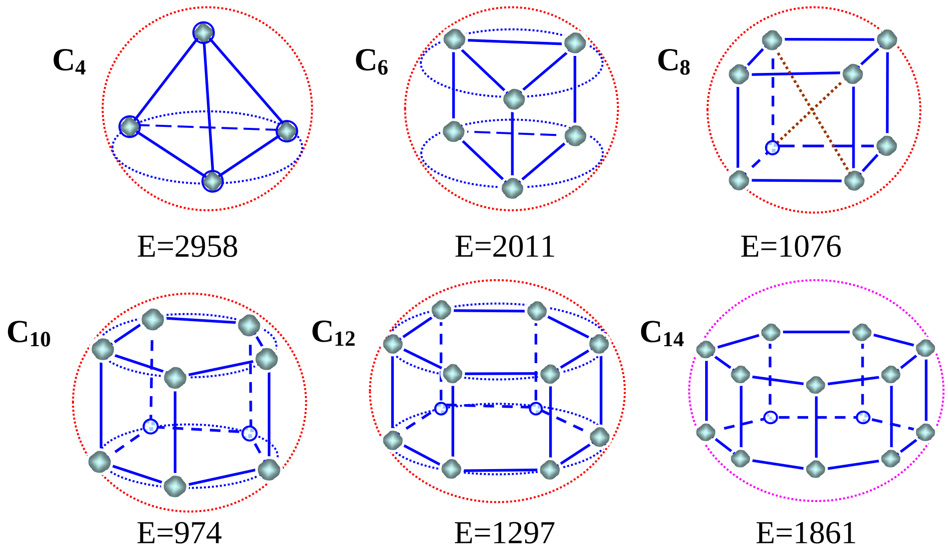

Fig. 1. Structure and energy (kJ/mol) of the Δn=2 series fullerenes with single bonds

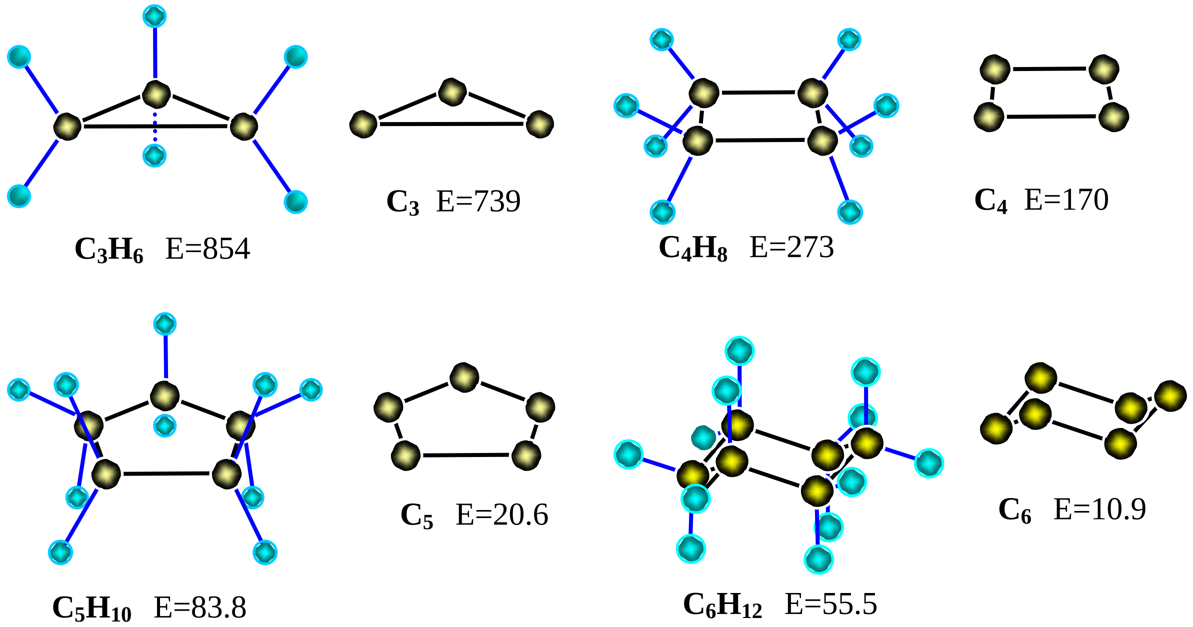

Fig. 2. Structure and energy (kJ/mol) of cyclic molecules and their cores

3. Fusion reactions and initial fullerenes

The fullerene formation is modeled on the basis of Arrhenius's postulate. It means that at first there forms an intermediate compound and only afterwards a usual chemical reaction is going on. Assuming this process being valid for two carbon molecules reacting with each other, it is possible to write fullerene reactions and illustrate them in figures. Suppose that two triangle carbon molecules react as $C_3 + C_3 \to (C_3C_3) \to C_6$. In Fig. 3 the atomic configurations illustrating this reaction are shown. At first two molecules C_3 are moving towards each other (Fig. 3a). Then the atoms of different molecules interact with each other and produce a compound (Fig. 3b). During this process new covalent bonds (red lines) are created and a triangular prism is generated (Fig. 3c), the electronic structure being turned into the ground state with single and double covalent bonds (Fig. 3d).

In a similar manner one can consider the reaction $C_4 + C_4 \to (C_4C_4) \to C_8$ (Fig. 4).

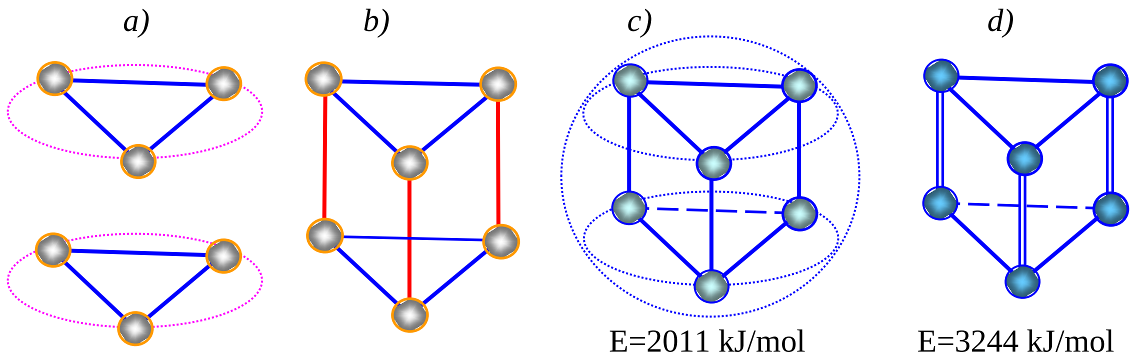

Fig. 3. Mirror-symmetry joining two triangles into a triangular prism
a) Separate triangles; *b*) Intermediate compound; *c, d*) Triangular prism;
Grey and blue balls are reacting and neutral atoms, respectively; red lines are new covalent bonds forming; blue lines are old and new covalent bonds

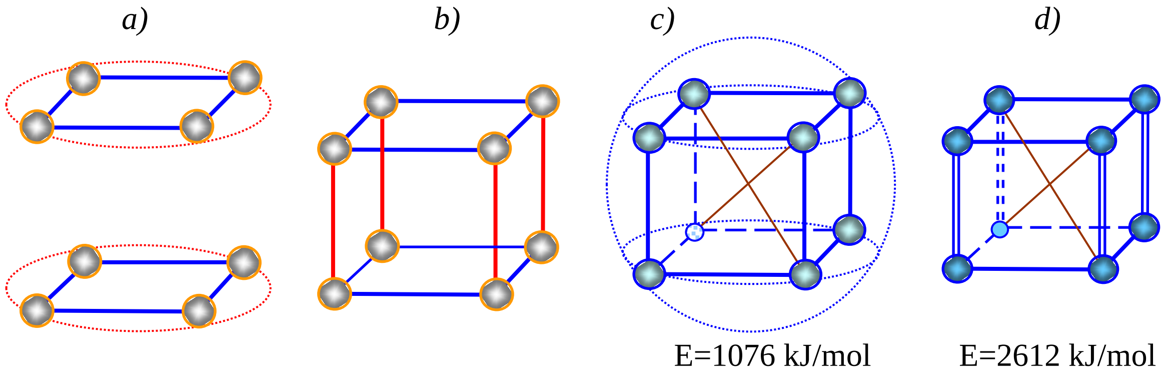

Fig. 4. Mirror-symmetry joining two squares into a cube
a) Separate squares; *b*) Intermediate compound; *c, d*) Cube;
Grey and blue balls are reacting and neutral atoms, respectively; red lines are new covalent bonds forming; blue lines are old and new covalent bonds

3. Growth of initial fullerenes

We can consider the initial fullerenes as simple words. Combining them with the 'letter' square, it is possible to create more complex words. In this manner we can analyze the reactions: $C_6 + C_4 \to (C_6C_4) \to C_{10}$, $C_{10} + C_4 \to (C_{10}C_4) \to C_{14}$, $C_8 + C_4 \to (C_8C_4) \to C_{12}$. They are illustrated in Figs. 5, 6 and 7.

From these figures it follows that only a part of the 'word' is changing during the reaction. In physics language it means that the number of fullerene reacting atoms is equal to the atom number of attacking molecule. In our case it equals four.

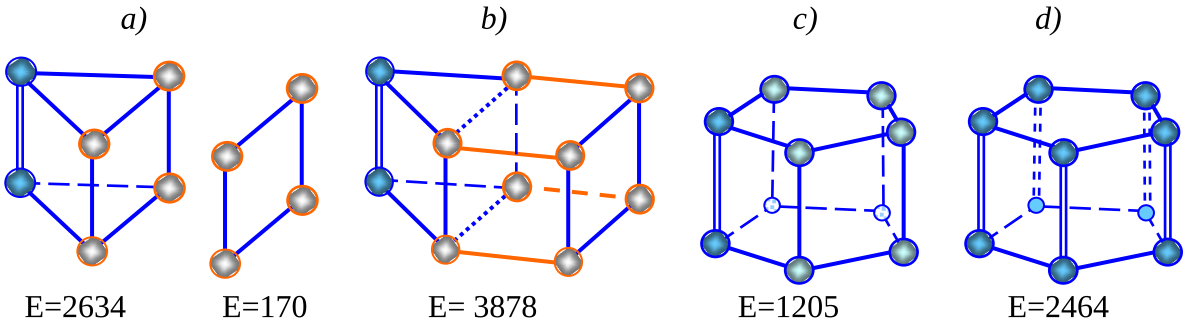

Fig. 5. Joining a square to a triangular prism (energy, kJ/mol):
a) Separate objects; *b*) Intermediate compound; *c, d*) Penta-angular prism;
Grey and blue balls are reacting and neutral atoms, respectively; red lines are new covalent bonds forming; blue lines are old and new covalent bonds; blue dot lines are covalent bonds to be destroyed

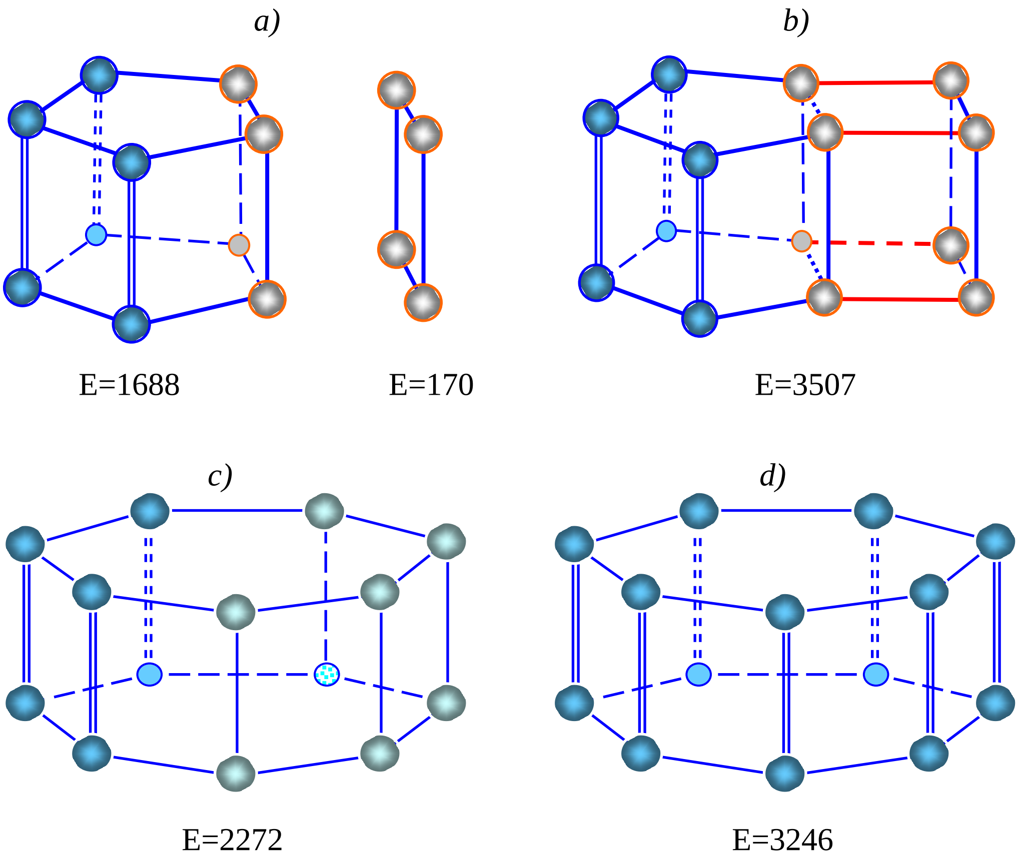

Fig. 6. Joining a square to a penta-angular prism (energy, kJ/mol):
a) Separate objects; *b*) Intermediate compound; *c, d*) Hepta-angular prism;
Grey and blue balls are reacting and neutral atoms, respectively; red lines are new covalent bonds forming; blue lines are old and new covalent bonds; blue dot lines are covalent bonds to be destroyed

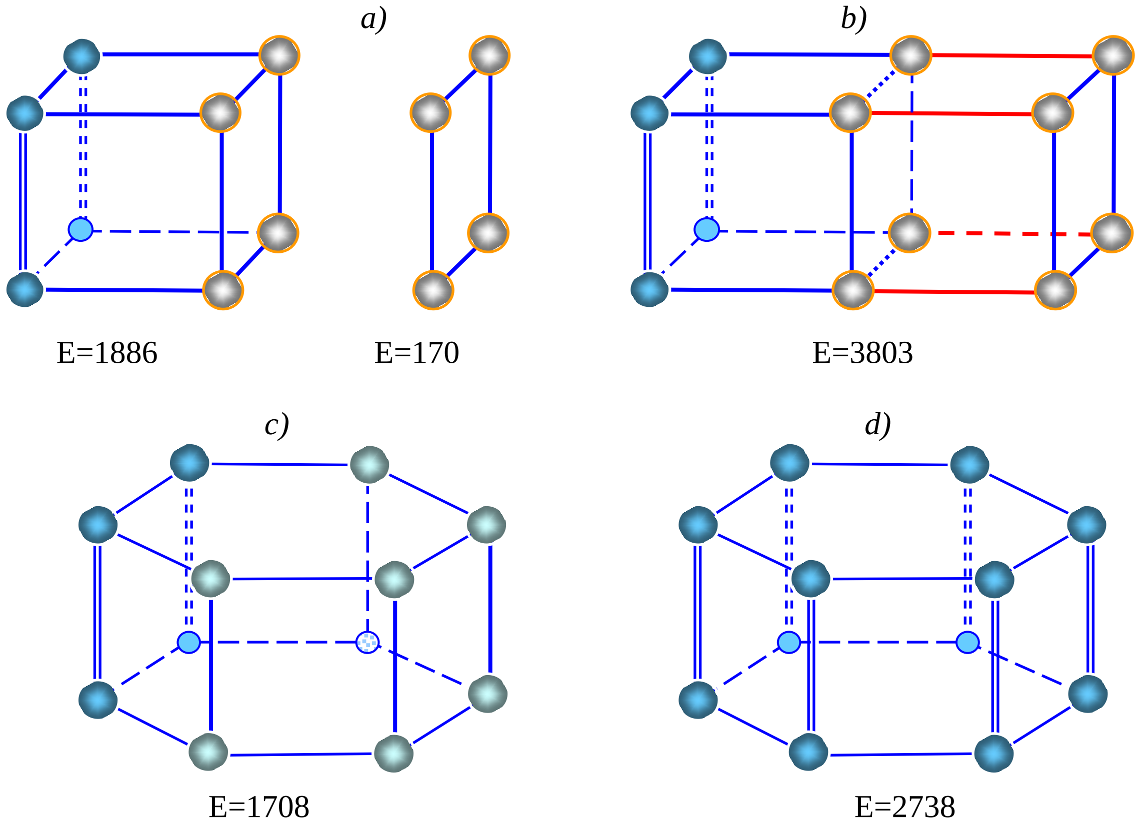

Fig. 7. Joining a square to a cube (energy, kJ/mol):
a) Separate objects; *b*) Intermediate compound; *c, d*) Hexa-angular prism;
Grey and blue balls are reacting and neutral atoms, respectively; red lines are new covalent bonds forming; blue lines are old and new covalent bonds; blue dot lines are covalent bonds to be destroyed

4. Folding a cluster

Strictly speaking the tetrahedron fullerene does not belong to the prism structures. It is included into the Δn=2 series temporally, for completeness sake. Similar to the previous reasoning, we are able to suggest the formation mechanism of this ugly duckling. We can think over a carbon molecule isobutane HC $(CH_3)_3$ as an ancestor of this fullerene (Fig. 8a). Removing hydrogen atoms from it, we obtain a core (Fig. 8b).

According to Aristotle (384-322 BC) every thing is the unity of form (ειδος) and matter; the form being an active element [5]. The things harbour elements of quiet and movement. In nature there are different forms for the same matter and the matter transforms constantly under the influence of different reasons. In our case the matter (core) consists of four carbon atoms and exists at first in the form of a tetrahedral molecule. However it can transform into a cluster (Fig. 8c) or a tetrahedron (Fig. 8d). The reasons of transforming are electric interaction of bond charges as well as thermal vibrations of atoms.

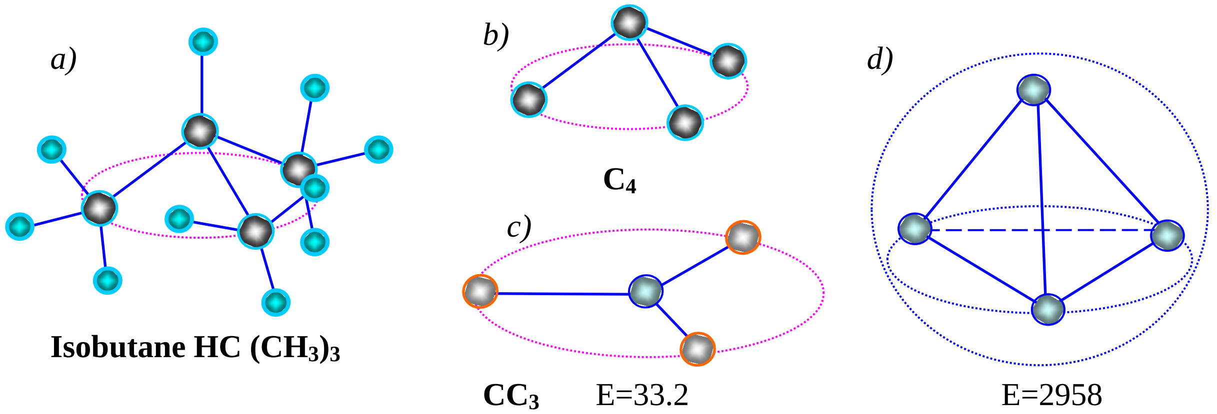

Fig. 8. Structure of isobutene (a), its core (b), cluster (c) and a carbon tetrahedron (d); their energy in kJ/mol:
Blue and grey balls of the molecules are neutral and reaction atoms, respectively

5. Periodic system of fullerenes

In Ref. [2] the periodic system of basic perfect fullerenes is presented. It contains the series from Δn= 6 to 18. Now we can enlarge the system from above adding the series Δn= 2 and 4; these series are given in the Table 1. The upper line corresponds to the molecules only with single bonds, the lower one refer to the molecules with single and double bonds. The series Δn= 4 was obtained and discussed early. Consider the series Δn= 2.

Table 1. Periodic System of Basic Perfect Fullerenes

Symmetry of Fullerenes						
Series Groups	3-fold S Δm=6	3-fold T Δm=6	4-fold Δm=8	5-fold Δm=10	6-fold Δm=12	7-fold Δm=14
Δn=2	**C_2** 19.8 34.7	**C_6** 2011 3244	**C_8** 1076 2611	**C_{10}** 974 2464	**C_{12}** 1297 2738	**C_{14}** 1861 3246
Δn=4	**C_8** 17.5 54.2	**C_{12}** 1689 3465	**C_{16}** 671 2070	**C_{20}** 491 1647	**C_{24}** 697 1778	**C_{28}** 946 2264
Δn=6	**C_{14}**	**C_{18}**	**C_{24}**	**C_{30}**	**C_{36}**	**C_{42}**

It should be emphasized that we did not include into the system the tetrahedral fullerene C_4. The reason is that because of its symmetry, it needs a special consideration. Instead of it we incorporated into the system dimers C−C and C=C; their energies are taken from Ref. [6]. From the table it follows that the least formation energies are characteristic for the groups Δm= 6 and 10, having threefold and fivefold symmetry, in comparison with their neighbors. This characteristic feature is intrinsical to all fullerenes of these columns. The results need further investigation.

4. Conclusion and discussion

We have considered fusion reactions of triangle C_3 and square C_4 carbon molecule with each other. The reactions create elementary fullerenes C_6 and C_8. The process is similar to fusion of bubbles in a soap solution. In its turn surface reactions of the square C_4 carbon molecule with the fullerenes formed produce other elementary prism fullerenes C_{10}, C_{12} and C_{14}. These surface reactions $C_6 + C_4 \to (C_6C_4) \to C_{10}$, $C_{10} + C_4 \to (C_{10}C_4) \to C_{14}$, $C_8 + C_4 \to (C_8C_4) \to C_{12}$

are modeled on the basis of Arrhenius's postulate. It means that at first there forms an intermediate compound and only afterwards a usual chemical reaction is going on. It is supposed that during the reactions new covalent bonds are formed and old covalent bonds between the reacting atoms are destroyed. The reaction zone takes into account the fact that forming covalent bonds exist only between nearest-neighbor reactive atoms. Together with the Δn= 4 series this series finishes designing the periodic system from above.

Today there is no clear and unique theory of fullerene growth. "The problem here is not the lack of imagination, because quite numerous models have been proposed. What is rather lacking is a model using quantities that might be evaluated and measured" [7]. There are a lot of papers on fullerene properties [8, and 277 references therein]. Using different computational methods (there are also a lot of programs), the authors calculate the properties of the most popular fullerenes which structure is known. As a result, the numbers obtained contradict to each other and only increase information entropy. To our mind, the absence of appreciable progress in understanding fullerene nature is determined by the domination of numerical calculations on the known structures. Consequently, it is necessary not to do various calculations only on the known structures which are poorly connected with each other, but to study simultaneously the definite series or columns of the fullerene periodic system suggested in Refs. [1, 2] and enlarged here.

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