# THERMOCHEMISTRY MODELING OF HYDROGEN AND WATER INFLUENCE ON $C_{20}$ CAGE DECAY

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**Introduction.** Nanoscale materials based on fullerenes have a high density of covalent carbon–carbon bonds storing a great amount of energy, thus providing a high heat release upon their spontaneous explosion, as it is shown in the detailed theoretical analysis /1/ of nitrofullerene $C_{60}(NO_2)_{12}$ decomposition by using of nonequilibrium reactive molecular dynamics. The initiation temperature of this explosion was found to be $\approx 1000$ K and full decomposition into 96 individual atoms was achieved at temperature $\approx 5000$ K, yielding energy release of $(3/2)k_B(96\times5000\,\text{K} - 1\times1000\,\text{K}) \approx 62$ eV, where $k_B$ is the Boltzmann constant. We propose to consider a decomposition of hydrogenated $C_{20}$ cage molecule as a more stable form of nanoscale explosive. The fullerene $C_{20}$ can be effectively hydrogenated unlike the fullerene $C_{60}$, which is typically hydrogenated to $C_{60}H_{36}$ molecule /2/. It is known that a metastable state of the $C_{20}$ cage molecule is thermally stable due to the considerable potential barrier between this state and the equilibrium state of the $C_{20}$ bowl /3/. We propose to use this relative stability of the metastable state of the $C_{20}$ cage covered by 20 hydrogen atoms (i.e. each carbon atom is bonded with one hydrogen atom). A detailed description of formation and decay of the hydrogenated $C_{20}$ molecule requires to take into account a great number of processes like vibrations of atomic systems, thermodynamic processes, kinetics of carbon nanostructure hydrogenation, nonequilibrium statistical processes, electromagnetic radiation effects etc. Here we limit ourselves to an elementary thermochemistry consideration.

Fullerenes being highly symmetric molecules /4/ undergo a spontaneous deformation (the Jahn–Teller effect). It was shown /5/ by means of a comparison of the computational results with the Raman scattering data that there may be the Fermi resonance between the totally symmetric vibrations of fullerene $C_{60}$. Charged fullerenes can be distorted by Coulombic forces /6/.

It is shown in /7/ that the activation energy of a chemical process differs significantly from the height of a barrier which separates the atomic configurations of the initial and the final states of the transition. Concepts of a “phase” and a “phase transition” for stable and metastable states of matter are discussed in /8/. While condensed matter physics primarily considers equilibrium states and treats metastable phases as exceptions, organic chemistry overwhelmingly deals with metastable states. A theoretical analysis of continuous light absorption in the visible, IR, and UV spectral ranges in a quasi-equilibrium hydrogen plasma with an effective temperature between 1500 and 25000 K was made in /9/. There also the relative contribution of positive molecular $H_2^+$ ions and negative atomic $H^-$ ions to the total photoabsorption coefficient of quasi-equilibrium hydrogen plasmas is emphasized.

The studies of the open questions concerning the nature, kinetics, and limit values of hydrogen sorption by carbon nanostructures is presented in review /10/. The thermodynamic and diffusion characteristics and the micromechanisms of the processes of chemical and physical sorption of hydrogen by graphite and related carbon nanomaterials are considered there in addition to the various methodological aspects of studying and optimizing such hydrogen adsorbents. The properties of hydrogenated low-dimensional systems, in particular made from fullerenes and nanotubes, are reviewed in /11/.

A modified phenomenological model for calculating the formation energy of carbon nanoclusters, which makes it possible to analyze the regions of existence of clusters in various forms, is proposed in /12/. A parameter corresponding to passivation of broken carbon bonds is introduced in the model, which affects the shape of the equilibrium optimum clusters.

The results of computer simulation of the dynamics of the fullerene $C_{20}$ at different temperatures presented in /13/ show that a cage isomer is very stable with respect to the transition to a lower energy configuration (bowl) and retains its chemical structure under heating to very high temperatures, $T \approx 3000$ K. The fullerene $C_{20}$ decay to a defected $C_{20}$ isomer is considered in /14/. Calculations by the use of a combination of the molecular dynamics and Monte Carlo techniques show that the lifetime of the fullerene $C_{20}$ at $T = 1500$ K becomes less than a second and exponentially decreases with temperature.

**Calculation results**. The linear combination of atomic orbitals (LCAO) method realized in software package Gaussian 09 /15/ was chosen for quantum chemical calculations as the most suitable and widely used to calculate the properties of molecules or clusters. The calculations were performed within the hybrid functional exchange-correlation UB3LYP (unrestricted Becke, Lee, Yang, and Parr) potential and basis wave functions 6-31G (d, p) for open electron shells. A full optimization of the $C_{20}$ molecule structure with the given neutral state (multiplicity $M = 1$) and temperature was performed (with an accuracy in the energy of 0.01 eV per molecule). A quasi-Newton ion relaxation implemented in the Broyden–Fletcher–Goldfarb–Shanno method was used for the optimization. The parameter Freq was used to calculate the frequency spectrum of optimized molecules and to output thermochemical data.

The results are presented in the Figures 1 and 2. Figure 1 shows the change of Gibbs energy ($\Delta G$) between products and reactants in each indicated reaction. There are considered a reaction *1* of the synthesis and a reverse reaction *3* of the decay. The reaction *2* is shown for a comparison with the reaction *3* indicating the influence of the hydrogenation explicitly. The reaction *4* is the hydrogenated $C_{20}$ cage decay in the presence of water yielding CO and $H_2$ as the products.

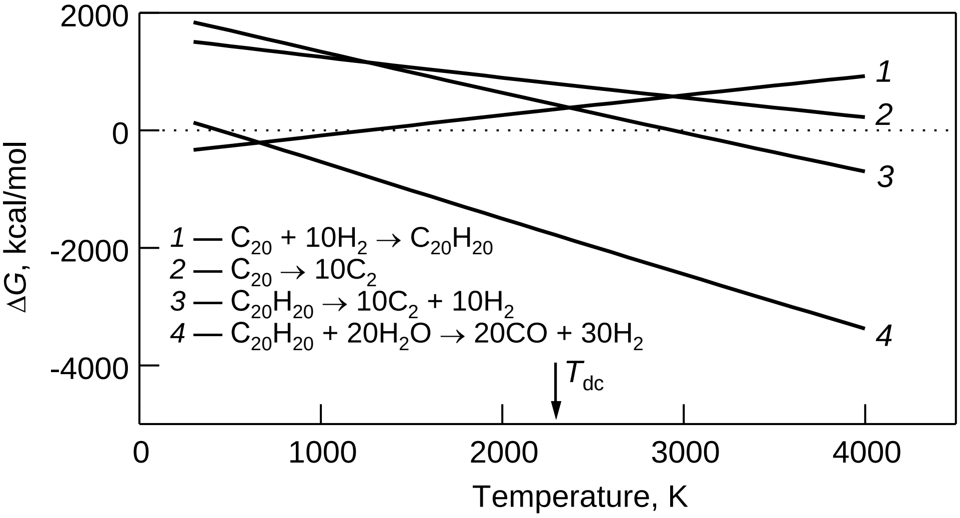

Fig. 1. Change of the Gibbs energy between product and reactant as a function of temperature calculated at DFT level (Gaussian 09). Temperature $T_{dc} \approx 2300$ K is an experimental value of fullerene formation temperature in the carbon arc discharge plasma /16/.

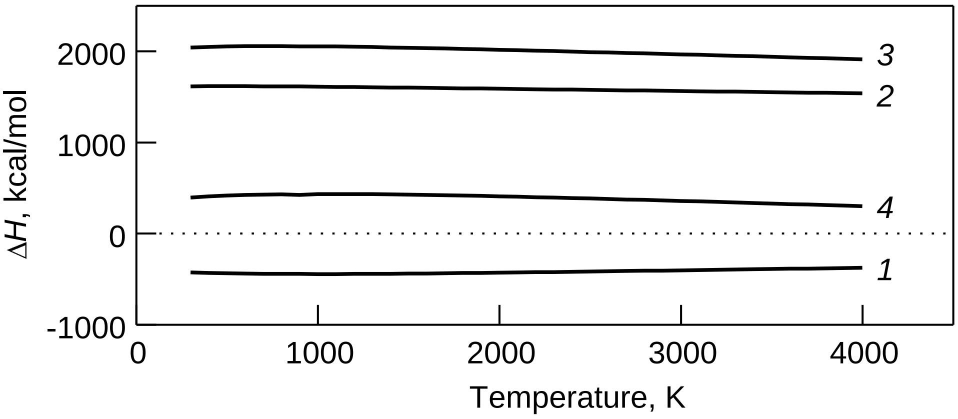

Fig. 2. Enthalpy of the reactions *1–4* as a function of temperature.

A reaction can pass spontaneously at $\Delta G < 0$. It is seen from the Figure 1 (reaction *3*) that the decay of the $C_{20}H_{20}$ molecules is possible at temperatures $T > 3000$ K (leading to formation of molecular hydrogen $H_2$ as a byproduct). Reaction *1* shows that a synthesis of $C_{20}H_{20}$ by molecular hydrogen $H_2$ addition to the $C_{20}$ occurs at temperatures $T < 1200$ K. Thus, the $C_{20}$ spontaneously decays by hydrogenation at high temperatures ($T > 3000$ K), that is larger than the initiation temperature for nitrofullerene explosion /1/. In order to enhance the effectiveness of the $C_{20}H_{20}$ decay we propose to add water (reaction *4*). It is seen that this reaction passes at temperatures $T > 500$ K, providing a great amount of molecular hydrogen as a product.

Figure 2 shows the enthalpy $\Delta H$ of reactions *1–5* as a function of temperature: $\Delta H = H_f(\text{products}) - H_f(\text{reactants}) = \Delta G + T\Delta S$, where $H_f$ is the heat of formation. The negative sign of $\Delta H$ corresponds to the energy release, while the positive sign of $\Delta H$ corresponds to the energy absorption as a result of reaction. It is seen that $C_{20}H_{20}$ decays with energy absorption $\Delta H \approx 2000$ kcal/mol = 87 eV (reaction *3*). By addition of a water the reaction *4* of the $C_{20}H_{20}$ decomposition passes with energy absorption $\Delta H \approx 400$ kcal/mol = 17 eV.

**Conclusion.** We obtain the initiation temperature for the $C_{20}H_{20}$ decomposition of $\approx 3000$ K and the heat absorption of $\approx 87$ eV. Addition of a water considerably enhances the conditions for the $C_{20}H_{20}$ decomposition (initiation temperature of $\approx 500$ K and the heat absorption of $\approx 17$ eV), providing a great output of molecular hydrogen (30 molecules of $H_2$ hydrogen for a single $C_{20}H_{20}$ molecule).

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