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## HEAT AND MASS TRANSFER AND PHYSICAL GASDYNAMICS

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# A New Model for Carbon Nanoparticle Formation in the Pyrolysis Process behind Shock Waves

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**Abstract**—A new conceptual model for carbon nanoparticle formation in shock waves that is based on recent data of the temperature dependence for finite sizes of resulting particles and an abrupt increase in their refractive index during the change in particle sizes from 5 to 15 nm. The model is based on the two following physically distinct assumptions. First, the volumetric fraction of condensed carbon remains constant from complete decomposition temperatures for the initial carbon-containing molecules (1600–2000 K) up to evaporation temperature for carbon nanoparticles (3000–3500 K). Second, the surface growth rate for particles is determined by the rate of collisions between vapor molecules and particles. The proposed model allows an explanation of all observed regularities of the carbon nanoparticle growth, including a decrease in finite sizes of particles at a rise in temperature and a corresponding decrease in the time of particle formation.

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## INTRODUCTION

Carbon nanoparticles occupy a highly important place both in nature and in the most various technical applications. Recently there has been a great advance in carbon nanoparticles because of the discovery of fullerenes, various types of nanotubes, graphenes, and because of the outstanding capabilities of carbon nanoparticles for adsorbing liquids and gases, in particular, hydrogen, which opens up unique possibilities for the advancement of hydrogen energy.

For these reasons, processes of carbon nanoparticle formation are investigated in a huge number of works. Particular attention in them has been given to experimental investigation of kinetics of carbon nanoparticle formation behind shock waves [1]. The high uniformity of parameters behind the shock wave in a shock tube, the simplicity of variation in temperature, pressure, and the mixture composition in wide limits, and the possibility for the reliable control of these and other general parameters of the experiment resulted in the situation in which investigations into shock tubes became one of the most widespread tools not only for the investigation of gas phase processes, but also for such heterogeneous processes as condensation, evaporation, and surface reactions with the participation of nanoparticles.

Based on a great number of investigations conducted in various leading world scientific laboratories, they were stable concepts of kinetics of formation and properties of carbon nanoparticles generated during pyrolysis of various carbon-containing compounds behind shock waves. The most significant results obtained in the shock waves are temperature dependences for the formation of condensed carbon parti-

cles in the gas phase [1–7]. Most of these results were obtained by means of the measurements of temporal profiles for laser radiation extinction by particles generated after passing the shock wave in a mixture containing a gaseous carbon-containing substance.

As a result of such investigations, beginning from the very first works, it was determined that the temperature dependence

$$f_v = \frac{\ln[I_0/I]}{\varepsilon l}, \quad (1)$$

for the finite level of extinction, which is expressed as the volumetric fraction of the condensed phase, has a bell-shaped form (Fig. 1) [3]. The maximum of this dependence in various substances lies in the region of 1600–2000 K. In (1),  $I_0$  and  $I$  are the initial and passed signals of a probing laser,  $\varepsilon$  is the extinction coefficient in  $\text{cm}^{-1}$ , and  $l$  is the absorption length, i.e., the diameter of the shock wave.

The analysis for the nature of such a bell-shaped temperature dependence for the volumetric fraction of condensed particles up to now has been reduced to the idea that the ascending branch of the dependence was explained by an increase in the degree of decomposition for the initial molecules as the temperature rises and the decrease in the volumetric fraction of particles with a subsequent temperature increase was connected with the competition between the reaction of growth and decomposition of various polyaromatic hydrocarbon compounds being the main material for the subsequent formation of condensed carbon particles [8]. However, a similar decrease in the volumetric particle fraction as the temperature rises is also observed during pyrolysis of hydrogen-free precursors [1, 9], where carbon particles grow without hydrogen participation

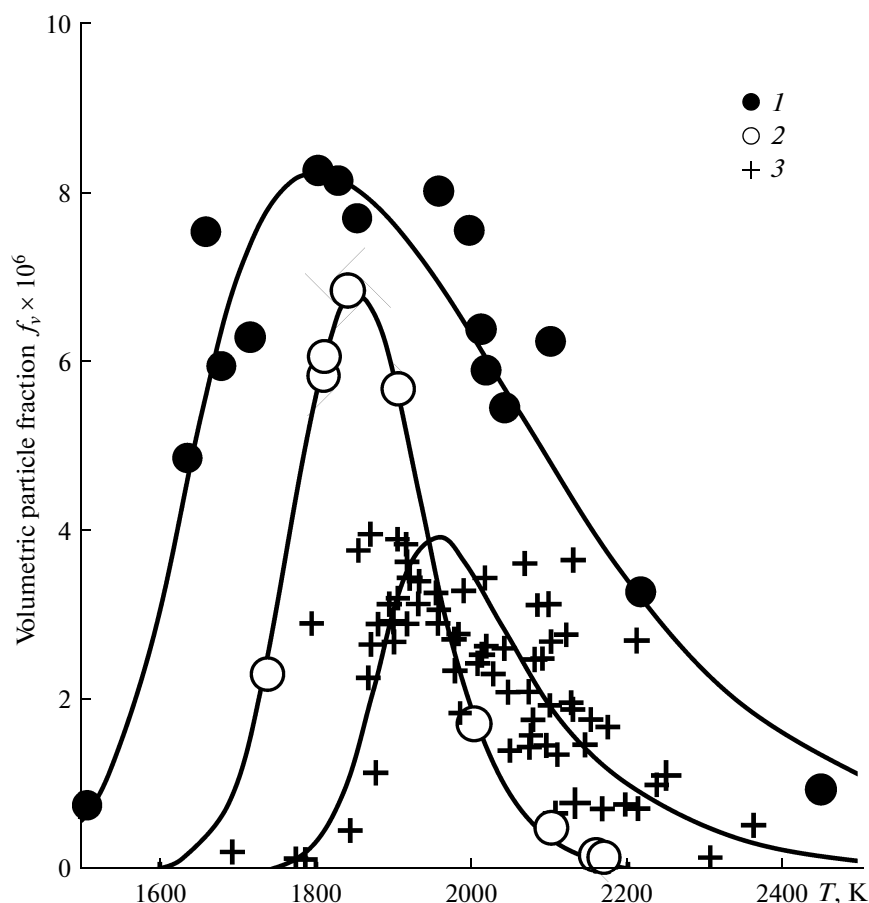


Fig. 1. Temperature dependences of the volumetric particle fraction at shock-wave pyrolysis of benzene (1), ethylene (2), and n-hexane (3) [3].

and no hydrocarbon compounds form. In addition, it is well known that a temperature rise above 2000 K necessarily leads to the decomposition of any hydrocarbon compounds, and the thermodynamically equilibrium state of carbon is the condensed phase up to phase transition temperatures lying above 3000 K. Therefore, the question of what state carbon is in at temperatures of 2000–3000 K, where a decrease in the volumetric fraction of condensed particles is observed, up to now has remained without an answer.

Another very significant characteristic of the nanoparticle growth process is the effective particle growth rate constant  $k_f$  determined by the approximation of the temporal profile for the volumetric fraction of the condensed phase by the relaxation equation

$$\frac{df_v}{dt} = k_f(f_v^\infty - f_v).$$

In a whole series of works, it was shown that the particle growth rate abruptly increased as the temperature rose, and the temperature dependence for  $k_f$ , which was measured during pyrolysis of a great variety of carbon compounds, was described well by a relationship of the Arrhenius type (see Fig. 2)

$$k_f = A \exp(-E/kT).$$

The effective activation energy  $E$  for this process, which is determined by the slope of Arrhenius dependences, lies in the range of 100–200 kJ/mol [1, 5, 6, 9, 10].

On the other hand, it is well known that the general reactions determining the particle growth rate are the recombination of atoms and carbon clusters, and hydrocarbon radicals. Such reactions run without activation energy; i.e., their rate increases very weakly as the temperature rises, reflecting only an increase in collision frequencies as  $T^{1/2}$ . Therefore, the observed Arrhenius dependence of the effective particle growth rate constant at a high activation energy is presented strangely enough.

Thus, the above-described two significant empirical characteristics for the particle growth—temperature dependences of the volumetric fraction and the particle growth rate—have no clear physical justifications. Therefore, the objective of the present work is critical analysis of the accumulated data of temperature dependences of the carbon nanoparticle growth and the development of the qualitative conceptual model allowing construction of a physically distinct

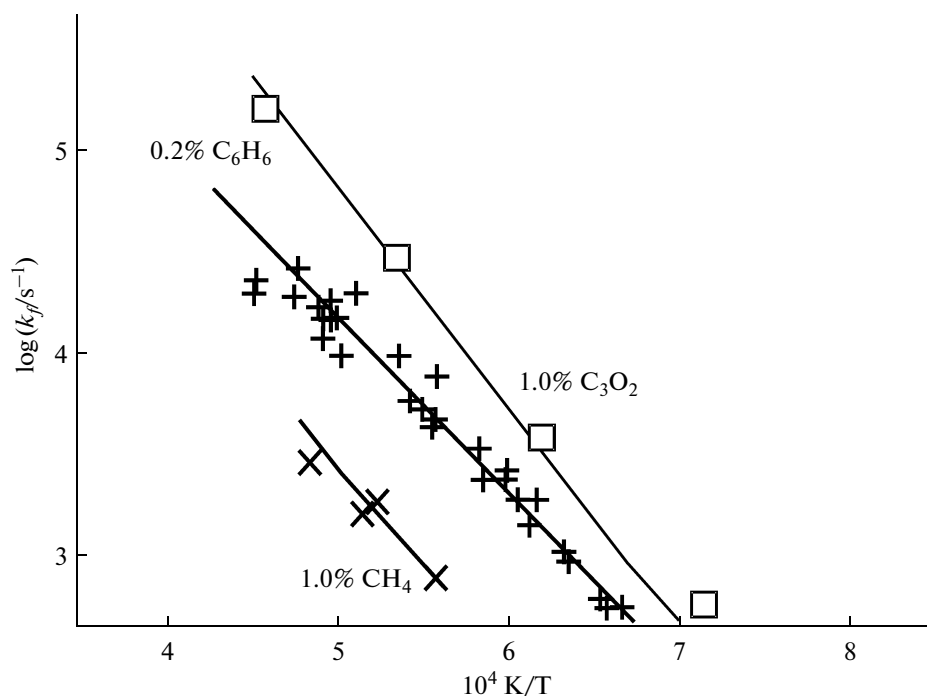


Fig. 2. Particle growth rate constant at pyrolysis of different compounds [4].

pattern of relationships determining the formation of carbon particles behind shock waves with a temperature increase from 2000 up to 3000 K.

#### ANALYSIS OF EXPERIMENTAL DATA OF RECENT YEARS

Formulation of general concepts for the proposed model is based on important experimental data obtained during investigations of particle growth at the shock-wave pyrolysis of carbon-containing compounds in recent years.

A whole series works on measuring the temperature dependences for finite sizes of carbon nanoparticles demonstrated that these dependences vary similarly to the temperature dependences for the volumetric fraction of particles [1, 11–13]. They also have the bell-shaped form, and the maximum particle sizes are attained about at the same temperatures, 1600–2000 K (Fig. 3). At the same time, the maximum particle sizes (diameters) are 10–18 nm, and as the temperature increases up to 2300–2500 K, their size decreases to 3–8 nm.

Other significant information was recently obtained from measuring the optical properties of carbon nanoparticles, depending on their size [1, 13–15]. Figure 4 represents dependences for the function of the constant  $E(m)$  of refraction

$$E(m) = \frac{\varepsilon\lambda}{6\pi}$$

on the size of particles generated during acetylene pyrolysis behind shock waves ( $\lambda$  is the wave length). It is quite evident that particles with a diameter less than 10 nm are more translucent than particles with common soot sizes of more than 20 nm.

Thus, it becomes apparent that the analysis of extinction data for determining the volumetric particle fraction is absolutely unjustified with the use of the invariable optical properties of particles. In other words, a decrease in the extinction level as the temperature rises above 2000 K, which is observed simultaneously with a decrease in the particle size, reflected no decrease in the volumetric particle fraction or a reduction in their refraction index. Based on the above described new experimental data on the temperature dependence for a finite particle size and on the abrupt change in the optical properties of particles at their growth from 10 up to 20 nm, let us attempt at this sight angle to revise all the data on the temperature dependences of kinetics of carbon nanoparticle formation. Based on such an analysis, one can formulate a new conceptual model describing the regularities of the condensed particle growth during pyrolysis of various carbon compounds behind shock waves.

#### MODEL

The foundation of the proposed model contains two fundamental assumptions.

First, it is believed that the volumetric fraction of the condensed phase remains constant, beginning from temperatures corresponding to the complete

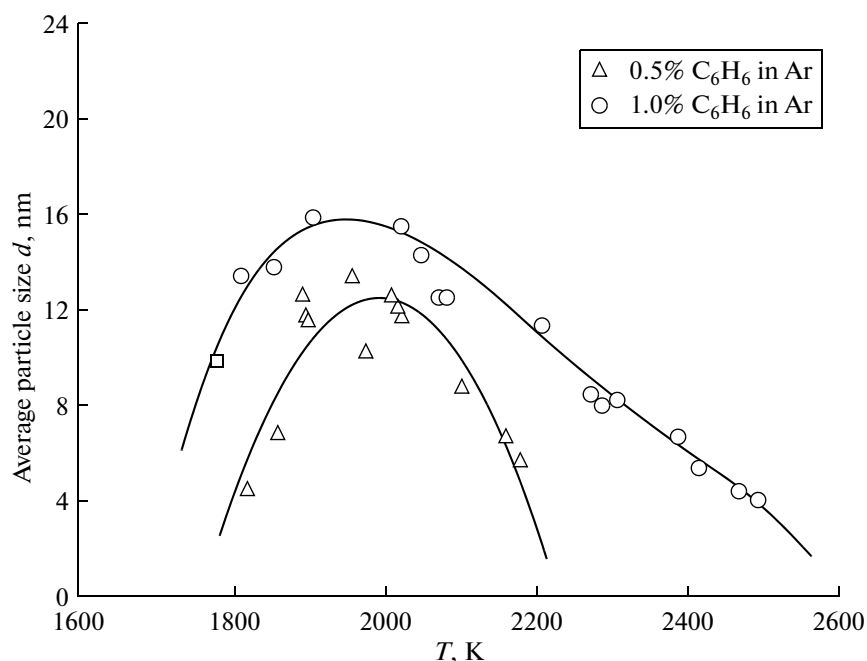


Fig. 3. Temperature dependence of the finite particle size during pyrolysis of  $C_6H_6$  [11].

release of carbon from the initial carbon-containing molecules (1600–2000 K) and up to evaporation (sublimation) temperatures of condensed carbon (3000–3500 K depending on the nanoparticle sizes).

The second fundamental assumption is that the particle growth (increase in sizes) in pyrolysis behind shock waves is completely determined by mechanisms of the surface growth, i.e. recombination of small gas

radicals (atoms C, small cluster  $C_2-C_n$ , etc., and carbon radicals  $C_nH_m$ , where  $n \leq 6$ ) at the surface of growing particles. It is well known that the surface growth reactions run in a barrierless way and their rate is determined by the gas kinetic collision frequency

$$z = N_R \sigma_p v_R,$$

where  $N_R$  and  $v_R$  are the concentration and the thermal velocity of recombining radicals and  $\sigma_p$  is the gas kinetic particle cross section. From the assumption it follows that the condensation rate at the given concentrations and sizes of particles with increasing temperature may increase only as  $T^{1/2}$ , reflecting an increase in the thermal velocity of radicals.

Let us note that the first assertion of the model is based on well-known facts mentioned in the Introduction relative to the loss of the thermodynamic stability of all hydrocarbon compounds at temperatures above 2000 K and the phase diagram of carbon according to which it must be in the condensed state up to temperatures above 3000 K.

In addition, as experimental verification of the validity of the first assertion relative to the constancy of the volumetric particle fraction, one can cite data of measuring the temperature dependence of the normalized optical density of particles,

$$D_p = \frac{\ln[I_0/I]}{l[C]} = \frac{f_V \varepsilon}{[C]},$$

where  $[C]$  is the total carbon concentration in the mixture. Figure 5 represents results of measuring  $D_p$  during pyrolysis of  $C_3O_2$ , which are carried out simultaneously in various spectral ranges [9]. It is quite evi-

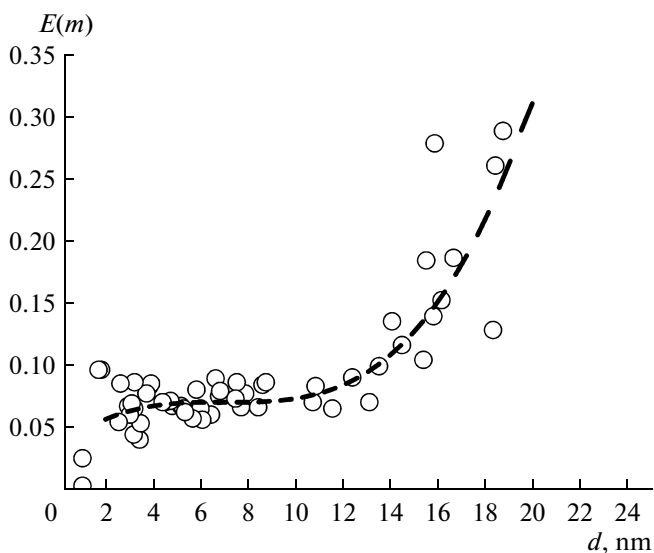


Fig. 4. Dependence of the constant of refraction on the growing particle diameter at  $\lambda = 1064$  nm [13].

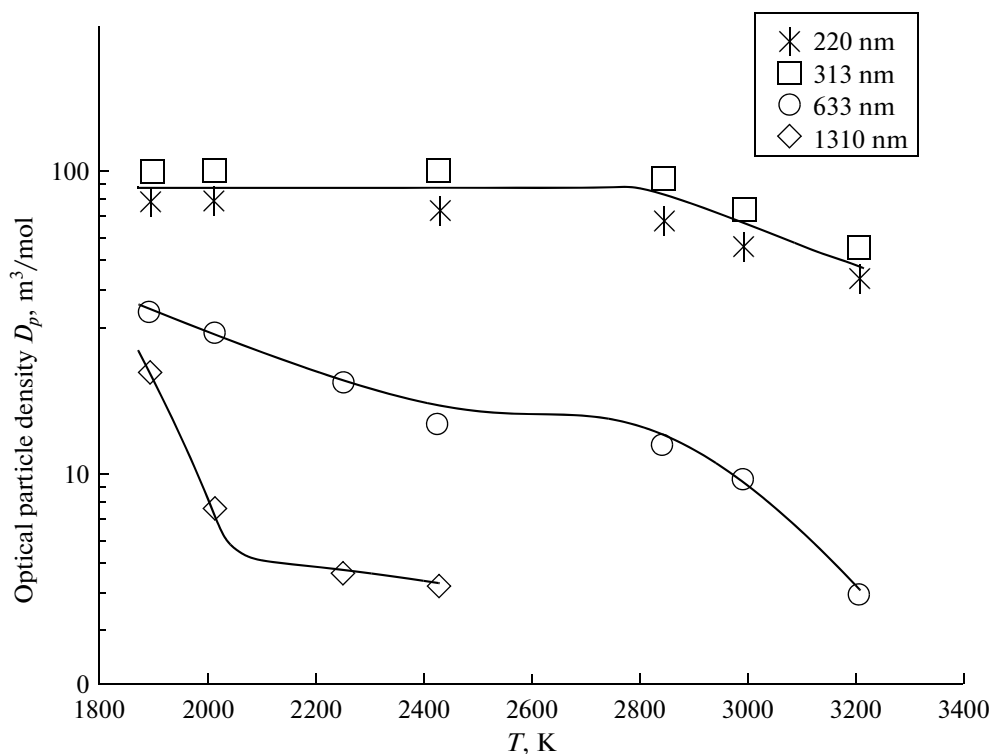


Fig. 5. Temperature dependences of the finite optical density of particles in different spectral ranges during pyrolysis of the mixture 0.2%  $C_3O_2$  + Ar [9].

dent that in the temperature range of 1900–2900 K the optical density in the visible and IR regions decreases substantially, reflecting the behavior of the high-temperature wing of the bell-shaped dependence of the volumetric particle fraction (see Fig. 2), and remains practically constant in the UV region. Because pyrolysis of  $C_3O_2$  forms no radicals or compounds, absorbing radiation in this spectral region, apart from growing carbon particles, such data may be considered as verification that as the temperature increases carbon is condensed into increasingly fine nanoparticles transparent in the visible region, but as before, actively absorbing UV radiation [16].

The second assertion of the model is obviously verified by data of the change in the particle size during pyrolysis of acetylene [13]. Figure 6 demonstrates the comparison of temporal profiles for particle size measures at various temperatures. The profile coincidence indicates that the particle size increase rate is invariable with a rise in temperature, although, according to the data of [6, 17], the particle growth rate constant  $k_f$  during pyrolysis of acetylene with an increase in temperature from 1850 to 2050 K increases by about two times.

## RESULTS AND DISCUSSION

Let us now consider consequences of the proposed model with respect to the description of temperature

dependences of the finite size of particles and their numerical density.

If particles grow by the mechanism of surface condensation, the increase rate for the atom number in the particle in the kinetic mode is determined by the relationship [18]

$$\frac{dn}{dt} = N_R \sigma_p v_R = N_R n^{2/3} r_W^2 \sqrt{\frac{8\pi kT}{m_R}}.$$

Here,  $m_R$  is the mass of the atom or active radicals participating in particle formation and  $r_W$  is the Wigner–Seitz radius. At the same time, knowing the particle growth time  $\tau$  and neglecting the atom loss in this time, one can roughly determine the finite atom number in the particle or its size

$$n_{fin} = \left( \frac{8\pi kT}{m_R} \right)^{3/2} \frac{N_R^3}{27} \tau^3.$$

Supposing further that the particle growth time can be evaluated from data of their growth rate constant

$$\tau^{-1} \sim k_f = A \exp(-E/kT),$$

and taking into account that  $d \sim n_{fin}^{1/3}$ , for spherical particles, we obtain the temperature dependence for the particle size,

$$d(T) \sim \sqrt{T} \exp(E/kT). \quad (2)$$

Figure 7 represents a comparison of the temperature dependence for the particle size with experimental data obtained from particle formation in acetylene

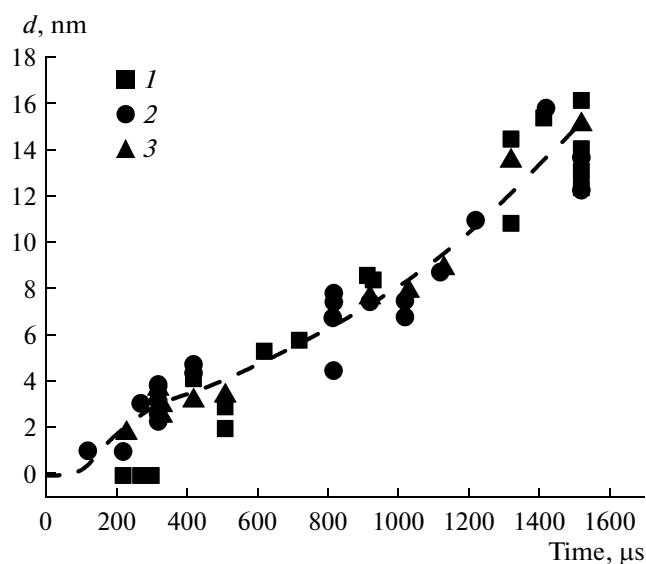


Fig. 6. Measurement results for the particle size growth during pyrolysis of acetylene at various temperatures [13].

and carbon suboxide. Activation energies determined by measuring the particle growth rate constants are taken from one work and compared with the measurements of the particle size in other works. It is quite evident that in both cases the found dependence describes well the character of the change in the particle size with an increase in temperature.

Thus, this analysis verifies that the observed increase in the effective constant for the particle growth rate as the temperature increases is completely caused by a reduction in the time of their growth up to a finite size.

Further, the obtained temperature dependence (2) for the finite particle size under the condition of the consistency of the volumetric particle fraction

$$f_V = N n_{fin} \frac{4\pi r_W^3}{3} = \text{const}$$

with allowance made for

$$n_{fin} \sim T^{3/2} \tau^3 \sim T^{3/2} \exp(3E/kT),$$

allows for determining the temperature dependence of the numerical particle density

$$N = \frac{\text{const}}{n_{fin}} \sim \frac{1}{\sqrt{T}} \exp(-E/kT). \quad (3)$$

Thus, obtained relationship (3) indicates that the observed growth for the particle formation rate and the decrease in finite particle sizes with increasing temperature, which is determined by formula (2), actually express the law of an increase in the numerical particle density  $N$ . Let us note that the particle density for surface growth is invariable and reflects the numerical density of condensation nuclei.

In order to find out the physical meaning of the dependence, let us consider general processes determining the numerical density of condensation nuclei. It is well known that nucleation processes in a strongly supersaturated vapor are poorly described in the framework of the classical theory of condensation and, therefore, should be considered on the basis of the kinetic approach. In this case, the specificity of the shock-wave experiment lies in the fact that atoms and active radicals  $R_i$  participating in nucleation appear at the dissociation of the initial molecules, which begins after passing the shock wave and have a rate constant described by the Arrhenius relationship

$$k_d = A \exp(-E_d/kT), \quad (4)$$

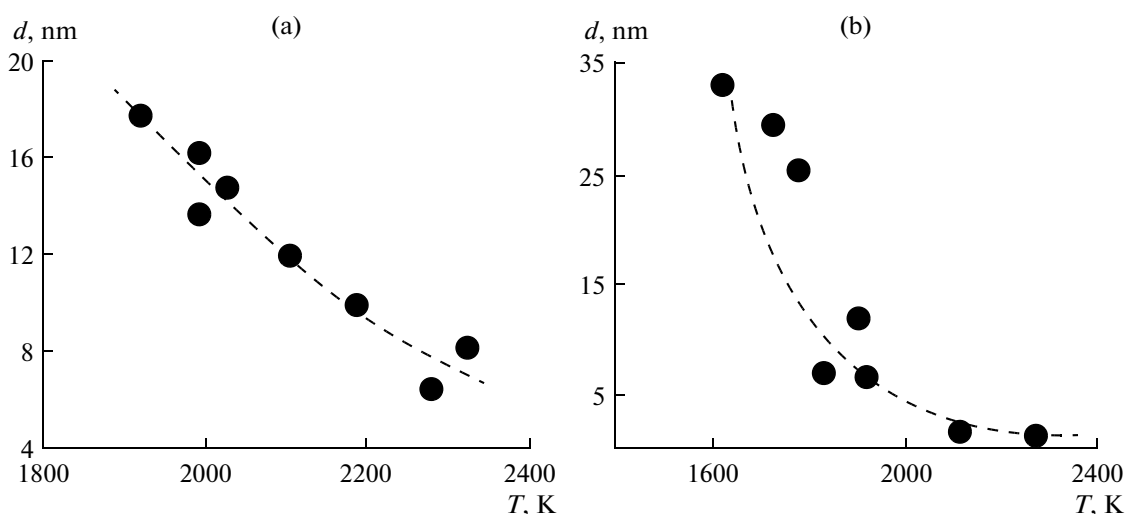


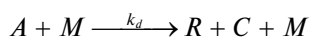
Fig. 7. Temperature dependences of the particle size in  $C_2H_2$  [12] (a) and  $C_3O_2$  [19] (b). The dotted line is calculations by (2): (a) at the activation energy  $E = 101$  kJ/mol from [10], and (b)  $E = 211$  kJ/mol from [4].

Comparison of temperature dependences for the vapor (or active radicals) generation rate with the proposed model assumption

Reaction of generation of vapor or active radicals	Activation energy $E_d$ , kJ/mol	Model $3E - (kT \ln T)$ , kJ/mol	Footnotes
$C_3O_2 \rightarrow C + 2CO$	490 [20]	$\sim 620$ [6] ( $>E_d$ )	exothermal process
$2C_2H_2 \rightarrow C_4H_3 + H$	276 [21]	$\sim 300$ [9] ( $>E_d$ )	exothermal process
$CCl_4 \rightarrow C + 4Cl$	773 [22]	$\sim 570$ [5] ( $<E_d$ )	endothermic process

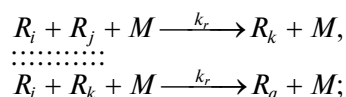
where  $E_d$  is the activation energy of dissociation. Subsequently, the fluctuation growth of condensation nuclei begins as long as they form clusters with the critical size at the numerical density  $N$ . Generally, these processes can be represented as the following:

(i) dissociation of initial molecules  $A$  with the formation of active radicals  $R$  and passive molecules or radicals  $C$  not participating in condensation processes:

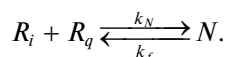


( $M$  is the concentration of diluent gas);

(ii) nucleation processes including the sequential (fluctuating) growth of nuclei with the subcritical size by recombination collisions of active radicals  $R_i$



(iii) further growth of nuclei as long as they reach the critical size with the numerical density  $N$ :



Because it is known [1] that the “bottleneck” of the whole process is just dissociation reactions of initial molecules and processes of nucleation and the surface growth of particles run with great rates, it is appropriate to accept the quasi-stationary approximation for the evaluation of concentrations of active radicals and critical nuclei. Under qualitative consideration, the stationary concentration  $N$  of nuclei is determined from the relationship

$$N(T) = \frac{k_d k_N}{2k_r k_f} [A] = \text{const } T^{-1/2} \exp(-E_d/kT). \quad (5)$$

When writing relationship (5), it was accepted that nucleation processes (ii) and (iii) are barrierless and their rate constants  $k_r$ ,  $k_N$ , and  $k_f$  rise with increasing temperature by  $T^{1/2}$ , whereas the rate constant for initial molecule dissociation (4) has a substantial activation energy  $E_d$ , usually more than 250–300 kJ/mol.

The table lists the comparison of the obtained kinetic dependence (5) with the model relationship (3).

It is interesting to note that exact concordance is not observed, but there is a defined regularity. The question is that both model consideration (3) and kinetic relationship (5) suppose that particle growth proceeds at an invariable temperature. Actually, the process in the first two substances is strongly exother-

mal [17, 23] and the model numerical particle density rises with an increase in temperature rather than by kinetic predictions; i.e., the process is self-accelerating because of heat release in the course of the reaction that leads to additional temperature growth. On the other hand, the process in strongly endothermic  $CCl_4$  [1, 9] goes more slowly, evidently, because of the temperature drop caused by heat absorption during the reaction.

## CONCLUSIONS

Analysis of the results of measuring the temperature dependences of sizes of carbon particles and their optical properties allowed critical revision of the prevailing conceptions relative to a decrease in the volumetric fraction of particles and the acceleration of their growth as the temperature increases from 2000 up to 3000 K. As a result, a new conceptual model for particle growth that is based on fundamental conceptions taken no account in the preceding works is proposed. The proposed model eliminates the existing contradictions and describes all known experimental data of temperature dependences of particle growth during pyrolysis in a wide range of parameters.

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## REFERENCES

1. Eremin, A., *Prog. Energy Combust. Sci.*, 2012, vol. 38, no. 1, p. 1.
2. Bronin, S.Ya., Emel'yanov, A.V., Eremin, A.V., and Khrapak, A.G., *High Temp.*, 2011, vol. 49, no. 3, p. 349.
3. Alexiou, A. and Williams, A., *Fuel*, 1994, vol. 73, no. 8, p. 1280.
4. Dörge, K.J., Tanke, D., and Wagner, H.Gg., *Z. Phys. Chem.*, 1999, vol. 212, p. 219.
5. Bauerle, S., Karasevich, Y., Slavov, St., Tanke, D., Tappe, M., Thienel, T., and Wagner, H.Gg., *Proc. Combust. Inst.*, 1994, vol. 25, no. 1, p. 627.
6. Knorre, V.G., Tanke, D., Thienel, T., and Wagner, H.Gg., *Proc. Combust. Inst.*, 1996, vol. 26, no. 2, p. 2303.
7. Kellerer, H., Muller, A., Bauer, H.-J., and Wittig, S., *Combust. Sci. Technol.*, 1996, vol. 113, p. 67.

8. Frenklach, M., Taki, S., and Matula, R.A., *Combust. Flame*, 1983, vol. 49, p. 275.
9. Emelianov, A., Eremin, A., Gurentsov, E., Makeich, A., Jander, H., and Wagner, H.Gg., *Proc. Combust. Inst.*, 2005, vol. 30, p. 1433.
10. Tanke, D., *Dissertation*, Göttingen: Göttingen Universität, Germany, 1994.
11. Starke, R. and Roth, P., *Combust. Flame*, 2001, vol. 127, no. 4, p. 2278.
12. Gurentsov, E.V. and Eremin, A.V., *High Temp.*, 2011, vol. 49, no. 5, p. 667.
13. Eremin, A., Gurentsov, E., Popova, E., and Priemchenko, K., *Appl. Phys. B: Lasers Opt.*, 2011, vol. 104, no. 2, p. 285.
14. Basile, G., Rolando, A., D'Alessio, A., D'Anna, A., and Minatolo, P., *Proc. Combust. Inst.*, 2002, vol. 29, p. 2391.
15. Snelling, D., Liu, F., Smallwood, G.Ö., and Gülder, Ö., *Combust. Flame*, 2004, vol. 136, p. 180.
16. D'Anna, A., Rolando, A., Allouis, C., Minatolo, P., and D'Alessio, A., *Proc. Combust. Inst.*, 2005, vol. 30, p. 1449.
17. Emelianov, A.V., Eremin, A.V., Jander, H., and Wagner, H.Gg., *Proc. Combust. Inst.*, 2011, vol. 33, p. 525.
18. Smirnov, B.M., *Phys.—Usp.*, 2011, vol. 54, no. 7, p. 691.
19. Starke, R., Kock, B., Roth, P., Eremin, A., Gurentsov, E., Shumova, V., and Ziborov, V., *Combust. Flame*, 2003, vol. 135, nos. 1–2, p. 77.
20. Friedrichs, G. and Wagner, H.Gg., *Z. Phys. Chem.*, 1998, vol. 203, no. 1, p. 1.
21. Benson, S.W., *Int. J. Chem. Kinet.*, 1989, vol. 21, p. 233.
22. Kumaran, S.S., Su, M.C., Lim, K.P., Michael, J.V., Klippenstein, S.J., DiFelice, J., Mudipalli, P.S., Kiefer, J.H., Dixon, D.A., and Peterson, K.A., *J. Phys. Chem. A*, 1997, vol. 101, no. 46, p. 8653.
23. Emel'yanov, A.V., Eremin, A.V., Makeich, A.A., and Fortov, V.E., *High Temp.*, 2010, vol. 48, no. 6, p. 823.

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