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Temperatures of the Attainable Superheat of Some Thermally Unstable Liquids

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The paper gives the results of measuring the temperatures of the attainable superheat of some liquids that are thermally unstable at these temperatures. The technique of heating a thin wire probe placed into a liquid under study with electric-current pulses has been used. The length of pulses is from 10^{-5} to 10^{-3} s, which corresponds to a heating rate of 10^5 to $10^8\ \mathrm{K \cdot s^{-1}}$. The influence of a chemical reaction in the liquid phase on the temperature of the attainable superheat has been considered. In particular, it has been shown that boiling initiated by an elementary act of an exothermic chemical reaction is of a low probability. A method of calculating the temperature of the attainable superheat of thermally unstable liquids under conditions of quick heating has been developed. A method for the determination of the kinetic parameters of thermal decomposition from the measurements of the temperature of the attainable superheat is discussed.

KEY WORDS: attainable superheat; boiling; homogeneous nucleation; kinetic parameters; pulse heating; thermal decomposition; wire probe.

1. INTRODUCTION

A chemical reaction in the liquid phase affects the bubble formation in a superheated liquid. The method of describing nucleation in multicomponent systems with chemical reactions suggested by Cherepanova and Ushkans [1] is too general and does not allow numerical calculations. The aim of the present paper is to develop a simple method for estimating the temperature of the attainable superheat of thermally unstable substances

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using the results of experiments. We restrict ourselves to the reactions of thermal decomposition, although some of the conclusions of this paper are true for reactions of an arbitrary type. We also assume that a chemical reaction is a primary process and nucleation is a secondary one in the sense that bubble formation does not influence the course of a chemical reaction.

If a chemical reaction has nonzero heat as a result of the reaction in the liquid phase, domains appear for which the temperature and the composition differ from those of the bulk. The initial size of these domains is very small; it is of the order of molecule dimensions. Then these domains spread out over the whole liquid volume as a result of molecule interactions. So this inhomogeneity should be taken into account in developing a rigorous nucleation theory in chemically reacting systems.

However, we consider only two limiting cases: (i) the critical bubble arises as the result of a single, elementary act of an exothermic chemical reaction, and (ii) the products and the heat of a chemical reaction have spread over the whole volume so that such a system can be considered as a mixture, the temperature and the composition of which are uniform but time dependent.

Only several new molecules may be born due to an elementary act, which does not change considerably the composition of the critical nucleus because, even at the temperature of the attainable superheat, it consists of no fewer than 100 molecules [2–4]. However, if a chemical reaction is exothermal, the originated molecules may have energy that is sufficient for the formation of the critical bubble. Several approaches have been developed for calculating the conditions under which a local heat release leads to the birth of the critical bubble. One of these approaches is known as the thermal theory of the initiation of boiling-up of superheated liquids with high-energy particles [5, 6]. According to the thermal theory, zones or so-called thermal spikes are formed in the liquid along the track of the particle. The temperature in the spikes is higher than that in the bulk. To form the critical bubble, it is necessary to evaporate the volume of liquid that is equal to

$$V_1 = \frac{4}{3}\pi r_c^3 \frac{\rho''}{\rho'}$$

Here ρ' and ρ'' are the densities of the liquid and the vapor, respectively, and r_c is the radius of the critical bubble at the temperature of the bulk. In the framework of the thermal theory it is suggested that if the volume V_1 has the energy $W_a + W'$, the formation of the critical bubble occurs with a probability that is equal to 1. Here W_a is the adiabatic work of the critical bubble formation, and W' is the irreversible energy losses connected with the thermal conductivity and the viscosity of the liquid. The work W_a may be written as follows:

$$W_a = W_c \alpha$$

where W_c is the work of formation of the critical-size bubble at $P = \text{const}$, $T = \text{const}$,

$$W_c = \frac{16\pi\sigma^3}{3(P'' - P')^2}$$

and the factor α is equal to

$$\alpha = 1 + \frac{2\rho'' L}{P'' - P'} - 3\frac{d \ln \sigma}{d \ln T}$$

Here σ is the surface tension, P' is the pressure in the liquid, P'' is the pressure in the critical bubble, L is the heat of vaporization, and T is the temperature.

In the spirit of the thermal theory, the condition of critical bubble formation due to an elementary act of an exothermal chemical reaction may be written in the following form:

$$\Delta H > W_a + W'$$

where ΔH is the heat of the reaction per act. The values of W_a and W_c decrease quickly with increasing liquid superheat [2], so initiation is most likely to occur near the boundary of the homogeneous nucleation of the liquid. Figure 1 gives as an example the pressure dependence of the adiabatic work W_a in *n*-hexane at $J = 1\ \mathrm{m}^{-3} \cdot \mathrm{s}^{-1}$, where J is the rate of homogeneous nucleation calculated using the theory developed by Derjaguin et al. [7]. Figure 1 shows that the work W_a decreases quickly under tension of the liquid ($P' < 0$). However, even at negative pressures, the work W_a exceeds the heat of highly exothermal reactions such as the decomposition of the azides of lead, copper, and mercury, for which ΔH is from 0.8×10^{-18} to 1×10^{-18} J [8]. In addition, in accordance with the estimations made in Ref. 2, irreversible energy losses W' range from $0.15 W_a$ to $0.3 W_a$.

Another approach was developed by Pavlov [9, 10]. Here, in comparison with the thermal theory, the later stage of thermal spike evolution is considered. It is assumed that the volume of a thermal spike V_1 is already large enough to use the traditional theory of homogeneous nucleation.

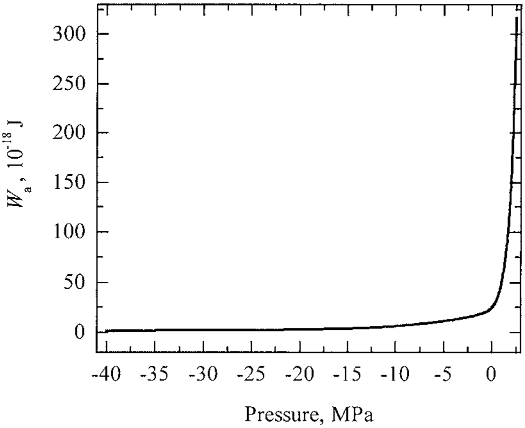

Fig. 1. Pressure dependence of the adiabatic work of the critical bubble formation in *n*-hexane at the rate of homogeneous nucleation $J = 1\ \mathrm{m}^{-3} \cdot \mathrm{s}^{-1}$.

In such a situation, the rate of homogeneous nucleation in a thermal spike may be written as follows [2]:

$$J(T + \Delta T) = J(T)\exp(G_T\, \Delta T) \tag{1}$$

where T is the temperature in the bulk, ΔT is the temperature increment in a thermal spike, and $G_T = \partial \ln J/\partial T$. The number of bubbles formed in the bulk V in the time t is equal to

$$N_g = J(T)\, Vt \tag{2}$$

The number of bubbles formed in the thermal spikes is equal to

$$N_i = J(T + \Delta T)\, V_1 t_1 v V t \tag{3}$$

Here $t_1 = V_1^{2/3}/a'$ is the time of disappearance of the thermal spike, a' is the thermal diffusivity of the liquid, and v, in $\mathrm{m}^{-3} \cdot \mathrm{s}^{-1}$, is the rate of the thermal spike formation, in this case the rate of a chemical reaction. The initiated nucleation is of importance when

$$N_i \geqslant N_g \tag{4}$$

The temperature increment in the thermal spike is of the order

$$\Delta T = \frac{\Delta H}{V_1 \rho' c'} \tag{5}$$

where c' is the heat capacity of the liquid. For boiling-up of the liquid, the bubble formed in the thermal spike should grow to the size of $r_c(T)$, consuming the heat of the thermal spike. The condition of survival of the bubble may be written approximately as follows [9]:

$$\frac{V_1}{V_c} \approx \frac{L}{(T-T_s)\,c'} \tag{6}$$

Here $V_c = \frac{4}{3}\pi r_c^3(T)$ is the volume of the critical bubble and T_s is the saturation temperature.

Solving Eqs. (1)–(6) simultaneously we find that the nucleation initiated by the elementary acts of exothermal chemical reactions is of importance if the heat of a reaction satisfies following condition:

$$\Delta H \geqslant \frac{\rho' V_c L}{G_T(T-T_s)} \ln\left[\frac{(T-T_s)\,c'}{V_c L v t_1}\right] \tag{7}$$

This condition is valid only at $P' > 0$ and a moderate rate of a chemical reaction $v < (T-T_s)\,c'/(V_c L t_1)$. Figure 2 gives as an example the reaction heat calculated using Eq. (7) as a function of the pressure and the reaction rate for n-hexane at the rate of homogeneous nucleation $J = 1\ \mathrm{m^{-3}\cdot s^{-1}}$. Even at such a high rate of a chemical reaction $v = 10^{20}\ \mathrm{m^3\cdot s^{-1}}$, the value of ΔH is of the order of 10^{-17} J.

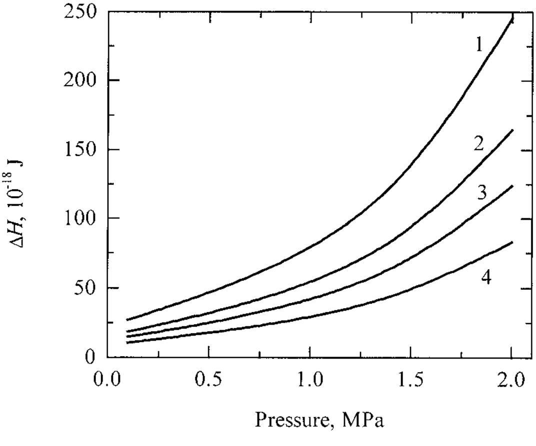

Fig. 2. Exothermal chemical reaction heat as a function of pressure and the reaction rate v ($\mathrm{m^{-3}\cdot s^{-1}}$): 1–1, 2–$10^{10}$, 3–$10^{15}$, and 4–$10^{20}$. For n-hexane, the rate of homogeneous nucleation $J = 1\ \mathrm{m^{-3}\cdot s^{-1}}$.

So, according to both the thermal theory and the model suggested by Pavlov, the initiation of boiling-up of superheated liquids by elementary acts of exothermal chemical reactions is of a low probability.

In the second limiting case, if the kinetic equation for a chemical reaction is well known, the time dependences of the temperature and the mole fractions may be calculated and then, using the homogeneous nucleation theory, the rate of nucleation may be estimated. The main problem with this method is that under the thermal decomposition of many substances of practical importance, so many products are formed that it is difficult to find in the literature or to calculate with satisfactory accuracy the properties of the gas and liquid needed for the application of the nucleation theory. To develop a simple method for estimating the temperature of the attainable superheat of thermally unstable liquids, we carried out an experimental investigation of boiling-up of those liquids under conditions of quick heating.

2. MEASUREMENT OF THE TEMPERATURES OF THE ATTAINABLE SUPERHEAT

We measured the temperature of the attainable superheat by the method of pulse heating of a wire probe placed into the liquid under study. We widely used this method for investigating the superheating of organic liquids, water, liquid oligomers, and polymers. It is described in detail elsewhere [2, 3, 11, 12].

The liquid under study filled the chamber, the pressure in which was created with a piston and measured with a dial gauge. A measuring probe (platinum wire 2×10^{-3} cm in diameter and from 1 to 3 cm in length) served simultaneously as a heater and a temperature element. The probe was included in a low-inductance bridge. Square potential pulses were applied to the bridge from a generator. During pulses the probe was heated; at the moment of boiling, the conditions of the heat transfer from the probe to a liquid changed. This resulted in a change in the functional dependence of the probe temperature on time. There arose a certain temperature perturbation connected with boiling. The potential difference on the probe was uniquely connected with its temperature; so at the moment of boiling-up, one could observe a voltage perturbation. This perturbation was isolated with the help of an amplifying filter with a controllable bandwidth. Low frequencies were filtered out. Then the signal was applied to an oscilloscope. The bridge was adjusted with a resistance box in such a way that its balance corresponded to the beginning of boiling-up. For an exact determination of the moment of balance, one made use of a potential difference comparator which at that moment gave a potential step that went to the other beam of the oscilloscope.

The average probe temperature corresponding to the beginning of boiling was calculated from the condition of the bridge balance and by the well-known temperature dependence of the resistance of platinum. Then the temperature of the surface of the probe in its middle part was calculated, and that temperature was taken as the temperature of the attainable superheat. The time from the beginning of a heating pulse to the moment of boiling-up t^* ranged from 10 to 1000 μs, which corresponded to heating rates from 10^5 to 10^8 $K \cdot s^{-1}$.

The measurements were carried out with various classes of chemical compounds: normal alkanes C_nH_{2n+2} ($n = 19$ to 36), 1-alkanols $C_nH_{2n+1}OH$ ($n = 13$ to 22), 1-alkenes C_nH_{2n} ($n = 13$ to 20), polyethene glycols $H(CH_2CH_2)_nOH$ ($n = 1$ to 13.2), some methylphenylsiloxanes, oligoethylsiloxanes produced in an industrial way [13], aqueous solutions of hydrogen peroxide [14], glycerin, mixtures (n-alkane + isoprene rubber) [15], benzene sulfurazide, mixtures (benzene sulfurazide + benzene), petroleum fractions, fuels for cars and jet airplanes, transformer oils [16], and others.

The effect of a chemical reaction on the boiling of a liquid depends on the amount and the composition of the reaction products. The more the reaction products differ in their critical properties from the initial liquid, the greater is the change in the temperature of boiling-up. The temperature of the attainable superheat of benzene sulfurazide that we used as a model substance is shown in Fig. 3. Between 130 and 150°C this substance decomposes in accordance with the following equation [17]:

$$C_6H_5SO_2N_3 \rightarrow C_6H_5SO_2N + N_2 \tag{8}$$

At higher temperatures in parallel with the reaction given by Eq. (8), the decomposition of $C_6H_5SO_2N$ takes place because sulfur dioxide is found among the products of the decomposition.

Figure 3 is typical of the boiling-up of thermally unstable liquids; the lower the heating rate, the lower is the temperature of the attainable superheat and the higher is the critical pressure P_c of the mixture consisting of the initial substance and the products of decomposition. This is explained by the decomposition of a liquid and the saturation of it with highly volatile substances, in the case of benzene sulfurazide, with nitrogen and sulfur dioxide. For many substances studied—normal alkanes, alkanols, and alkenes—the thermal decomposition did not show itself in our experiments, although the temperature of the attainable superheat of such a substance was considerably higher than the temperature of the onset of decomposition. The temperature of the attainable superheat of triacontane is given in Fig. 4. Here we have a pattern characteristic of the boiling-up of thermally stable liquids. The lines of the attainable superheat corresponding

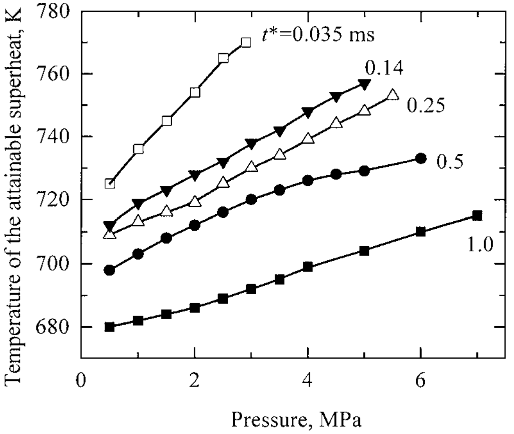

Fig. 3. Temperature of the attainable superheat of benzene sulphurazide versus pressure at selected times from the beginning of heating to the moment of boiling-up t^*.

to the different values of t^* and, thus, to the different rates of homogeneous nucleation convergence to the critical point. However, normal alkanes are unstable above 650 K and the temperatures of the attainable superheat of triacontane are from 800 to 850 K. The explanation of this fact is the following. The rate of the decomposition of normal alkanes at temperatures from 650 to 850 K in the liquid phase is not very high. Due to

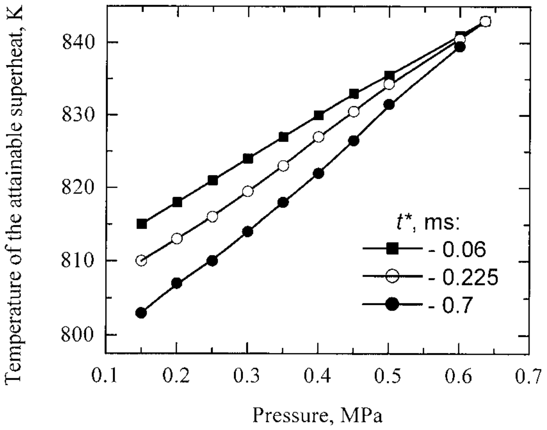

Fig. 4. Temperature of the attainable superheat of *n*-triacontane versus pressure at selected times from the beginning of heating to the moment of boiling-up t^*.

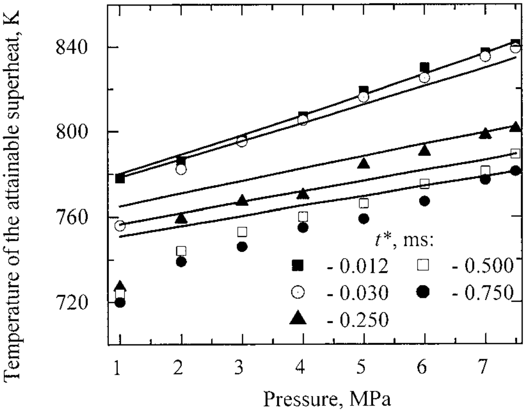

Fig. 5. Temperature of the attainable superheat of glycerin as a function of pressure and the time from the beginning of heating to the moment of boiling-up t^*. Solid lines correspond to calculations using Eq. (11) for the same set of heating times.

the small length of the heating pulses, the mass of decomposition products at the moment of boiling-up was so small that the change in the temperature of the attainable superheat produced by the decomposition was less than the apparatus sensitivity (about 0.5 K).

One further variant was observed (see Fig. 5). It is characteristic of glycerin and aqueous solutions of hydrogen peroxide. Here, as in Fig. 3, the lower the heating rate, the lower the temperature of the attainable superheat at a given pressure. However, in contrast to Fig. 3, the pressure to which we observed the temperature perturbation connected with boiling is approximately independent of the heating rate.

3. METHOD OF CALCULATING THE TEMPERATURES OF THE ATTAINABLE SUPERHEAT

Let us consider a mixture, the mole fraction of a thermally unstable substance for which is x_0. The mixture is heated at a constant pressure from the temperature T_0 at a constant rate: $T = T_0 + \dot{T}t$. In the process of heating the unstable substance decomposes in accordance with the following equation:

$$dC/dt = -C^m B \exp(-E/(RT)) \tag{9}$$

Here C is the mole concentration, t is time, m is the order of reaction, B is the pre-exponential factor, E is the activation energy, and R is the universal gas constant. The mole fraction of the thermally unstable substance is equal to $x = C/\sum C_i$, where C_i are the mole concentrations of the components of the mixture. The temperature of the attainable superheat can be expanded into a power series and delimited by the linear member,

$$T_*(x) = T_*(x_0) + \beta(x - x_0) \tag{10}$$

where β is a constant. By integrating Eq. (9) with an allowance for Eq. (10) and with the condition $E/kT_0 \gg E/kT_* \gg 1$, we obtain the dependence of the temperature of the attainable superheat on the heating time [11, 14, 15]:

$$T_*(t^*) = T_*(x_0) + \beta x_0 \left[1 - \exp\left\{ \left(-\frac{BRT_*^2}{E\dot{T}} \right) \exp\left(-\frac{E}{RT_*} \right) \right\} \right] \qquad (m = 1)$$

$$T_*(t^*) = T_*(x_0) + \beta \left[x_0 - \left\{ x_0^{1-m} - (1-m) \left(\frac{BRT_*^2}{E\dot{T}} \right) \exp\left(-\frac{E}{RT_*} \right) \right\}^{\frac{1}{1-m}} \right]$$

$$(m \neq 1) \tag{11}$$

To obtain Eq. (11) we used the obvious condition $T_*(x_0) = T_*(t^* = 0)$. An equation that is identical to Eq. (11) can be obtained for the dependence of the critical pressure on the heating time [18]. For it, the factor β in Eq. (11) should be replaced by γ, which must satisfy the following equation:

$$P_c(x) = P_c(x_0) + \gamma(x - x_0) \tag{12}$$

We suggest the following method for estimating the temperature of the attainable superheat of thermally unstable liquids in the processes of quick heating.

(1) The critical temperature T_c and the critical pressure P_c of a substance are measured or calculated. The techniques of measuring the critical constants of thermally unstable substances were reviewed by Ambrose and Young [19] and by Nikitin [20]. Various calculation methods were given, for example, in Refs. 21 and 22.

(2) The acentric factor $\omega = \lg[P_c/P_s(T/T_c = 0.7)] - 1$ is calculated, where P_s is the vapor pressure. If the experimental vapor pressures are unknown, rough estimates of the acentric factor are made using well-known methods [21].

(3) The liquid under study is considered stable, and the pressure dependence of the temperature of the attainable superheat is calculated using the principle of corresponding states [23]:

$$T_*(P, t^*=0) = 1 - \frac{1-P_r}{8.0698-1.73\ln A} + (0.01622+0.00778A-0.00049A^2) \times (1-P_r)^q - \frac{(35.7-8P_r)(1-P_r)^{1.34}}{1760-314.9\ln A} \times \ln\left(1-\frac{\lg J}{35.7-8P_r}\right) \tag{13}$$

Here $P_r = P/P_c$, $q = 1.7 - 0.1A$, $\ln A = 1.391 - 3.466\omega$, and $J/\mathrm{m}^{-3}\cdot\mathrm{s}^{-1}$ is the rate of nucleation.

(4) Now the liquid under study is considered unstable. The dependence of the temperature of the attainable superheat on the heating rate (the heating pulse length) is calculated by Eq. (11) if the kinetic parameters of the reaction of thermal decomposition m, E, B, and the factor β are well known. Otherwise, the dependence $T^*(t^*)$ is measured, as a minimum, at one pressure and the parameters m, E, B, and β are determined from it.

Let us calculate, as an example, the temperature of the attainable superheat of glycerin. The critical constants of glycerin have been measured in our laboratory [11]: $P_c = 7.5$ MPa and $T_c = 850$ K. The vapor pressures of glycerin are well known [24]; the estimated acentric factor is $\omega = 0.535$. The main products of the thermal decomposition of glycerin are water and acrolein but we failed to find in the literature the kinetic parameters of the decomposition reaction in the liquid phase at high temperatures. We calculated them from the experimental dependence of the temperature of the attainable superheat on the heating time at a pressure of 7.5 MPa using Eq. (11): $E = 75\ \mathrm{kJ\cdot mol^{-1}}$, $B = 3.177 \times 10^9\ \mathrm{s^{-1}}$, $m = 1$, and $\beta = 80$ K. The solid lines in Fig. 5 were calculated in the manner discussed above. Figure 5 shows that the proposed method describes the results of measurements well for high pressures and short heating times t^*. For long times and comparatively low pressures, the experimental temperatures of the attainable superheat are lower than the calculated ones. We see two reasons for this. First, at long times the molar fraction of the decomposition products is not small, and in Eq. (10) the second member should be taken into account. Second, at low pressures boiling-up does not go exclusively through homogeneous nucleation. The example with glycerin also demonstrates that estimation of the temperature of the attainable superheat of thermally unstable substances is difficult without direct measurements of this temperature at, at least, one pressure; for such substances, as a rule, the critical constants and the kinetic parameters of thermal decomposition are unknown.

4. METHOD FOR DETERMINATION OF THE KINETIC PARAMETERS OF THERMAL DECOMPOSITION REACTIONS

The kinetic parameters of a thermal decomposition reaction can be calculated using Eq. (11) from the experimental dependence of the temperature of the attainable superheat on the time t^* at a certain pressure. The advantage of the method, suggested over well-known ones, is the possibility to determine the kinetic parameters at high rates of heating (to $10^8\ \mathrm{K \cdot s^{-1}}$) and, therefore, at higher temperatures. Under heating at lower rates, the substance under investigation may decompose before sufficiently high temperatures are achieved. The shortcoming of the method is in the complex mathematical processing of the experimental data. In addition, the kinetic parameters determined in such a way are averaged over the interval from the temperature of the onset of decomposition to the temperature of the attainable superheat.

An example of calculating the kinetic parameters of the reaction of thermal decomposition for glycerin was given in the previous paragraph. The processing of the dependences $T_*(t^*)$ for aqueous solutions of hydrogen peroxide which were obtained for different mole fractions and pressures gave values of m from 0 to 0.66 and for E from 27 to 52 $\mathrm{kJ \cdot mol^{-1}}$ [25]. Literature data for the kinetics of decomposition of hydrogen peroxide in the liquid phase are rather contradictory. For the reaction order m , different authors [26, 27] give values from 0 to 2.3, and for molar activation energy E from 48 to $60.2\ \mathrm{kJ \cdot mol^{-1}}$. In the course of the homogeneous thermal decomposition of hydrogen peroxide, the reaction is unimolecular ($m = 1$) and begins with the disruption of the O–O bond, whose molar energy in a liquid phase by Serbinov's estimation [28] is 125 $\mathrm{kJ \cdot mol^{-1}}$. Thus, in our experiments the heterogeneous decomposition of hydrogen peroxide occurred at the surface of the platinum probe.

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