

THE PHENOMENON OF SUPERADIABATIC TEMPERATURES IN PROCESSES OF HOMOGENEOUS COMBUSTION OF GASES CAUSED BY FORMATION OF SUPER EQUILIBRIUM CONCENTRATION OF WATER

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Super adiabatic temperature (SAT) is commonly appreciated as the phenomenon observed upon combustion during which in the zone of chemical transformation the temperature is reached which exceeds the equilibrium one for the given system and conditions. The mechanisms of SAT formation, the forms of its existence, the systems in which it is recorded, are quite different [1]. The phenomenon of SAT is based on the heat exchange in two-phase systems, on the competition between the processes of molecular diffusion and thermal conductivity, and on the selective diffusion of fuel and oxidant. The striking examples of SAT are observed in the heterogeneous systems of filtrational combustion where SATs are determined by the heat-diffusion and convective characteristics of the system [2].

The present paper reports the SAT phenomenon of the poorly known type which is realized in homogeneous, gaseous systems and determined by formation of super equilibrium concentration of water as a result a competition between elementary chemical reactions in combustion zone (the kinetic phenomenon of SAT). The phenomenon of this type is taken as the nontrivial, natural property of the combustion process itself.

Manifestations of the kinetic SAT phenomenon have been observed earlier. Thus, the SAT was recorded in a series of works on the production of thin diamond films using rich flames $C_2H_2/H_2/O_2$ or CH_4/O_2 [3-5]. The study of the SAT by numerical methods [6] indicates that the phenomenon occurs in rich hydrocarbon mixtures: CH_4/air , CH_4/O_2 ; $C_2H_2/H_2/O_2$; C_2H_4/O_2 ; C_3H_8/air . It is concluded then that the phenomenon of SAT manifests itself only in hydrocarbon

flames. The superadiabatic temperatures in these hydrocarbon flames are associated with the processes of heat absorption caused by the endothermal reactions of dissociation of these large hydrocarbon molecules and H_2O in H_2 and OH .

It should be noted that the phenomenon under study is closely related to flame propagation limits. Figure 1 shows the dependences of equilibrium $T_{b,eq}$ and maximal $T_{b,max}$ flame temperatures on propane concentration in a mixture with air [7]. It is seen that the maximal flame temperature starts to exceed the equilibrium value in a mixture, containing 7% of propane. As

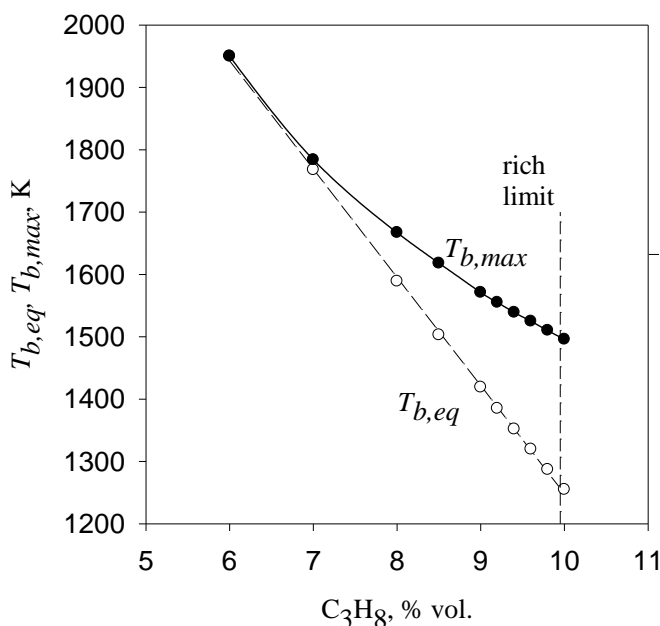


Fig. 1. Dependence of T_{max} and T_{eq} on propane concentration in flame C_3H_8/air . $T_0=298$ K, $p_0=0.1$ MPa.

the propane concentration increases, this difference increases and attains a maximal value of 241 K at the limit of flame propagation. In this work, also as well as in other our works mentioned in the text well checked methods, models, kinetic constants and codes were used.

It is demonstrated [8] that the extension of rich limit in methane-air mixtures at high pressures depends on the nonequilibrium of chemical processes at the limit, i.e., the development of SAT

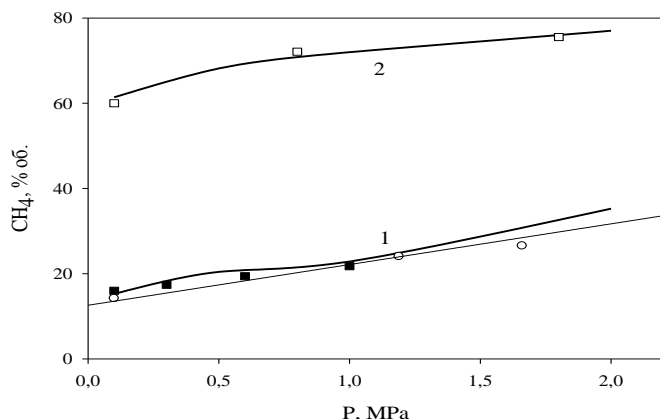


Fig. 2. Dependence of the rich flame propagation limit in CH_4/air (1) and CH_4/O_2 (2) mixtures on the initial pressure

in the zone of these flames [8]. This conclusion was verified using the methods of numerical flame simulation with regard to the kinetics of chemical reactions. The rich limits in the mixtures of methane with air and oxygen were determined within the pressure range of 0.1 – 2.0 MPa.

Figure 2 presents the experimental and calculated data on methane concentration in the limiting mixtures CH_4/air and CH_4/O_2 depending on the initial pressure P_0 at $T_0=300$ K [8]. The experimental and

calculated values of the limits are observed to be in fair agreement. In both of the cases, the limits expand with increasing initial pressure. The coefficients of diffusion and temperature conductivity are the determining parameters of laminar flame propagation velocity. In this regard, there is an interesting problem about possibility of manifestation of SAT in processes of burning without molecular heat and a lot of transfer. For this purpose we studied a problem of adiabatic spontaneous ignition of rich mixes of dimethyl ether with air with a constant pressure

without use of coefficients heat and a lot of transfer. This system has been chosen owing to the possibility of comparison: it is shown [9] that the flames of rich DME/air mixtures exhibit substantial SAT effect. The studies were performed using numerical methods. A 30% DME/air mixture was used ($\phi=6.12$) with the initial temperature $T_0=600$ K and constant pressure $p_0=0.1$ MPa [10]. The concentration of 30% DME corresponds to the near limiting mixtures (the rich limit of flame propagation under standard conditions equals 26.7% DME).

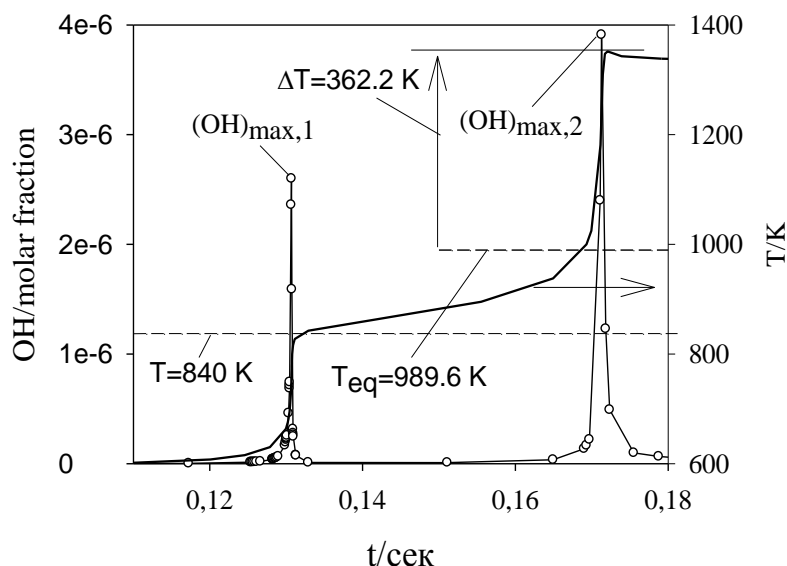


Fig. 3. Time dependences of OH concentration and temperature at adiabatic self-ignition of the mixture of 30% DME with air; $T_0=600$ K, $P_0=0.1$ MPa=const

temperature and OH concentration dependences on time upon self-ignition which includes two stages. At the end of the first stage the temperature is 840 K. The first maximum in the temporary profile of OH hydroxyl is reached after 0.13 s. The second peak is observed after a

short period of time (≈ 0.04 s). At the end of the second stage, the temperature reaches 1351.8 K and remains maximum during the entire process. This temperature exceeds equilibrium value by 362.2 K. Between the maxima, the hydroxyl concentration tends to zero. The character of hydroxyl peaks indicates that these are determined by the chain-thermal ignition. The two-stage self-ignition is recorded at the initial temperatures varying from 520 to 900 K. In this temperature range, the first stage runs out almost at a constant temperature of 840 K. With higher initial temperatures, the first stage degenerates.

Figure 4 depicts the dependences of H_2O , H_2 , CO , and CO_2 concentrations normalized to equilibrium values on current temperature upon self-ignition. Of interest are some peculiarities of concentration dynamics and first of all the rapidly increasing (direction is denoted with arrow) and abnormally high water concentrations. The equilibrium value of H_2O is reached already at $T=710$ K. When $T_{b,eq}=989.6$ K, the water concentration is almost three times as high as the equilibrium value. At maximal temperature, it is 6 times higher. On the contrary, no increase is actually observed in CO_2 concentration up to a first maximum of 1351.8 K. At this temperature the CO and CO_2 concentrations fail to reach their equilibrium values: the normalized value of CO concentration is 0.76, and that of CO_2 concentration amounts to 0.25.

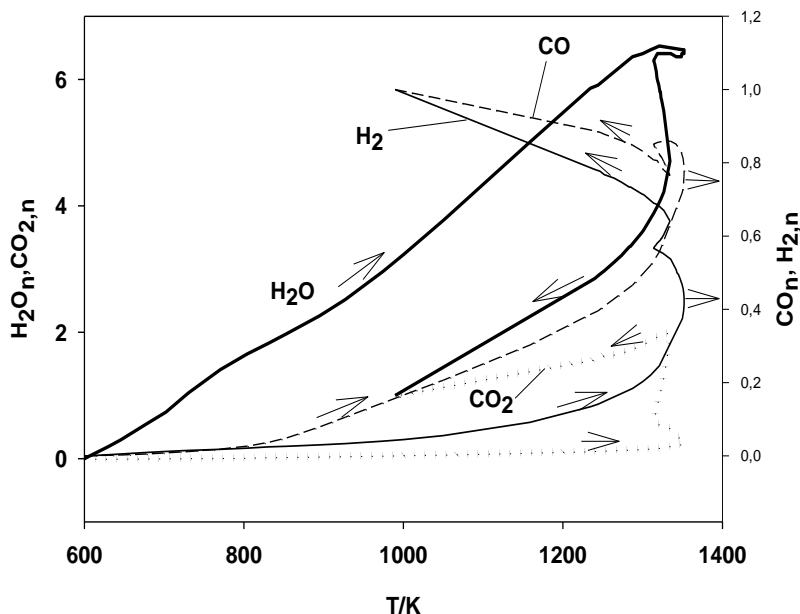


Fig. 4. Temperature dependence of H_2O , H_2 , CO , and CO_2 concentrations, normalized to equilibrium values, upon self-ignition. The mixture of 30% dimethyl ether with air. $T_0=600$ K, $p_0=0.1$ MPa=const.

This review discusses a novel, original type of SAT, the mechanisms and conditions of its formation, the origin of this phenomenon. The main peculiarity is the kinetics of chemical reactions with appearance of superadiabatic concentration of water as the dominating factor of the phenomenon. As for the processes of heat- and mass exchange, these are of secondary importance. Therefore, the SAT of this type may be called the kinetic SAT.

The SAT is based on the competition between chemical reactions for the rate and maximal heat emission at the exothermal stage of combustion processes (up to $T_{b,max}$).

In the rich hydrocarbon/oxygen mixtures, water is the basic product whose formation is followed by emission of the maximal amount of heat. Indeed, the oxygen concentration, in our case, determines the amount of emitted heat. One mole of oxygen may give either two moles of water or one mole of CO_2 , or two moles of CO . It is readily seen that water formation results in the greater amount of heat than CO or CO_2 formation. The formation of water in super equilibrium concentration is sure to lead to SAT. Consequently, the heating of combustion products and the contribution into $T_{b,max}$ are mainly caused by water formation. As compared to the slow processes of CO and CO_2 formation, a faster process of water production results in temperature rise and in greater amount of heat.

The studies on SAT in gradient-free concentration and temperature conditions (upon self-ignition) testify to a feasible formation of super equilibrium water at the early stages of the process up to $T_{b,max}$, whereas the CO and CO_2 concentrations compose only minor fractions of

equilibrium concentrations. These results are in agreement with the two determining characteristics of the competition responsible for SAT, that is, the rate and the maximal heat emission at the first stage of the process. The second stage after point with $T_{b,max}$ is of minor importance.

The proposed principle mechanism of kinetics SAT formation does not restrict the formation of SAT only to the rich hydrocarbon mixtures with oxygen and air. We have mentioned a feasible formation of SAT in the mixtures with ether and alcohols. Moreover, this mechanism allows the formation of SAT in the systems with other substances, fuels, and oxidants and not only at $\phi > 1$.

It is concluded then that taking account of SAT properties is rather promising for academic and practical applications due to a number of circumstances. First, many important combustion processes, e.g., laminar flame, propagation limits, flame ignition and extinction, etc., are determined, on the one hand, by the rate of Arrhenius reactions and, on the other hand, by maximal temperature, for our case, by $T_{b,max}$ rather than by $T_{b,eq}$. In this case, $T_{b,max}$ depends on both the thermodynamic and the kinetic data of elementary, chemical reactions, most of which are to be determined. On the other hand, the value of $T_{b,max}$ may be considered as a new parameter to control combustion processes. Thus, the kinetic phenomenon of superadiabatic temperatures should be taken as one of the actual problems of the up-to-date chemical physics.

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