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Quantum Phenomena in Ignition and Detonation at Elevated Density

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The influence of quantum effects on the processes of initiation of combustion and detonation of hydrogen and acetylene near the low-temperature limits at elevated pressures is analyzed. A theoretical consideration which allows quantification of the quantum corrections to the rate constants of endothermic reactions associated with an increase in the high-energy tail of the equilibrium momentum distribution function at high pressures is presented. This quantum effect is caused by a manifestation of the principle of uncertainty for the energy of the colliding particles at a high frequency of collisions. It is shown that significant deviations of experimentally observed ignition and detonation delay time from the predictions of kinetic calculations are quite well described by the proposed quantum corrections. This general mechanism should be considered in the safety problem with emergency emissions of hydrogen at nuclear power stations, as well as problems of the safe production and storage of hydrogen and acetylene, which have a fundamental importance for industry and power engineering.

Introduction.—Safety problems with the emergency emission of hydrogen at nuclear power stations, as well as problems of safe storage of hydrogen, which has fundamental importance for the development of hydrogen power engineering, are seriously complicated by the significant deviations of the experimental measurement of the detonation threshold and ignition delay time with the predictions of modern kinetic models [1–5]. With temperature decreasing and increasing of pressure, this divergence increases, and, at 700–800 K, the difference between the measured and calculated ignition delay reaches 10^2–10^3 [1,5]. Similar problems associated with the disagreement of experimental and theoretical results are observed when analyzing the explosion of other gaseous fuels [6].

Serious difficulties also raise the problem of the acetylene explosion hazard, dramatically increasing with growth of pressure [7,8]. Acetylene, widely used for various technical applications, has some important features. In contrast to other hydrocarbons, acetylene self-ignition and detonation could happen spontaneously without an oxidant. That feature originates from the high heat release of carbon condensation during pyrolysis of acetylene:

$$C_2H_2 \rightarrow 2C(\text{graphite}) + H_2 (+227 \text{ kJ/mol}). \quad (1)$$

Formation of a detonation wave of condensation during the thermal decomposition of acetylene was thoroughly investigated in recent work [9]. Such acetylene features significantly complicate the technologies of its production and storage.

It is notable that, in all these cases, the temperature dependence of the ignition delay time or induction of detonation initiation abruptly flattens as it approaches the low-temperature limit and with growth of pressure. Various

authors have attempted to explain the observed effects by the influence of unaccounted active impurities [1] or the inaccuracy of the measurements [5]. Nevertheless, a reasonable explanation for such a general and practically important phenomenon has not been proposed.

In recent papers [10,11], it was shown that, in view of quantum effects, the high-energy tail of the equilibrium particle velocities distribution function can have significant deviations from the classical Maxwell type, which leads to essential quantum corrections in the values of rate constants of the threshold reactions. These situations include the processes of vibrational-translational relaxation in low-temperature plasma, nuclear fusion in dense relatively low-temperature environments, and chemical reactions at elevated pressures. This effect is caused by the manifestation of the principle of uncertainty for the energy of the colliding particles at high collision frequency, so, as the role of quantum corrections increases with the growth of pressure, the energy threshold of the reaction and the mixture temperature decrease. A quantitative measure of the significance of the quantum correction is the ratio of the uncertainty of energy equal to the crossed Planck's constant, multiplied by the collision frequency to the threshold energy of the reaction E_r. This ratio is small compared with unity, but the contribution of quantum corrections to the reaction rate is obtained by multiplying this ratio by an exponential with exponent E_r/T [see (13) below]. Theoretically, the increase of the rate of threshold reactions was justified in the papers [10,11] for exothermic reactions. For the reverse reactions in the numerical calculations the equilibrium constants were used, which vary slightly due to the studied quantum effects in these conditions. This intuitive approach is justified in the present Letter for the

endothermic reactions, principally important for initiation of ignition and detonation.

   This Letter presents an analysis of the observed deviations in the hydrogen ignition delay time and the induction of detonation initiation of acetylene from the predictions of classic kinetic calculations by taking into account the quantum corrections to the rate constants of inelastic processes in the modeling approach developed in Refs. [10,11].

   The analysis of quantum corrections to the rates of chemical reactions.—The velocities of threshold chemical reactions are defined substantially by the kinetic energy of colliding particles, increasing with energy growth. Therefore, the dependence of the distribution function on the kinetic energy in the asymptotic region is extremely important when calculating the reaction rate. This is a particularly important area for endothermic reactions with high-threshold energy. As it is shown in Ref. [10], in a dense medium, where the mean free path of particles is small, quantum mechanics predicts the existence of the distribution function's power law of kinetic energy in the asymptotic region.

   The description of kinetic processes in dense matter must be based on a generalized distribution function of particles in the energy and momentum [11]. In a sufficiently general form, the equilibrium distribution function of the energy and momentum can be written as

$$f(E, \varepsilon) = n(E)\delta\gamma(E - \varepsilon, \varepsilon). \qquad (2)$$

Here $n(E)$ are the occupation numbers of levels with energy E [11], $\delta\gamma(E - \varepsilon, \varepsilon)$ is the spectral function describing the relationship between the total E and kinetic ε energy of the particle:

$$\delta_\gamma(E - \varepsilon) = \frac{1}{\pi}\frac{\gamma(E, \varepsilon)}{[E - \varepsilon - \Delta(E, \varepsilon)]^2 + \gamma(E, \varepsilon)^2} \qquad (3)$$

for an ideal gas—it is the δ function, for nonideal medium $\delta\gamma$ represents the Lorentzian linewidth; γ is the imaginary part of the retarded mass operator of the particle in the medium. The energy shift $\Delta(E, \varepsilon)$ is determined by its real part.

   The reaction rate under such a description is determined by a multidimensional integral [10], but for moderate temperatures the essential simplifications can be made:

$$\begin{aligned}
\langle\sigma V\rangle N_a N_b =& \frac{(4\pi)^2\sqrt{2m_a^3}\sqrt{2m_b^3}}{h^6}\exp\left\{-\frac{Q}{kT}\right\} \\
&\times \int_0^\infty dE_a \int_0^\infty d\varepsilon_a\sqrt{\varepsilon_a}\int_0^\infty dE_b \int_0^\infty d\varepsilon_b\sqrt{\varepsilon_b} \\
&\times n(E_a)\delta\gamma_a(E_a - \varepsilon_a, \varepsilon_a)n(E_b) \\
&\times \delta\gamma_b(E_b - \varepsilon_b, \varepsilon_b)V_{ab}\sigma(\varepsilon_p). \qquad (4)
\end{aligned}$$

Here Q is the energy absorbed in the reaction on one formed particle (reaction heat). The distribution function of the kinetic energy can be obtained by integrating the generalized distribution function:

$$\begin{aligned}
f(\varepsilon) &= \int_0^\infty f(E, \varepsilon)dE = \int_0^\infty n(E)\delta\gamma(E - \varepsilon)dE \\
&= \frac{1}{\pi}\int_0^\infty n(E)\frac{\gamma(E, \varepsilon)}{[E - \varepsilon - \Delta(E, \varepsilon)]^2 + \gamma(E, \varepsilon)^2}dE.
\end{aligned}$$

$$(5)$$

The interval of integration in (4) is divided on 2 areas: the region where the values of the total energy are less than the plasma temperature and the rest interval:

$$\begin{aligned}
f(\varepsilon) =& \frac{2}{\sqrt{\pi}(kT)^{3/2}}\left[\frac{1}{\pi\varepsilon^2}\int_0^{kT}\exp\left\{-\frac{E}{kT}\right\}\gamma(E, \varepsilon)dE \right. \\
&\left. + \exp\left\{-\frac{\varepsilon}{kT}\right\}\right] = f_{qp}(\varepsilon) + f_0(\varepsilon). \qquad (6)
\end{aligned}$$

For small values of the total energy E, the width of the Lorentzian function is defined as the sum of contributions of the elastic interaction with various components of the mixture. The linewidth of the component a can be calculated as follows, by using the approximation of the Lorentz gas [10]:

$$\gamma_a = \frac{\hbar}{2}\sum_l N_l\sigma_l(\varepsilon_{\text{pal}})V_{\text{al}}. \qquad (7)$$

Here ε_{pal} is the energy of the colliding particles of kinds a and l in the center of mass. To estimate the cross section of the adiabatic interaction of the molecules $\sigma_l(\varepsilon_{\text{pal}})$, the Lennard-Jones model is used, and then the scattering cross section depends on the energy of a power law:

$$\sigma_l(\varepsilon_{\text{pal}}) = \sigma_{0\text{al}}(E_r)\left(\frac{E_r}{\varepsilon_{\text{pal}}}\right)^t. \qquad (8)$$

The exponent is $t = 1/6$. As a result, the full distribution function can be written as

$$\begin{aligned}
f(\varepsilon_a) =& \frac{2}{\sqrt{\pi}(kT)^{3/2}}\left(\exp\left\{-\frac{\varepsilon_a}{kT}\right\} \right. \\
&\left. + \frac{\hbar(kT)^{3/2}}{2\sqrt{2\pi}\varepsilon_a^2}\sum_l\frac{N_l\sigma_{0\text{al}}E_r^t}{\sqrt{\mu_{\text{al}}}\varepsilon_{\text{pal}}^t}\right). \qquad (9)
\end{aligned}$$

Here μ_{al} is the reduced mass of interacting particles. The examples of the distribution function at different pressures and fixed temperature versus kinetic energy are shown in Fig. 1.

   Substituting the formula for the distribution function (9) in the expression for the rate constant of reaction (4), we get

$$\begin{aligned}
\langle\sigma V\rangle =& e^{-Q/kT}\int_0^\infty d\varepsilon_a\sqrt{\varepsilon_a}[f_0(\varepsilon_a) + f_{qp}(\varepsilon_a)] \\
&\times \int_0^\infty d\varepsilon_b\sqrt{\varepsilon_b}[f_0(\varepsilon_b) + f_{qp}(\varepsilon_b)]V_{ab}\sigma(\varepsilon_p). \quad (10)
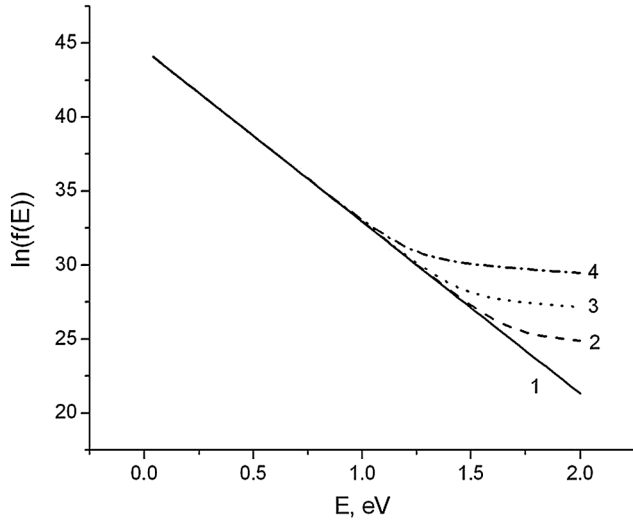\end{aligned}$$

FIG. 1.   The distribution functions versus kinetic energy. Line 1 is the Maxwellian distribution, and curves 2–4 are the distributions taking into account quantum corrections at different pressures: 2–1 bar, 3–10 bar, and 4–100 bar. The temperature is always 1000 K.

The reaction cross section with threshold energy E_r in the center of mass can be represented as

$$\sigma(\varepsilon_p) = \begin{cases} \sigma_r = \sigma_{r0}\left(\dfrac{E_r}{\varepsilon_p}\right)^r, & \varepsilon_p > E_r, \\ 0, & \varepsilon_p < E_r. \end{cases} \quad (11)$$

The summand with the classical Maxwellian distribution function in Eq. (10) determines the standard expression for the reaction rate constant. The following summands describe the role of the quantum effect and are asymptotically connected with the power-law distribution function. The reaction rate is defined by the following expression:

$$\langle \sigma V \rangle = \frac{2}{\sqrt{\pi}} V_T \left(\frac{E_r}{kT}\right) \sigma_{r0} e^{-(Q+E_r)/kT} + \frac{1}{r+t} \frac{\hbar \sigma_{r0}}{\pi}$$
$$\times \sum_l N_l \left[\frac{\sigma_{0al}}{m_a}\left(\frac{\mu_{ab}}{\mu_{al}}\right)^t + \frac{\sigma_{0bl}}{m_b}\left(\frac{\mu_{ab}}{\mu_{bl}}\right)^t\right] e^{-Q/kT}$$
$$= \langle \sigma V \rangle_{cl}\left\{1 + \frac{\hbar}{2\sqrt{\pi}(r+t)} \frac{P}{E_r} \frac{1}{V_T} e^{E_r/kT}\right.$$
$$\left.\times \sum_l C_l\left[\frac{\sigma_{0al}}{m_a}\left(\frac{\mu_{ab}}{\mu_{al}}\right)^t + \frac{\sigma_{0bl}}{m_b}\left(\frac{\mu_{ab}}{\mu_{bl}}\right)^t\right]\right\}. \quad (12)$$

Here, C_l is the share of the l component in the gas mixture and P the gas pressure.

Suppose that an endothermic reaction takes place only if the energy of colliding molecules is not lower than some threshold value, which is usually called activation energy $\Delta E_0 = E_r + Q$, and it is equal to the heat of reaction Q or over it. Therefore, the formula for calculating the reaction rate constant can be written like

$$k = k_0 e^{-\Delta E_0/kT}(1 + \varphi e^{E_r/kT}), \quad (13)$$

where $k = k_0 e^{-\Delta E_0/T}$ is the classical rate constant and φ the quantum correction:

$$\varphi = \frac{0.61 \cdot P^{(\text{atm})}}{(E_r^{(\text{grad})} + T)\sqrt{T}} \sum_l C_l\left[\frac{\sigma_{0al}}{10^{-15}} \frac{1}{\sqrt{A_a}}\left(\frac{A_b}{A_a + A_b}\right)^{2/3}\right.$$
$$\times \left(\frac{A_a + A_l}{A_l}\right)^{1/6} + \frac{\sigma_{0bl}}{10^{-15}} \frac{1}{\sqrt{A_b}}\left(\frac{A_a}{A_a + A_b}\right)^{2/3}$$
$$\left.\times \left(\frac{A_b + A_l}{A_l}\right)^{1/6}\right]. \quad (14)$$

It follows from these considerations that the deviation of the actual rate constant from its classical value increases linearly with the growth of pressure and decreasing of $T^{1/2}$.

When $\varphi e^{E_r/kT} \gg 1$, the temperature dependence of the rate constant flattens, and the effective activation energy becomes equal to the heat of reaction.

Analysis of results.—Before analyzing the influence of quantum effects on the process of hydrogen ignition, a careful analysis of existing kinetic mechanisms describing ignition of hydrogen-air and hydrogen-oxygen mixtures near low-temperature limits has been made.

To check the eligibility of various kinetic mechanisms, the most reliable experimental data of ignition delay in the mixture 4% H_2+ 2% O_2 + Ar behind a shock wave, presented in Ref. [3], has been selected (Fig. 2, black triangles). As a first approximation, the commonly accepted Gas Research Institute (GRI) mechanism [12] that includes 200 direct and reverse reactions, which is considered to be the most complete and reliable kinetic mechanism describing processes of ignition, combustion, and detonation, in various gaseous combustible mixtures, was chosen. Results of calculations of ignition delay for the same conditions as experiments [3] are shown in Fig. 2 by curve 1. A serious discrepancy between the results of experiments and calculations increasing with decrease of temperature is clearly seen. For the next approximation, the calculations on the improved GRI mechanism proposed in Ref. [5] has been performed (curve 2). One can see a much better coincidence of experiment and calculations; however, for temperatures lower than 1000 K, the discrepancy still increases.

Further analysis included the determining of key reactions that define temperature dependence of ignition delays. For this, the sensitivity of the chosen kinetic model to the most important basic reactions of the process having the greatest activation energies was analyzed. As a result of this sensitivity analysis, the 30 most important high-threshold reactions producing active radicals OH, H, O, HO_2, and H_2O_2 have been determined. The calculations of ignition delays with the rate constants of all these 30 reactions corrected by Eqs. (13) and (14) are shown in Fig. 2 by curve 3. It is clearly seen that accounting for quantum corrections essentially reduced the ignition delays at $T < 1000$ K; nevertheless, agreement with experimental data was not achieved. Therefore, the additional reaction
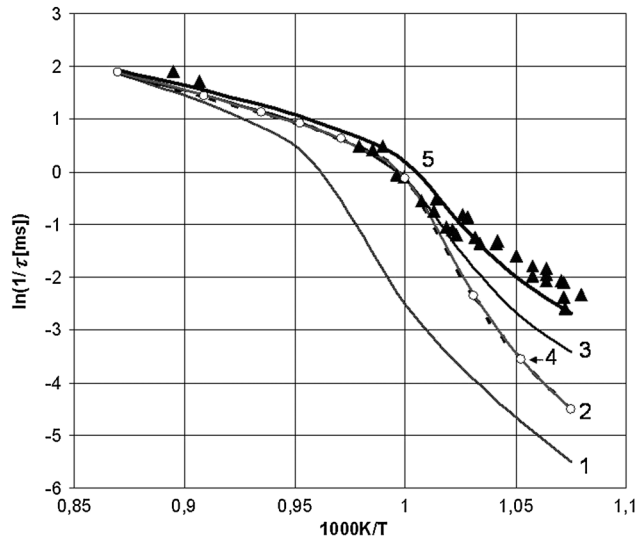
FIG. 2.   Arrhenius dependence of ignition delay in 4% H_2 + 2% O_2 + Ar mixture. ▲—experimental data [3]; curve 1—calculation with classical kinetic model (GRI-Mech-III) [12]; curve 2—calculation on modified GRI-Mech [5]; 3—calculations accounting for quantum corrections to modified GRI-Mech [5] for 30 high-threshold reactions; small empty circles 4—modified GRI-Mech with additional reaction [15]. Curve 5—calculations of ignition delays by modified GRI-Mech [5] + reaction (15) quantum corrected for all relevant reactions.

$$H_2 + O_2 \rightarrow 2OH,$$
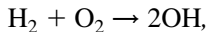
$$k = 1.3 \times 10^{13} \exp(-2.42 \times 10^4 K/T)[\text{cm}^3/\text{mol s}]$$

$$(Q = -9355 \text{ K}), \qquad (15)$$

which was not included in the improved GRI mechanism, due to very high activation energy, was considered. The calculations without quantum corrections have confirmed that reaction (15) really has no influence at these conditions (see circles 4 in Fig. 2). On the other hand, an account of quantum correction for this reaction (see curve 5) completely eliminates the contradiction between the experiment and calculation, i.e., makes it possible to correctly describe the process of ignition of hydrogen near the low-temperature limit.

The analysis of results of the initiation of detonation in acetylene has led to similar conclusions. The results of measurements of the induction time of condensed particle formation in mixtures containing 10% C_2H_2 in argon at pressures of 6 and 30 bar are shown in Fig. 3. The same graph for comparison shows the data of the classical study of Tanzawa and Gardiner [13], in which similar measurements were carried out in a mixture of 10% C_2H_2 in argon at much lower pressures, 0.3–0.75 bar. It is clearly seen that all data in the temperature range from 3200 to 2000 K are described with a high degree of accuracy by a single relation:

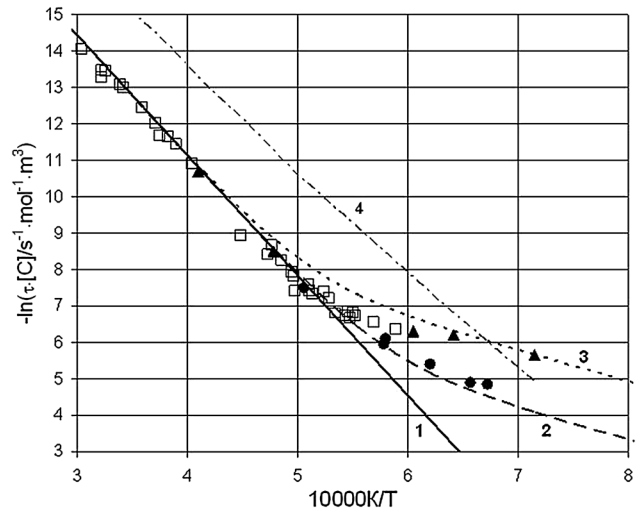$$\ln(\tau[\text{C}]) = -24.4 + 3.32 \times 10^4 \text{ K/T} \quad [\text{m}^3/\text{mol s}], \quad (16)$$

FIG. 3.   Arrhenius dependence of the induction periods of growth of the condensed phase in pyrolysis of C_2H_2. 1—Eq. (16). 10%C_2H_2 + Ar, $P = 6$ bar: ●—experiment, 2—calculation. 10%C_2H_2 + Ar, $P = 30$ bar: ▲—experiment, 3—calculation. 10%C_2H_2 + Ar, $P = 0.3$–0.75 bar: ☐—experiment [13]. 4—kinetic simulation of the rate of C_4H_2 formation.

where [C] is the total concentration of carbon (line 1 in Fig. 3). However, toward lower temperatures, all data indicate a significant flattening of the temperature dependence, and the induction times measured at a pressure of 30 bar are noticeably shorter than measured at 6 bar.

It is important to note that the activation energy of the processes determining the induction time at the temperatures of 2000–3200 K practically coincides with the activation energy of the primary reaction of pyrolysis of acetylene:

$$C_2H_2 + C_2H_2 \rightarrow C_4H_3 + H \quad (Q = -201 \text{ kJ/mol}). \tag{17}$$
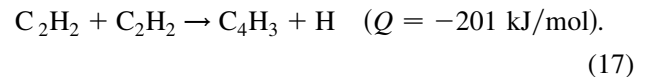
The rate constant of this reaction at similar conditions was measured with high accuracy in Ref. [14]:

$$k_{C_2H_2} = 1 \times 10^6 \ e^{-276[\text{kJ/mole}]/RT}[\text{m}^3/\text{mol s}]. \tag{18}$$

In accordance with the conclusions of Refs. [15,16], reaction (17) is the most high-threshold reaction, which determines the entire subsequent process of forming a detonation wave condensation at low temperatures and high concentrations of the reacting molecules. At temperatures below 2000 K, the experimental data show a flattening of the temperature dependence of the induction time, and at higher pressures this effect is stronger. The asymptotic behavior of the experimental data can be well approximated by straight lines with a slope, according to (13), determining the effective barrier of the reaction (including quantum corrections) equal to

$$Q_{\text{quant}} = 12\,700 \text{ K} \approx 106 \text{ kJ/mol}. \tag{19}$$

Checking the possible role of secondary reactions in the flattening of the temperature dependence of acetylene decomposition was carried out by a kinetic modeling scheme of 5 reactions from Ref. [16] including secondary reactions of C_2H_2 molecules with H atoms and C_2H radicals. The dash-dotted line 4 in Fig. 3 presents the results of calculations of the induction period of formation of the radical C_4H_2, which is considered as the basic "building block" in the further polymerization of hydrocarbons and the formation of carbon particles [9,13,16]. It is clearly seen that the decrease in temperature does not affect the activation energy for this process. Further calculations were made of the rate constants for reaction (17) taking into account the quantum corrections (13), which are presented in Fig. 3 as dashed curves 2 and 3. It is evident that, in this case, the calculations very well reproduce both the temperature at which the influence of the quantum effects begins and the stratification of pressure observed in experiments.

Conclusion.—Results of this work show that the essential discrepancy between the experimental data on the ignition delay time of hydrogen and the induction time of initiation of detonation in acetylene and classic kinetic calculations can be eliminated by accounting for the quantum corrections caused by the increase in the high-energy tail of the equilibrium momentum distribution function at high pressures. The developed model accounting for the quantum corrections to the rates of endothermic reactions allows evaluation of the delays of ignition and detonation correctly. Thus, the hazard of unpredictable explosions from hydrogen emission at nuclear stations, and from storage and production of hydrogen and acetylene, can be essentially reduced.

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