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CONDITIONS FOR SPHERICAL DETONATION IN HYDROGEN-OXYGEN MIXTURE

PACS 47.40.Rs

Initial detonation conditions required for fast chemical reactions to take place at the front of a spherical explosive wave have been determined. A simple relation describing the critical detonation temperature for various pressures in the hydrogen-oxygen mixture was obtained. Using the known formulas for a shock transition, the critical temperature was coupled with the initial conditions in a static environment, such as the pressure, temperature, and hydrogen content in the mixture.

Keywords: gas dynamics, a strong point explosion, blast, detonation, the system of Hugoniot equations, Semenov formula, Chapman–Jouguet regime, hydrogen-oxygen mixture, Haber scheme, Lewis scheme, kinetics of chemical reactions.

1. Introduction

A lot of researches were devoted to the emergence of detonation in a hydrogen–oxygen mixture [1–3]. At the same time, there are no works in the scientific literature dealing with the influence of initial conditions on the detonation process, when the blast wave propagates in the gas environment. In the previous work [4], a model was proposed for the transformation of an explosive spherical wave into a detonation wave in the course of a strong point explosion. The transition into the Chapman–Jouguet regime occurs at a certain distance R_x from the center, when the energy of the system becomes almost twice as high. The model supposes that the pressures at the front and in the explosion region are equal, which results in the appearance of a high temperature at the transition point behind the shock front, since the main part of the substance mass is concentrated in a thin layer of the blast wave. A simple formula was also proposed to determine the detonation wave velocity

in the explosive gas mixture. It allows one to calculate the velocity of a spherical wave, D , when some “portion” $c\%$ of a combustible gas burns out:

$$D = \left[\frac{(\gamma + 1)^2 (\gamma - 1)}{4\gamma} \frac{Qc\%}{\mu} \right]^{1/2}. \quad (1)$$

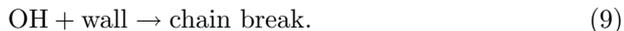
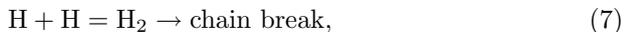
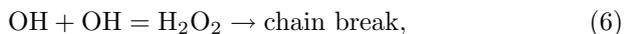
Here, Q is the combustion energy per mole of a combustible gas, $c\%$ the fraction of the burned-out gas (in percent), μ the molar mass of the mixture, and γ the adiabatic exponent for the given gas mixture. However, this model does not answer the question of whether the detonation will happen or not. For example, it is impossible to say whether the detonation will take place if the stoichiometric composition of the hydrogen–oxygen mixture is changed, and, if so, under which temperature conditions. This paper is aimed at solving this problem. Formula (1) turns out in relation with some formulas, in particular, with Semenov’s formula [5] concerning the probability of a branching in the chain reaction of hydrogen and oxygen, and allows the criterion for the transformation of a blast wave into detonation to be determined.

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2. Some Issues Concerning the Chemical Reaction Kinetics

The process of shock wave propagation is very fast. For instance, at the shock wave velocity $D = 2500$ m/s and the gas layer thickness $r = 0.005$ m, the shock compression of the substance lasts $t = 2 \times 10^{-6}$ s. This means that the dominant part of a compressed substance must react within such a short time interval; only in this case, we may talk about the supersonic burning as a self-supporting process [6]. Proceeding from this viewpoint, let us consider some issues of the kinetics of the chemical reaction of H_2 and O_2 .

First of all, it should be emphasized that the matter concerns chain reactions. The Haber scheme [5] and the development of a chain reaction with the Haber cycle look like



Reactions (2) and (3) correspond to the chain continuation, reactions (4) and (5) to the chain branching, and reactions (6)–(9) to the chain break. For reaction (2), the corresponding activation energy is supposed to be high, with not every collision of OH and H^2 resulting in the reaction between them. On the contrary, reaction (3) runs at every ternary collision [5]. The cycle of reactions (2) and (3) composes a repeating chain link. According to Haber, five to ten, on the average, cycles must pass before reaction (4) occurs and there emerges a branching in the chain. Let us consider reactions (3) and (4), which compete with each other. Denoting the rate of reaction (4) as W_4 and that of reaction (3) as W_3 , the probability of branching δ can be defined as the rate ratio

$$\delta = \frac{W_4}{W_3}. \quad (10)$$

In Semenov's book [5], the expression for δ is given as

$$\delta = \frac{2.5 \times 10^5 \times e^{-E_4/K^*T_2}}{[H_2]}, \quad (11)$$

where $[H_2]$ is the partial pressure of hydrogen in units of mm Hg (the numerical coefficient of 2.5×10^5 in the nominator is multiplied by 1 mm Hg; therefore, the pressure in the denominator is expressed in terms of mm Hg units), E_4 is the activation energy of reaction (4), K^* the gas constant, and T_2 the medium temperature (in Kelvin degrees). According to Semenov's data [5, 7], $E_4 = 16$ kcal/mol. Formula (11) shows that δ strongly depends on the temperature, so that the process can be substantially accelerated as the temperature grows. Moreover, it turns out that the cycle of reactions (2) and (3) with branching (4) does not describe the fastest mechanism. There may exist a case where

$$W_4 = W_3 \quad (12)$$

or

$$\delta = 1. \quad (13)$$

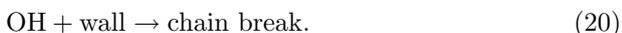
From the physical viewpoint, this means that the probability reaches the maximum, and the branching occurs at every chain link. Then the interaction scheme changes, reaction (4) substitutes reaction (3), and a transformation to the Lewis scheme takes place. In this case, we obtain



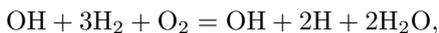
and so on, i.e. the temperature T_x , at which $\delta = 1$, is a critical one, when the kinetics of the interaction between hydrogen and oxygen undergoes qualitative changes.

Let us write down the Lewis scheme in the complete form [5],





In the summarized form, the cycle reaction looks like



and just this reaction is associated with the first fastest initial chain transformations that give rise to detonation.

3. Medium State at the Shock Wave Front. Critical Temperature

Let a point explosion took place in a gas medium. In our case, the matter concerns the reacting gas media; therefore, the blast wave extinction may occur more slowly than usually; or it can be absent altogether, because a strong mechanism of chain reactions between hydrogen and oxygen starts to play its role. The ultimate result depends on the physico-chemical properties of the gas mixture and the initial energy of explosion. From this point of view, the most interesting is the model of a transition of the strong (over-compressed) detonation into the Chapman–Jouguet regime.

The shock wave propagates from a region with a higher pressure into a region where the pressure is lower. The gas dynamics usually considers waves that have a sharp front. The region of shock-induced transition is a discontinuous surface, the shock wave front. The nonperturbed state is designated by subscript 1 and the perturbed one by subscript 2. The density ρ , pressure P , and temperature T change in a jump-like manner across the front. The relations between the parameters (P_1, T_1, ρ_1) and (P_2, T_2, ρ_2) follow from the Hugoniot relations (the conservation laws) and the equation of ideal gas [8]. It is known that

$$\frac{\rho_2}{\rho_1} = \frac{(\gamma + 1)M^2}{2 + (\gamma - 1)M^2}; \quad (21)$$

$$\frac{P_2}{P_1} = \frac{2\gamma M^2 - \gamma + 1}{\gamma + 1}; \quad (22)$$

$$\frac{T_2}{T_1} = \frac{(2\gamma M^2 - \gamma + 1)(2 + (\gamma - 1)M^2)}{(\gamma + 1)^2 M^2}, \quad (23)$$

where $M = D/c$ is the Mach number, D the shock wave velocity, c the sound velocity in the gas mixture, and $\gamma = C_p/C_v$ is the adiabatic exponent (for a two-atom ideal gas, $\gamma = 1.4$ [9]). The sound velocity can be determined by the formula $c = \sqrt{\gamma \frac{P}{\rho}}$, where P is the pressure in the medium, and ρ is the medium density. In such a manner, when a shock wave propagates in gases, we should consider the medium near (subscript 1) and at the front (subscript 2). To characterize the latter, we must know an important parameter, the shock wave velocity or the Mach number. In our case, using expression (1) and the formula for sound velocity,

$$c = \sqrt{\gamma \frac{P_1}{\rho_1}} = \sqrt{\gamma \frac{K^* T_1}{\mu}},$$

we obtain

$$M = \left[\frac{(\gamma + 1)^2 (\gamma - 1)}{4\gamma^2} \frac{Q c_{\%}}{K^* T_1} \right]^{1/2}. \quad (24)$$

Formula (24) describes the dependence of the Mach number on the adiabatic exponent γ , the combustion heat Q , the fraction (in percent) of the burned-out gas $c_{\%}$, and the initial medium temperature T_1 . By varying those quantities, it is possible to control the shock transition intensity.

Now, let us carry out a simple gedanken experiment. Let a spherical reactor contain a hydrogen–oxygen mixture with the initial parameters $(P_0, T_0 = 293 \text{ K})$. Let us heat up the mixture to the temperature $T_1 < T_1^*$, where T_1^* is the ignition temperature of the static medium, and initiate the reaction with the use of an explosion. We should observe a continuous transformation of a blast wave into the detonation of the hydrogen–oxygen mixture. At the wave front, the medium parameters are (P_2, T_2) . Let

$$T_2 = T_x, \quad (25)$$

i.e. the critical temperature T_x is attained, and the reaction develops, being driven by the chain reaction mechanism according to the Lewis scheme. In order to determine the critical temperature T_x , let us use formula (11),

$$\delta = \frac{2.5 \times 10^5 \times e^{-E_4/K^* T_2}}{[\text{H}_2]} = \frac{2.5 \times 10^5 \times e^{-E_4/K^* T_x}}{[\text{H}_2]}.$$

Taking into account that $\delta = 1$, we obtain the transcendental equation for the critical temperature T_x

$$\frac{2.5 \times 10^5 \times e^{-E_4/K^*T_x}}{[\text{H}_2]} = 1, \quad (26)$$

where

$$[\text{H}_2] = c\% P_2 \quad (27)$$

is the partial hydrogen pressure (in mm Hg units) at the shock wave front [10], P_2 is the total pressure in the mixture (in mm Hg units) at the shock wave front, and $c\%$ the hydrogen content in the mixture (in percent). With regard for Eq. (27), we obtain

$$\frac{2.5 \times 10^5 \times e^{-E_4/K^*T_x}}{c\% P_2} = 1. \quad (28)$$

Let us express P_2 in the denominator of Eq. (28) in terms of known quantities. Before the reaction started (the initiation of the explosion), the gas mixture pressure was P_0 , and its temperature was $T_0 = 293$ K. As the mixture is heated up to T_1 , its pressure increases to

$$P_1 = P_0 \frac{T_1}{T_0}. \quad (29)$$

From Eq. (22), it follows that

$$P_2 = \frac{2\gamma M^2 - \gamma + 1}{\gamma + 1} P_1, \quad (30)$$

or, in view of Eq. (29),

$$P_2 = \frac{(2\gamma M^2 - \gamma + 1)P_0 T_1}{(\gamma + 1)T_0}. \quad (31)$$

The temperature T_1 in formula (31) is expressed in terms of T_x and the Mach number M as follows:

$$\frac{T_x}{T_1} = \frac{(2\gamma M^2 - \gamma + 1)(2 + (\gamma - 1)M^2)}{(\gamma + 1)^2 M^2}. \quad (32)$$

Whence, we obtain

$$T_1 = \frac{(\gamma + 1)^2 M^2 T_x}{(2\gamma M^2 - \gamma + 1)(2 + (\gamma - 1)M^2)}, \quad (33)$$

or, taking Eq. (33) into account,

$$P_2 = \frac{(\gamma + 1)M^2 T_x P_0}{T_0(2 + (\gamma - 1)M^2)}. \quad (34)$$

The denominator in formula (28) also includes the hydrogen content $c\%$. If we assume that all hydrogen in the gas mixture burns out, we can express $c\%$ using the Mach number (Eq. (24)) and the temperature of the gas medium T_1 ,

$$c\% = \frac{4\gamma^2 M^2 K^* T_1}{(\gamma - 1)(\gamma + 1)^2 Q}, \quad (35)$$

or, in accordance with Eq. (33),

$$c\% = \frac{4\gamma^2 M^4 K^* T_x}{(\gamma - 1)(2\gamma M^2 - \gamma + 1)(2 + (\gamma - 1)M^2)Q} \quad (36)$$

(in this case, we impose a restriction on the gas mixture composition, $0 < c\% \leq 0.66$). From Eq. (27) and using Eqs. (36) and (34), we obtain the partial pressure of hydrogen at the shock wave front,

$$[\text{H}_2] = \frac{4\gamma^2(\gamma + 1)M^6 K^* P_0}{(\gamma - 1)(2\gamma M^2 - \gamma + 1)(2 + (\gamma - 1)M^2)^2 Q T_0} T_x^2. \quad (37)$$

Then, formula (26) reads

$$\begin{aligned} \frac{2.5 \times 10^5 \times e^{-E_4/K^*T_x}}{[\text{H}_2]} = 1 &\Rightarrow T_x^2 = \\ &= \frac{2.5 \times 10^5 Q T_0 (\gamma - 1)(2\gamma M^2 - \gamma + 1)(2 + (\gamma - 1)M^2)^2}{4\gamma^2(\gamma + 1)K^* P_0 M^6} \times \\ &\times \exp\left(-\frac{E_4}{K^*T_x}\right). \end{aligned}$$

Hence, we obtained the dependence

$$\begin{aligned} T_x^2 &= \frac{2.5 \times 10^5 Q T_0 (\gamma - 1)}{4\gamma^2(\gamma + 1)K^* P_0} \times \\ &\times \frac{(2\gamma M^2 - \gamma + 1)(2 + (\gamma - 1)M^2)^2}{M^6} \exp\left(-\frac{E_4}{K^*T_x}\right), \end{aligned} \quad (38)$$

which connects the initial pressure in the medium and the Mach number with the critical temperature at the shock wave front.

4. Results and Their Discussion

After the substitution of the corresponding numerical values of physical parameters of the hydrogen-oxygen mixture and taking into account that $\gamma = 1.4$, $Q = 286.5$ kJ/mol, $K^* = 8.31$ J/mol/K, $E_4 = 16 \times 10^3 \times 4.19$ J/mol, and $T_0 = 293$ K, Eq. (38) reads

$$T_x^2 = \frac{5.38 \times 10^{10}(2.8M^2 - 0.4)(2 + 0.4M^2)^2}{P_0 M^6} \times e^{-8067/T_x}. \tag{39}$$

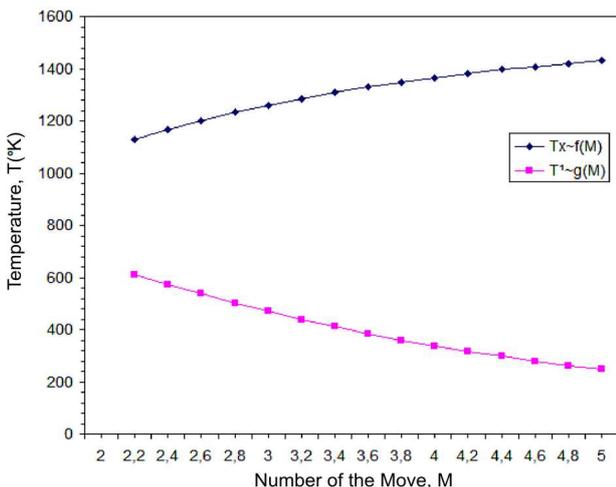
Using this expression, let us calculate the critical temperature for two Mach numbers, (i) $M = 2.15$ and (ii) $M = 4.78$, i.e. for shock waves of two types, but at the fixed initial pressure $P_0 = 60$ mm Hg. From practical reasons, let us select a certain interval and assume $M = 2.15$ to be a minimum in it. At the same time, the value $M = 4.78$ was selected as the largest one obtained from expression (24) at the following parameters: $c\% = 0.66$, $T_1 = T_0 = 293$ K, and $\gamma = 1.4$.

In the first case ($M = 2.15$ and $P_0 = 60$ mm Hg),

$$T_x^2 = 1.69 \times 10^9 \times e^{-8067/T_x}. \tag{40}$$

In the second one ($M = 4.78$ and $P_0 = 60$ mm Hg),

$$T_x^2 = 5.93 \times 10^8 \times e^{-8067/T_x}. \tag{41}$$



Dependences of the critical temperature at the shock wave front, $T_x \sim f(M)$, and the temperature of static medium $T^1 \sim g(M)$, at which the detonation is possible, on the Mach number at a fixed pressure $P_0 = 60$ mm Hg

The transcendental equations were solved with the use of the software package “Consortium Scilab (Inria, Enpc)” with the program code “Scilab-4.1.2”. After the corresponding calculations, we obtained $T_x = 1120$ K for the first case and $T_x = 1420$ K for the second one.

The interval of researches can be expanded to determine the critical temperatures for Mach numbers within the interval [2, 5] with an increment of 0.2. Only real-valued roots, which have a physical sense, must be taken into consideration. The corresponding plot for the dependence $T_x = f(M)$ at $P_0 = 60$ mm Hg is shown in Fig. 1. One can see that the critical temperature grows nonlinearly with the Mach number. This behavior is not of surprise. The stronger the shock wave, the higher is the pressure at its front, and the higher is the probability of the chain break. As a result, we obtain the critical temperature growth, because the probability of chain break can be compensated only by the probability of chain branching, which increases with the medium temperature. However, this is not the main point. Knowing the critical temperature and the Mach number, it is possible to determine the initial temperature of the gas medium required for the detonation to take place. In other words, it is possible to determine such a temperature T^1 in front of the shock wave front that the corresponding wave would stimulate the detonation. Using expression (23), let us plot the dependence of T^1 on M at $P_0 = 60$ mm Hg (Figure). It allows us to determine the initial temperature of the medium, at which the detonation of the gas mixture becomes possible for the given Mach number. Moreover, in accordance with Eq. (24), the initial temperature and the known Mach number determine the hydrogen content. Hence, the critical temperature is unambiguously related with the Mach number and, therefore, with the initial parameters of the hydrogen-oxygen mixture.

5. Conclusions

The expression obtained for the critical temperature is the simplest criterion for the transformation of the blast wave into a detonation one. At this temperature, $T_2 = T_x$ if $\delta = 1$, i.e. the probability of branching becomes maximum for the scheme of chain reactions with the hydrogen-oxygen interaction, which was considered above. The obtained Eq. (38) allows

Table 1. Parameter changes at the shock transition ($T_1 = 273$ K and $P_0 = 60$ mm Hg)

| Gas mixture | T_1 , K | M | T_2 , K | T_x , K |
|---------------------------|-----------|------|-----------|-----------|
| 66.6% H_2 + 33.3% O_2 | 273 | 4.95 | 1558 | 1427 |
| 60% H_2 + 40% O_2 | 273 | 4.72 | 1438 | 1420 |
| 50% H_2 + 50% O_2 | 273 | 4.31 | 1241 | 1390 |

Table 2. Parameter changes at the shock transition ($T_1 = 373$ K and $P_0 = 60$ mm Hg)

| Gas mixture | T_1 , K | M | T_2 , K | T_x , K |
|---------------------------|-----------|------|-----------|-----------|
| 66.6% H_2 + 33.3% O_2 | 373 | 4.23 | 1648 | 1384 |
| 60% H_2 + 40% O_2 | 373 | 4.04 | 1523 | 1365 |
| 50% H_2 + 50% O_2 | 373 | 3,70 | 1339 | 1339 |

the sought value to be determined as a function of the Mach number, provided that the initial pressure is fixed.

The critical temperature is the threshold of a detonation in a gas mixture, because the supersonic burning is impossible at temperatures below it. For example, let us analyze gas mixtures with different hydrogen contents of 66.6, 60, and 50%, and the temperature of static medium $T = 273$ K (Table 1). Comparing the T_2 - and T_x -values, we come to a conclusion that the process, which is of interest for us, occurs only in the first two cases. However, it is enough to raise the initial temperature ($T_1 = 373$ K) for the detonation to become possible at lower hydrogen concentrations (Table 2).

The practical results testify that the conditions for the emergence of spherical detonation have a drastic dependence on the temperature and the mixture composition. The relation obtained in this work allows the critical values of those parameters to be determined and, in such a manner, to stimulate the regime of supersonic burning in the hydrogen-oxygen mixture.

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Received 08.01.13.

Translated from Ukrainian by O.I. Voitenko

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УМОВИ ВИНИКНЕННЯ СФЕРИЧНОЇ ДЕТОНАЦІЇ В ВОДНЕВО-КИСНЕВІЙ СУМІШІ

Резюме

Метою роботи було визначення початкових умов детонації, необхідних для швидких хімічних перетворень на фронті вибухової сферичної хвилі. Отримано просте співвідношення, що дозволяє визначити критичну температуру для різних тисків воднево-кисневої суміші. Використовуючи вже відомі формули ударного переходу, стало можливим пов'язати критичну температуру з початковими умовами нерухомого середовища і тим самим відповісти на запитання чи відбудеться детонація при заданих значеннях тиску, температури та процентного співвідношення водню в суміші.