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Reduction of the Hydrogen Oxidation Mechanism Using Thermodynamic Analysis †

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Abstract

The growing interest in hydrogen as an alternative fuel for advanced aviation engines highlights the need for simplified combustion mechanisms suitable for modeling complex hydrodynamic, flame propagation, and detonation processes. A thermodynamic analysis method, accounting for both thermodynamic and kinetic factors, was applied to identify the most significant reactions in the detailed hydrogen combustion scheme (68 reactions). This analysis highlighted eight key reactions, for which rate constants were refined by matching the calculated combustion kinetics of a stoichiometric $H_2 + O_2$ mixture to experimental data. The resulting reduced mechanism M-I (12 reversible reactions) shows only minor deviation from the experimental ignition limits. Further exclusion of the two least contributing reactions (mechanism M-II) leads to significant errors in the upper ignition limit at pressures above 10 mmHg. The proposed thermodynamic approach enables effective reduction of the hydrogen combustion mechanism while maintaining sufficient accuracy for applied modeling tasks.

Keywords: thermodynamic analysis; hydrogen oxidation; reduced kinetic mechanism; ignition limits; reaction rate constants

1. Introduction

Several methods have been proposed for reducing detailed mechanisms. One approach involves determining the relative significance of reactions by using the values of $\partial y_i/\partial k_j$ or $\partial \ln y_i/\partial \ln k_j$, which characterize the sensitivity of the concentration y_i of the i-th component to the uncertainty of the rate constant k_j of the j-th reaction. For the rapid calculation of these values, nonlinear Fourier analysis [1] and Green's function methods [2] have been suggested. However, due to their high complexity and low efficiency, this approach has not gained widespread application. The work [3] proposes a method for reducing the dimensionality of the kinetic scheme based on identifying slowly changing manifolds of certain combinations of variables corresponding to the eigenvalues of the Jacobian matrix of the kinetic scheme with the smallest negative real parts. Specifically, all linear manifolds corresponding to zero eigenvalues, i.e., conservation laws, are identified.

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Nevertheless, there are no documented examples in the literature of the consistent application of any method for reducing the kinetic scheme of hydrogen combustion and comparing it with experimental data under various conditions.

The present work aims to extract a simplified mechanism from the comprehensive hydrogen combustion mechanism, consisting of as few reactions as possible, while still adequately describing the experimental data. The experimental data selected include Koval'sky's kinetic experiment [4], and the ignition limits determined by Lewis and von Elbe [5] and by Egerton and Warren [6].

2. Methods

The oxidation reaction of hydrogen has been investigated both experimentally and theoretically [5,7]. The maximum mechanism, defined for the hydrogen–oxygen system with a set of species including H_2, O_2, OH, H, O, HO_2, H_2O, and H_2O_2, consists of all possible linearly independent reactions and includes 30 reversible reactions [8].

Using the maximum hydrogen combustion scheme (30 reversible reactions + 4 reactions involving radical-wall interactions), the upper and lower values of the ignition limits were obtained based on the data from [8]. A comparison of the results with the experimental data of Lewis and von Elbe [5] and Egerton and Warren [6] is presented in Figure 1. The observed variation in the ignition limits calculated using the maximum mechanism is attributed to the relatively low accuracy in determining the parameters of the elementary reactions within this mechanism. The use of the maximum mechanism [8] does not allow for a precise representation of the experimental data [5,6] and requires substantial computational resources, further highlighting the relevance of the present work.

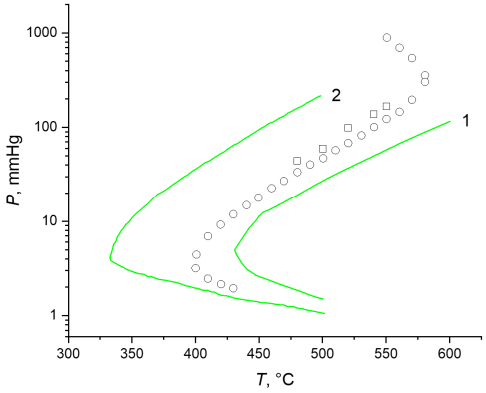


Figure 1. Ignition limits of a stoichiometric mixture of H_2 and O_2. Lines—calculation by the maximum mechanism [8]: curve 1—upper values of the rate constants; curve 2—lower values; ○—experimental data [5]; and □—experimental data [6].

The application of thermodynamic analysis methods [9] allows for the assessment of the thermodynamic contribution of each elementary stage of the maximum mechanism of hydrogen combustion with oxygen. This is achieved using the formula:

$$q_j = \frac{\left(\overline{\omega_j^+} - \overline{\omega_j^-}\right) ln\left(\overline{\omega_j^+} / \overline{\omega_j^-}\right)}{\sum_j \left(\overline{\omega_j^+} - \overline{\omega_j^-}\right) ln\left(\overline{\omega_j^+} / \overline{\omega_j^-}\right)} \quad (1)$$

where q_j is the non-equilibrium thermodynamic characteristic representing the thermodynamic contribution of the j-th stage and the j-th stage consists of both the forward and reverse reactions, with rates denoted as $\overline{\omega_j^+}$ and $\overline{\omega_j^-}$, respectively.

For the selection of elementary reactions, this quantity proved to be more representative than those mentioned earlier in the article, as it accounts for both the thermodynamic factor

$ln(\overline{\omega}_j^+/\overline{\omega}_j^-)$, which describes the deviation of the reacting system from equilibrium, and the kinetic factor $(\overline{\omega}_j^+ - \overline{\omega}_j^-)$, which characterizes the rate of approach to equilibrium.

The computed thermodynamic contributions of all reactions as functions of time for the maximum mechanism allow for conclusions regarding the role of specific reactions at different moments. Let us consider reactions 1, 18, 22, and 23, along with reaction 9 (from the maximum mechanism [8]), which can be regarded as initiating reactions. For the experimental conditions outlined in [4], the kinetic calculations of the combustion of a stoichiometric mixture at a temperature of 430 °C and 5 mmHg, along with the thermodynamic contributions of these reactions, indicated that reaction 1 undoubtedly plays a significant role at the onset of the process and serves as the primary initiating reaction.

3. Results and Discussion

Through thermodynamic analysis of the maximum mechanism [8], reactions were selected whose contribution within a certain time interval is at least 0.4, resulting in a reduced reaction scheme consisting of eight reactions (numbers 1, 2, 3, 4, 8, 11, 16, 32 according to [8]).

The parameters of the eight reactions describing the kinetics of hydrogen combustion were refined. All refined rate constants for the forward and reverse reactions are consistent with the thermodynamic equilibrium constants. By substituting the refined parameters of the eight hydrogen combustion reactions into the maximum mechanism, the refined maximum hydrogen combustion scheme [8] was obtained, which provides a good description of the experimental data [4] (Figure 2).

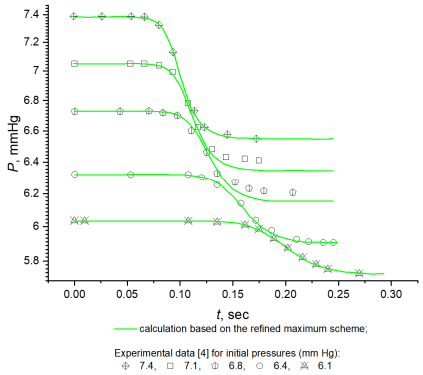


Figure 2. Kinetic curves of combustion of a stoichiometric oxygen–hydrogen mixture: lines—calculation by the refined maximum scheme and symbols—experimental data [4] for initial pressures of 7.4, 7.1, 6.8, 6.4 and 6.1 mmHg.

The results of calculating the ignition limits using the refined maximum mechanism and the reduced mechanisms M-I and M-II, as well as the ignition limit values obtained from the critical conditions analysis, are presented in Figure 3 in comparison with the experimental data of Lewis and von Elbe [5] and Egerton and Warren [6]. Reducing the scheme from 34 to 12 reversible reactions (mechanism M-I) results in a relatively small deviation from the experimentally established ignition limits. However, the exclusion of reactions 18 and 33 (mechanism M-II), which have the smallest contributions among the remaining reactions, leads to a significant deviation of the upper ignition limit at pressures above 10 mmHg (Figure 3, curve 3).

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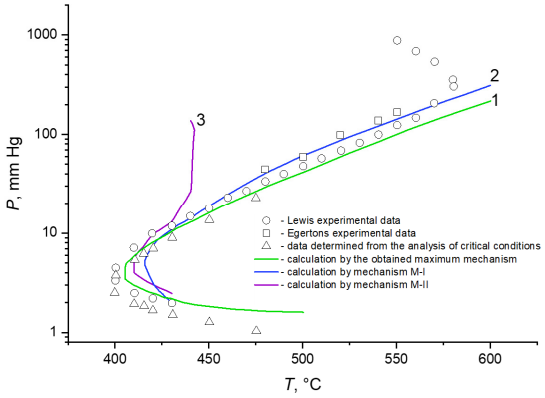


Figure 3. Ignition limits of a stoichiometric mixture of H_2 and O_2: ○—experimental data [5]; □—experimental data [6]; △—ignition limits determined from the analysis of critical conditions; and lines—calculation by the refined maximum mechanism (curve 1), by mechanism M-I (curve 2) and by mechanism M-II (curve 3).

4. Conclusions

The thermodynamic analysis conducted in this work on the maximum hydrogen combustion scheme (which includes 68 reactions) allowed for the identification of the eight most significant reactions. The use of the refined constants of these reactions in the maximum scheme enables the description of all experimental kinetic curves of Koval'sky [4] using a single set of reactions, thereby confirming the reliability of their determination. By excluding the reactions with a lower thermodynamic fraction, the M-I mechanism was obtained, which includes 12 reactions and allows a reliable description of the experimental data on ignition limits and kinetic curves of oxidation.

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