The effect of the composition of elementary chemical reactions and the uncertainty of the rate constants on the accuracy of calculating the rate of hydrogen oxidation

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Abstract. A table of twenty-four elementary reactions of the hydrogen-oxygen mixture combustion process is compiled. For each reaction, the published values of several rate constants are given, which can differ by tens of times. The influence of the uncertainty in the values of the rate constants on the accuracy of calculations of the hydrogen burning rate at temperatures of 2000 K, 2400 K, and 3000 K is determined. For each temperature, the initial composition of the mixture in calculating the combustion rate is assumed to be equilibrium. The evaluation of the influence of the rate constants on the rate of the hydrogen combustion reaction is determined by the adopted procedure by changing the reaction rate of the active centers and the reaction product depending on the values of the rate constants of the elementary reactions.

Introduction
In connection with the development of hydrogen energy issues of burning hydrogen are given a lot of attention. The combustion mechanism has been thoroughly studied. However, due to the high combustion temperature and explosion hazard, hydrogen combustion experiments were carried out mainly at low pressures. To reduce the combustion temperature, air is used as an oxidizer, as well as mixtures of oxygen diluted with inert gases (argon, helium). In recent years, studies have been carried out to burn hydrogen at higher pressures. When burning hydrogen, up to forty elementary chemical reactions are observed. At present, it is firmly established that hydrogen combustion takes place through a chain branching reaction, with the role of active centers played by the particles H, O, OH, HO₂ [1–3].

In studies on the combustion of hydrogen [4–10], for most elementary reactions, the values of several rate constants are published, which can differ by more than ten times. In the description of the studies [4] it is noted that the results of experiments that are performed on the same experimental installations under the same conditions can differ substantially. It is necessary to carefully compare the calculated models with the experimental data by carefully considering the uncertainties in the measurements, as well as the adopted initial conditions. It is necessary to carry out additional studies of reactions that have not received adequate attention.

To analyze the combustion mechanism, it is necessary to have an exhaustive list of reactions [4–8, 10–15, 19], since the sensitivity to the rate constants should be determined both at low temperatures and at high pressures. And the sensitivity of each elementary reaction can be different under different combustion conditions. The effect of the uncertainty of the rate constants of elementary reactions at low combustion temperatures of hydrogen carried out in [11, 14–19]. Most experiments are carried out at low pressures. At high pressures separate experiments were carried in [10].
In order to choose the composition of elementary reactions, it is necessary to determine their sensitivity to the rate constants for each elementary reaction, including for those little used in the studies. The rate constants of elementary reactions with high sensitivity should be determined with high accuracy, since they exert a decisive influence on the results of calculating the total rate of the combustion reaction. To reduce the uncertainty of the rate constants of elementary reactions over a wide range of pressures and temperatures for undiluted mixtures, additional investigations are required.

Methodical provisions

The most important quantitative kinetic characteristic is the rate of chemical reaction

$$\frac{dc}{dt} = - \frac{d}{dt} \left( \frac{N}{V} \right),$$

where \(N\) – the amount of substance, mol; \(V\) – the volume, cm\(^3\); \(t\) – the time, s; \(c\) – the concentration of the substance, mol/cm\(^3\).

The dependence of the chemical reaction rate on the temperature and concentration of reagents is given by

$$\frac{dc}{dt} = kc^n,$$

where \(k\) – the rate constant of the chemical reaction; \(c^n\) – the concentration of the substance, \(r\) – the order of the reaction, which may be equal to the stoichiometric chemical reaction coefficients.

The effect of the temperature and nature of the reactants on the rate of chemical reaction is described by the Arrhenius equation, which relates the rate constant of the chemical reaction to the temperature and activation energy \([1–4, 7]\).

$$k = Ae^{\frac{-E_a}{RT}} = A_n T^m \exp\left(\frac{-E_a}{RT}\right),$$

where \(A\) – the pre-exponential factor; \(E_a\) – the activation energy; \(R\) – the universal gas constant (1.986 cal/(mol·K)); \(T\) – the absolute temperature. The factor \(A\) is slightly dependent on the temperature (for the given reaction) and is assumed to be constant in individual calculations. \(A\) reflects the total number of collisions of particles per unit time, as well as the probability of the decay of the so-called “activated complex” into the initial substances. The temperature dependence of the factor \(A\) in \([7]\) is represented by the dependence \(A = A_0 T^m\), where \(m\) – the exponent, \(\exp\left(\frac{-E_a}{RT}\right)\) – the factor characterizes the fraction of particles that have sufficient energy to enter the reaction (the fraction of active molecules). The rate constants are determined experimentally.

To study the kinetics of hydrogen burning, an important indicator is the choice of the composition of the elementary combustion reactions, as well as the accuracy of the reaction rate constants.

To analyze the effect of the rate constants of elementary chemical reactions on the overall rate of the hydrogen combustion reaction, table 1 of elementary chemical reactions is compiled.

Table 1 lists twenty-four elementary chemical reactions. For each reaction, up to three of the rate constants published in \([3–19]\) are presented. Each of these reactions is regarded as an independent chemical reaction with its original reagents and products \([1–5]\). For each elementary reaction, the rate constants at 2000, 2400, and 3000 K are calculated from all available initial data. As follows from the table, even for the same elementary reaction and temperature, the rate constants can differ substantially. In the table at a temperature of 3000 K, the ratio of the maximum rate constant to the minimum value is calculated for each reaction. The value of these ratios for individual reactions can be from 1 to 100.

The rate of formation and death of the active particles of the hydrogen combustion reaction for the stoichiometric hydrogen-oxygen mixture at 2000, 2400 and 3000 K without dilution with the inert gas mixture is calculated using the rate constants of table 1 and the molar concentrations of table 2. The change in the combustion temperature is accomplished by cooling the combustible mixture.
Table 1. The rate constants of elementary chemical reactions of hydrogen combustion.

| No. | Reactions                        | A     | n      | E      | Ref     | 2000 K      | 2400 K      | 3000 K  |
|-----|---------------------------------|-------|--------|--------|---------|-------------|-------------|---------|
| 1   | \( H + O_2 = OH + O \)         | 2.06-10^14 | -0.097 | 15022  | 4       | 2.2×10^12  | 4.1×10^14  | 7.6×10^14 |
| 2   | \( O + H_2 = OH + H \)         | 5.06-10^8  | 2.67   | 6290   | 7       | 6.8×10^12  | 1.4×10^13  | 3.4×10^13 |
| 3   | \( H_2 + OH = H_2O + H \)      | 2.14-10^8   | 1.52   | 3450   | 8       | 9.3×10^12  | 1.4×10^13  | 2.2×10^13 |
| 4   | \( OH + OH = H_2O + O \)       | 3.34-10^8   | 2.42   | -1930  | 8       | 5.3×10^12  | 7.6×10^12  | 1.2×10^13 |
| 5   | \( HO_2 + O = OH + O_2 \)      | 1.60-10^13   | 0      | 500    | 9       | 1.4×10^13  | 1.4×10^13  | 1.5×10^13 |
| 6   | \( H + HO_2 = OH + OH \)       | 1.90-10^4   | 0      | 875    | 8       | 1.5×10^14  | 1.6×10^14  | 1.6×10^14 |
| 7   | \( H + HO_2 = H_2O \)          | 2.85-10^8   | 1      | -724   | 21      | 6.8×10^13  | 8.0×10^13  | 9.7×10^13 |
| 8   | \( H + HO_2 = H_2O + O_2 \)    | 1.40-10^2   | 0      | 2004  | 7      | 6.6×10^13  | 6.7×10^13  | 6.7×10^13 |
| 9   | \( H_2 + O_2 = OH + OH \)      | 1.45-10^1   | 0      | 2130  | 5      | 8.5×10^12  | 9.3×10^12  | 1.0×10^13 |
| 10  | \( O_2 = 2O \)                 | 2.09-10^14   | 0      | 1450  | 7      | 1.0×10^14  | 1.0×10^14  | 1.0×10^14 |
| 11  | \( HO_2 + O = OH + O_2 \)      | 1.03-10^4   | 0      | 11040 | 10     | 6.4×10^14  | 1.0×10^13  | 1.0×10^13 |
| 12  | \( H + HO_2 = H_2O + O \)      | 4.20-10^4   | 0      | 12000 | 19     | 2.0×10^13  | 3.4×10^13  | 5.6×10^13 |
| 13  | \( H_2O_2 + O = H_2O + O_2 \)  | 2.50-10^11   | 0      | -5200 | 5      | 9.3×10^11  | 7.4×10^11  | 6.0×10^11 |
| 14  | \( H_2O_2 + H = H_2O + H_2 \)  | 1.70-10^18   | 0      | 3755  | 8      | 7.1×10^14  | 8.1×10^14  | 9.1×10^14 |
| 15  | \( H_2O_2 + OH = HO_2 + H_2O \) | 4.82-10^13   | 0      | 7950  | 20     | 7.1×10^12  | 9.1×10^12  | 1.1×10^13 |
| 16  | \( H + H + M = H_2 + M \)      | 1.69-10^12   | 0      | 3980  | 5      | 6.1×10^11  | 7.1×10^11  | 9.1×10^11 |
| 17  | \( O + O + M = O_2 + M \)      | 1.00-10^17   | 0      | 0      | 15     | 5×10^13    | 4×10^13    | 3×10^13  |
| 18  | \( OH+O=O=H \)                 | 2.28-10^16   | -1     | 0      | 5      | 1×10^13    | 4×10^13    | 1×10^13  |
| 19  | \( OH+O=O=H \)                 | 1.71-10^16   | -0.6   | 0      | 5      | 8×10^14    | 7×10^14    | 6×10^14  |
| 20  | \( H=H+M=H+O+M \)              | 7.00-10^14   | -1     | 0      | 15     | 1×10^13    | 3×10^13    | 1×10^13  |
| 21  | \( H+H+M=H+O+M \)              | 1.00-10^17   | -1     | 0      | 5      | 1×10^13    | 3×10^13    | 1×10^13  |
| 22  | \( H+H+M=H+O+M \)              | 1.19-10^16   | -1     | 0      | 5      | 1×10^13    | 3×10^13    | 1×10^13  |
| 23  | \( O+O+H=O_2+O \)              | 1.20-10^17   | 0      | -5200 | 5      | 9.3×10^11  | 7.4×10^11  | 5.9×10^11 |
| 24  | \( OH+O=O=H \)                 | 2.50-10^11   | 0      | 45000 | 5      | 2.4×10^12  | 1.6×10^13  | 1.05×10^14 |

* in the table are taken the dimensions: pre-exponent A, cm^3/(mol·s); activation energy E, cal/mole
Components to form new active species. Using the elementary reactions
2
\[ \text{all reaction rate of the components} \]

\[ \text{consideration is} \ 2.1 \ \text{mol} \]

rate of formation of the hydrogen atom H at a temperature of 3000 K for the conditions under
3000 K. The reaction rates depend strongly on temperature. With

\[ \text{HO} \]
85% for the hydrogen atom H, 98% for the oxygen atom O, 48% for the radical OH. For this reaction,

\[ \text{times greater than the minimum value}. \]

Then the uncertainty of the reaction rate of the active centers is:

\[ \text{and the uncertainty of their values are presented in} \]

calculations. We exclude elementary reactions that change the over
second stage, the
smaller rate constants for each reaction were chosen for the calculation, published recently. Then, in the
combustion reaction, calculations of the rate of elementary reactions in two stages are performed. First,
stoichiometric coefficients; \( w \)

\[ \text{presented in table 1, we obtain kinetic equations for the rates of formation of the active particles H, OH,} \]

\[ \text{Combustion of the mixture in the reactor is considered at constant pressure. To calculate the molar} \]

concentrations (mol/l or mol/cm³), the equilibrium composition in mole fractions [20, 21], calculated at
a pressure of 0.1 MPa, is used. The change in specific volumes in the calculation of concentrations was
determined from the equation for calculating the properties of dissociated vapor [22], at temperatures
above 2200 K – according to the tables [21, 23].

The mechanism of hydrogen combustion includes elementary stages in which chemically active
particles are formed from stable components; chain propagation stages in which reaction intermediate
particles react with stable components to form new active species. Using the elementary reactions
presented in table 1, we obtain kinetic equations for the rates of formation of the active particles H, OH,
O₂, and HO₂.

The rates of reaction products are determined by expression

\[ \frac{\text{dc}_i}{\text{dt}} = \sum \beta_i - \gamma_i \ w_i , \]

where \( M \) – the number of elementary reactions; \( c_i \) – concentration of components; \( \beta_i \) and \( \gamma_i \) – the
stoichiometric coefficients; \( w_i \) – the rate of components.

To analyze the influence of the rate constants of elementary reactions on the rate of the hydrogen
combustion reaction, calculations of the rate of elementary reactions in two stages are performed. First,
smaller rate constants for each reaction were chosen for the calculation, published recently. Then, in the
second stage, the maximum rate constants of each reaction are used for the calculation. Comparing the
velocities of the active centers, we determine the composition of the elementary reactions for subsequent
calculations. We exclude elementary reactions that change the overall reaction rate of the components
by less than 0.1%. Reactions \( \text{H}_2\text{O}_2 = \text{H}_2\text{O} + \text{O}_2 \) (No. 20), \( 2\text{HO}_2 = \text{H}_2\text{O}_2 + \text{O}_2 \) (No. 23) are excluded.

The uncertainties of each elementary reaction are determined using the difference in the rates of the
active centers of each reaction of the first and second stages. Calculations of velocities of active centers
and the uncertainty of their values are presented in table 3, taking into account the analysis carried out.

For the elementary reaction \( \text{O} + \text{H}_2 = \text{OH} + \text{H} \) (No. 2), the maximum value of the rate constant is 34
times greater than the minimum value. Then the uncertainty of the reaction rate of the active centers is:
85% for the hydrogen atom H, 98% for the oxygen atom O, 48% for the radical OH. For this reaction,
further investigations are needed to refine the magnitude of the rate constant

For the reactions \( \text{HO}_2 + \text{OH} = \text{H}_2\text{O}_2 + \text{O}_2 \) (No. 10), \( \text{HO}_2 + \text{HO}_2 = \text{H}_2\text{O}_2 + \text{O}_2 \) (No. 11), \( \text{H}_2\text{O}_2 + \text{O} = \text{HO}_2 + \text{OH} \) (No. 14), \( \text{H}_2\text{O}_2 + \text{OH} = \text{HO}_2 + \text{H}_2\text{O} \) (No. 15), for which rate constants can differ by more
than 100 times, the uncertainty of the speed of active centers was less than 0.5%.

The reaction rates of the active centers are calculated at temperatures of 2000, 2200, 2400, 2800 and
3000 K. The reaction rates depend strongly on temperature. With an increase in temperature from
2000 K to 3000 K (by a factor of 1.5), the reaction rate of the O atom increased by a factor of 3000. The
rate of formation of the hydrogen atom H at a temperature of 3000 K for the conditions under
consideration is 2.1 mole/(cm³·s). The dependences of the rates of active centers on temperature are
shown in the figure 1.
According to the published data, a table of 24 elementary reactions was created. Up to three different rate constants are presented for each reaction.
The dependence of the accuracy of calculation of the reaction rate of the mixture components on the uncertainty of the rate constants of elementary reactions is determined. A table of the minimum number of elementary reactions is compiled to calculate the reaction rate of the components of the mixture.

The reaction \( \text{O} + \text{H}_2 = \text{OH} + \text{H} \) (No. 2) was determined, for which the maximum uncertainty in calculating the reaction rates of the active centers reaches 98% with an increase in the rate constant by 34 times in accordance with table 1.

For the reactions \( \text{HO}_2 + \text{OH} = \text{H}_2\text{O} + \text{O}_2 \) (No. 10), \( \text{HO}_2 + \text{HO}_2 = \text{H}_2\text{O}_2 + \text{O}_2 \) (No. 11), \( \text{H}_2\text{O}_2 + \text{O} = \text{HO}_2 + \text{OH} \) (No. 14), \( \text{H}_2\text{O}_2 + \text{OH} = \text{HO}_2 + \text{H}_2\text{O} \) (No. 15), for which the rate constants can differ by more than 100 times, the uncertainty of the reaction rate of the active centers was less than 0.5%.

The rates of formation and consumption of active centers depend strongly on temperature. With an increase in temperature from 2000 K to 3000 K (by a factor of 1.5), the reaction rate of the O atom increased by a factor of 3000.

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