

# Investigation of numerical methods in combustion theory

*Oleg P. Lopatin\**

Department of thermal engines, automobiles and tractors, Vyatka State Agrotechnological University, October prospect, 133, Kirov, 610017, Russian Federation

**Abstract.** The analysis of numerical methods in combustion theory considered in this paper allows us to find the optimal solution of systems of differential equations of kinetics of complex chemical reactions and provides an opportunity to obtain information on: - options for solving mechanisms at known values of velocity constants for various stages of a complex reaction; - on the concentration values of all components as a function of time throughout the reaction for each of the considered mechanism. Therefore, a comparison of calculated and experimental concentration values is possible for any component and any time intervals available for the experiment. The degree of sensitivity of the mechanism to changes in the rate constants of individual reaction stages and their various groups, as well as the degree of sensitivity to variations in reaction conditions (temperature, pressure, initial composition, etc.) of the mathematical model corresponding to the mechanism under consideration. It is essential that such a study can be conducted without any additional experimental data.

## 1 Introduction

Often, in combustion theories under consideration, the main task and criterion of applicability is the possibility of calculating the normal combustion rate. Undoubtedly, this parameter is practically important and easily measurable, however, the technological application of tribes poses new challenges, primarily related to the study of the mechanisms and kinetics of combustion processes, the study of heat and mass transfer processes in flames. The rapid progress of computer technology puts in the hands of researchers a modern and more effective means of solving these problems every year. Mathematical modeling is currently one of the fastest and most reliable methods for solving problems of chemical kinetics, in particular, the kinetics of combustion processes [1-2].

In the field of purely kinetic research, mathematical modeling allows us to solve two large classes of problems. The direct kinetic problem consists in finding kinetic curves, i.e. time dependences of concentrations of all components of the reacting system. To solve the problem, it is necessary to specify the initial composition of the mixture, the mechanism and conditions of the reaction, as well as the kinetic parameters (preexponents, activation energies) of all elementary stages of the mechanism.

---

\* Corresponding author: [nirs\\_vsaa@mail.ru](mailto:nirs_vsaa@mail.ru)

From a formal mathematical point of view, a direct kinetic problem is a system of first-order ordinary differential equations with given initial conditions

$$\dot{y}_i = f(y_i, k), \quad y_i(0) = y_o$$

where  $k$  – a set of parameters.

In most cases, these equations are nonlinear, and their solution is generally impossible without the use of modern computer technology.

The main mathematical problem that arises in the numerical solution of a direct kinetic problem is the problem of the so-called "rigidity" of the system of equations. The rigidity of the system lies in the fact that the time characteristics of various variables differ significantly from each other. This means that the rates of change in the concentrations of the various components of the reaction mixture can vary by several orders of magnitude. As a result, there are fast and slow-changing variables in the system. By equating the rate of change of "fast" variables to zero, it is possible to replace some differential equations with algebraic ones. Such a replacement simplifies the task and is the essence of the quasi-stationary concentration method. A large number of papers have been devoted to the peculiarities of solving rigid systems of ordinary differential equations, and by now there are a number of methods that allow us to successfully solve such systems. The most widely used in our country were the Pavlov-Povzner method [3], the method of slow combinations and the Geer method [4]. Consideration of the theory of these methods is not included in the task of this work, therefore we refer interested readers to the relevant sources.

Another serious difficulty in solving a direct kinetic problem is the frequent lack of reliable data on the kinetic parameters of elementary reactions [5-6].

Recently, a significant number of papers have appeared on measuring the rate constants of various elementary reactions. There are a number of reviews in which these data are discussed and systematized [7-8]. In [7], for example, the kinetic parameters of about 250 reactions involving 44 molecular and radical particles that can be observed in hydrocarbon flames are given. However, a significant number of these parameters cannot be considered definitively defined. Calculations carried out using literature data on the rate constants of elementary reactions often yield results that differ greatly from experimental ones [10].

## 2 Materials and methods

The inverse kinetic problem consists in constructing a mechanism describing experimentally obtained kinetic curves. Mathematically, this means constructing the right-hand sides of the differential equations of a direct problem. In this case, it is possible to obtain information about the kinetic parameters of the mechanism under study. To solve the problem, it is necessary to specify a set of substances involved in the reaction and the type of kinetic law. A sufficient condition for the uniqueness of the solution is the ability to measure the instantaneous concentrations of all components of the reaction mixture at any given time. It is clear that this condition cannot be met in a real experiment. Firstly, the experiment is conducted for a limited time. This time may not be long enough to determine the rate constants of slow reactions. Secondly, the experimental results are discrete measurement data. The time intervals between individual measurements may be too long to find the rate constants of fast reactions. Thirdly, concentrations of stable products are usually determined experimentally. Data on the concentrations of radical particles are always incomplete. All this leads to the ambiguity of the solution of the inverse kinetic problem, i.e. the proposed mechanism has a greater or lesser degree of reliability determined by the methods of mathematical statistics. As a result, a number of significantly different mechanisms are often proposed for the same process, describing experimental data equally well [11-13].

One of the first combustion processes, which became the object of research by mathematical modeling, was the high-temperature oxidation of methane [14-17]. The

combustion of methane, as the simplest hydrocarbon, has a relatively simple mechanism, and the kinetics of this reaction has been studied experimentally well enough. The calculations were based on the radical chain scheme proposed by Semenov. The initial composition of the gas mixture and the temperature of the process were set as initial data. The calculation results represented the dependence of the concentrations of the system components on time. The calculations were carried out in an isothermal approximation for various temperatures. The results showed that up to 1600-1700 K, the mechanism of the methane combustion reaction is chain-based, at higher temperatures it is free radical. The activation energies of the gross reaction were calculated depending on the temperature [14]. Several different specific mechanisms have been used in various works. Comparing the results of such calculations with the experiment does not allow us to give preference to any of them.

The described studies, despite the undeniable importance of the results obtained, still provide little to solve the problems discussed in this paper. The reason for this is that the works cited above considered an isothermal reaction in a homogeneous reactor, i.e. they assumed that the same set of chemical reactions takes place at every point in space at a constant temperature. Flames, on the other hand, are a reaction in a stream where temperature and chemical processes change, and very quickly, from point to point. Therefore, heat and mass transfer can play an important and even decisive role in flames.

### 3 Results and discussion

Attempts to calculate the flame propagation velocity, as well as the profiles of reagent concentrations and temperature, based on the thermodynamic and transport properties of the gas mixture, the assumed or known chemical mechanism and data on the kinetic parameters of elementary reactions, were first undertaken by researchers of the Herschfelder school. The flame of mixtures of hydrogen and bromine was considered as an object of modeling. These mixtures were chosen due to a fairly good experimental knowledge, as well as because their combustion proceeds by a fairly simple mechanism, at the same time possessing all the characteristic features of the chain process [18-19].

Initial attempts to solve the problem did not lead to success due to mathematical difficulties, but some results were obtained using a simplified model.

Spalding found a way out of the mathematical difficulties associated with solving stationary equations [20], who showed that the numerical solution of non-stationary equations is much easier, and if the integration procedure is continued for a sufficiently long time, then the solution becomes stationary. This method is called the establishment method. The object of Spalding research was the decomposition reaction of hydrazine, which is kinetically simpler than the combustion of a hydrogen bromide mixture [18-20].

The method of determination was consistently applied to study the flames of hydrazine and other reagents by Adams and Cook, Zeldovich and Barenblatt and Dixon-Lewis [18]. Lovachev and Kaganova [18] applied this method to solve the equations describing the flame  $H_2 + Br_2$ . For their calculations, they used simplified temperature dependences for transfer coefficients and thermodynamic quantities. So, they assumed for the thermal conductivity of the mixture and for the diffusion coefficients of the dependence

$$\lambda = \lambda_o(T/T_o)^{0.67}, \quad D_i = D_{i,o}(T/T_o)^{1.67},$$

where  $\lambda_o$  and  $D_{i,o}$  – accordingly, the thermal conductivity coefficient of the mixture and the diffusion coefficient of the  $i$ -th component at temperature  $T_o$ .

The heat capacity was assumed to be independent of composition and temperature. Spalding [20] considered the same problem using more realistic assumptions about the transport and thermodynamic properties of the reacting mixture. In addition, he applied a new computational procedure, which has a number of advantages over the establishment method, in particular, reducing the time required for calculation. In this case, the reaction rates are

described on the basis of the law of acting masses, and the velocity constants obey the Arrhenius dependence [21].

To consider diffusion, a simplified model was adopted, according to which the diffusion coefficients into a multicomponent mixture are calculated using the formula

$$D_i = \frac{1 - W_i}{\sum_{j \neq i} X_j / D_{ij}},$$

where  $W_i$  – mass fraction;  $X$  – molar fraction;  $D_{ij}$  – the coefficient of binary diffusion of the  $i$ -th substance in the  $j$ -volume.

It should be noted, however, that a stricter account of the dependencies of the mentioned characteristics on temperature and composition did not lead to a noticeable improvement in the agreement of the calculated data with the experimental ones. Apparently, the main reason for the discrepancy between the calculation and the experiment is the inaccurate values of the rate constants of elementary reactions.

The calculation was carried out for a one-dimensional flame. At first, it was assumed that the area occupied by the gas was divided into two half-spaces by a thin flat zone in which the temperature and concentration change steeply but continuously from values corresponding to fresh gas on one boundary to values characterizing a completely burnt mixture on the other. The shape of the initial profiles was set arbitrarily and did not affect the stationary solution. This decision is strongly influenced by the boundary conditions for fresh gas. Two types of such conditions were considered. One of them corresponded to a freely spreading flame, the other to a stabilized flame.

The solved system of equations had the form

$$\begin{aligned} \rho \frac{dn_i}{dt} + \rho v \frac{dn_i}{dx} &= \frac{d}{dx} \left( D_i \rho \frac{dn_i}{dx} \right) + \frac{d}{dx} \left( D_i \rho \frac{n_i \bar{M}}{M} \frac{d\bar{M}}{dx} \right) + K_i, \\ \rho \frac{dH}{dt} + \rho v \frac{dH}{dx} &= \frac{d}{dx} \left( \frac{\lambda}{c_p} \frac{dH}{dx} \right) + \frac{d}{dx} \left[ \sum H_i \frac{D_i \rho}{M} \frac{d}{dx} (n_i \bar{M}) \right] - \frac{\lambda}{c_p} \sum H \frac{dn_i}{dx}, \end{aligned}$$

where  $H$  – specific enthalpy of the gas mixture;  $\bar{M}$  – the average molecular weight of the mixture;  $K$  – the total speed of the  $i$ -th component.

The presented equations allow us to apply them to solve the computational method developed by Patankar and Spalding. This method reduces the required calculation time, and the accuracy results are no worse than those obtained by other methods. The suitability of this solution method for kinetically more complex circuits has also been shown.

A number of fundamental works devoted to the mathematical modeling of combustion processes of mixtures of hydrogen with oxygen and air, alkanes, acetylene were published by Warnatz [22]. To study the combustion of hydrocarbons, he considered a mechanism involving 130 elementary reactions, from which he then excluded non-essential reactions. The exclusion was carried out according to two criteria: firstly, reactions were discarded in which the rate of consumption or nucleation of all particles involved in it throughout the entire flame front was negligibly small (less than 5%) compared with the maxima of the corresponding velocities in other reactions. Secondly, a reaction was excluded in which the integral consumption of all reagents involved in it was less than 5% of the consumption of such reagents in all other reactions.

A model of a one-dimensional flame of a pre-mixed gas mixture was used for calculations. The laws of conservation of enthalpy and mass of the  $i$ -th component lead to the following system of equations:

$$\begin{aligned} \rho \frac{dT}{dx} &= -\rho v \frac{dT}{dx} + \bar{j} \frac{dT}{dx} - \frac{\sum K_i H_i}{c_p} + \frac{1}{Ac_p} \frac{d}{dx} \left( A \lambda \frac{dT}{dx} \right), \\ \rho \frac{dW_i}{dt} &= -\rho v \frac{dW_i}{dx} - \frac{1}{A} \frac{d(Aj_i)}{dx} + K_i, \end{aligned}$$

where  $W_i$  – mass fraction of the  $i$ -th component;  $H_i$  – specific enthalpy;  $A$  – relative expansion.

The boundary conditions introduced were different depending on whether the flame was considered to be freely propagating or stabilized. In the first case, the gradients at the cold

boundary are zero, in the second case they are determined by the conditions of heat dissipation and the course of reactions on the walls. At the hot boundary, the gradients are assumed to be constant in both cases. A significant disadvantage of Warnatz work [22] should be considered the absence of a low-temperature branching reaction in the mechanisms being driven. This leads to the fact that the proposed models incorrectly describe the low-temperature zone of hydrocarbon flames, although at high temperatures there is a fairly good agreement with the experiment.

## 4 Conclusion

Summarizing what was said in the previous sections of this work, it is safe to say that numerical methods for solving combustion theory equations have become one of the most important research tools in this field. There is no doubt that the further development of computational methods and computer technology and the obtaining of more reliable values of kinetic parameters will make the application of mathematical modeling in combustion theory even more widespread and fruitful.

## References

1. S.R.D. Akella, A. Yeswanth, P. Gayathri, Technical Journal of Daukeyev University **2(1)**, 11-20 (2022).
2. N. Yusupbekov, N. Bobomurodov, J. Sevinov, E3S Web of Conferences **431**, 02027 (2023).
3. B.V. Pavlov, A.Ya. Povzner, Journal of Computational Mathematics and Mathematical Physics **4**, 1056-1059 (1973).
4. C.W. Gear, *Numerical Initial Value Problems in Ordinary Differential Equations* (Prentice-Hall, Upper Saddle River, 1971).
5. K.V. Osintsev, Y.S. Prikhodko, M.M. Dudkin, Smart Innovation, Systems and Technologies **272**, 327-334 (2022).
6. E.V. Radkevich, N.N. Yakovlev, O.A. Vasilieva, Doklady Mathematics **102(3)**, 505-509 (2020).
7. J.C. Dechaux, Oxidation Communications **2(2)**, 95-126 (1981).
8. D.L. Baulch, D.D. Drysdale, D.G. Horne, A.C. Lloyd, Journal of Physical Chemistry Reference Data **9(3)**, 259-439 (1980).
9. W.P. Carter, A.C. Lloyd, J.L. Sprung, J.N. Pitts Jr., International Journal of Chemical Kinetics **11(1)**, 45-101 (1979).
10. R. Atkinov et al., Advances in Photochemistry **11**, 315 (1979).
11. M.R. Talaghat, N. Naamaki, International Journal of Hydrogen Energy **46(2)**, 2282-2295 (2021).
12. O.D. Nikolayev, I.D. Bashliy, Technical mechanics **2022(1)**, 3-15 (2022).
13. G.V. Kuznetsov, S.V. Syrodoy, N.Y. Gutareva, N.A. Nigay, Journal of the Energy Institute **96**, 280-293 (2021).
14. I.A. Vardanyan, C. Jan, A.B. Nalbandian, Kinetics and catalysis **4**, 825-851 (1981).
15. N. Bystrov, A. Emelianov, A. Eremin, B. Loukhovitski, A. Sharipov, P. Yatsenko, Combustion and Flame **218**, 121-133 (2020).
16. N.E. Afonina, G.D. Smekhov, A.N. Khmelevsky, Fluid Dynamics **57(S1)**, 151-163 (2022).

17. V. Srinivas et al., *Journal of the American Chemical Society* **142(33)**, 14249-14266 (2020).
18. G.I. Xandopulo, V.V. Dubinin, *Chemistry of gas-phase combustion* (1987).
19. V.V. Azatyan, *Review Journal of Chemistry* **7(2)**, 125-146 (2017).
20. D.B. Spalding, P.L. Stephenson, *Proceedings of the Royal Society of London* **A324**, 315-851 (1971).
21. A. Ushakova, M. Varfolomeev, D. Emelyanov, V. Zatsepin, *Journal of Combustion* **2017**, 2526596 (2017).
22. J. Warnatz, *Berichte der Bunsen-Gesellschaft für physikalische Chemie* **82**, 193-200, 643-49 (1978).