Spatial Features of Ignition and Combustion

Spatial Features of Ignition and Combustion:

Experimental and Theoretical Results

By

Nikolai M. Rubtsov, Kirill Ya. Troshin,
Alexander P. Kalinin and Michail I. Alymov

Cambridge
Scholars
Publishing

Spatial Features of Ignition and Combustion:
Experimental and Theoretical Results

By Nikolai M. Rubtsov, Kirill Ya. Troshin, Alexander P. Kalinin,
and Michail I. Alymov

This book first published 2025

Cambridge Scholars Publishing

Lady Stephenson Library, Newcastle upon Tyne, NE6 2PA, UK

British Library Cataloguing in Publication Data
A catalogue record for this book is available from the British Library

ISBN: 978-1-0364-4377-1
ISBN (Ebook): 978-1-0364-4378-8

This book presents new data on combustion with practical applications, including fire safety issues both in combustion control and in the use of noble metals in catalytically stabilized (CS) combustion, as well as the determination of catalytic ignition limits in noble metal-hydrogen-deuterium-carbon monoxide-methane systems; original results obtained by the authors in 2021-2024 are presented. The book also discusses the modes of spatial development of gas ignition over surfaces of various chemical nature and morphology, subsonic combustion in reactive flows and in volumes of complex geometry. The aim of the book is also to acquaint the reader with the main modern problems of multisensory data analysis and possibilities of hyperspectral imaging, visualization of subsonic combustion and catalytic combustion processes of flame propagation.

The book can be useful to students of higher courses and scientists dealing with problems of optical spectroscopy, visualization, digital recognition of images and gaseous combustion.

> "The development of science is such that while correctly established facts remain forever, theories are constantly changing, being extended, improved and specified”.
> —Piotr Kapitsa, Nobel Prize winner

CONTENTS

Preface x

Acknowledgments xvi

Introduction xvii

Chapter 1 1
Theory and qualitative mathematical interpretation of combustion and catalytic combustion processes
  References to Chapter 1 22

Chapter 2 27
Principles and areas of use of hyperspectral technologies
  §1. Hyperspectral and high–speed shooting technique 28
  §2. Characteristics of unstable flame propagation 42
  Conclusions to Chapter 2 61
  References to Chapter 2 61

Chapter 3 65
Homogeneous self-ignition or local ignition? Thermal ignition of a stoichiometric mixture of hydrogen and oxygen near the second ignition limit
  Conclusions to Chapter 3 80
  References to Chapter 3 81

Chapter 4 83
The use of hyperspectral analysis and high–speed filming methods for establishing the patterns of catalytic ignition of deuterium–air, deuterium-methane-air, and deuterium-carbon monoxide-air mixtures over the surfaces of metallic rhodium and palladium
  §1. Catalytic ignition of deuterium-air mixtures over the surface of metallic rhodium 86

§2. The use of hyperspectral analysis and high–speed filming methods to establish the patterns of catalytic ignition of deuterium-carbon monoxide mixtures with air over the surface of metallic rhodium at pressures of 1-2 atm 95
§3. Using the method of high-speed filming to establish the patterns of catalytic ignition of deuterium-air mixtures over the surface of palladium metal 103
§4. Catalytic ignition of deuterium-methane mixtures with air over palladium metal at pressures up to 2 atm 111
§5. Changes in the morphology of the surface of noble metals under the action of ignitions of mixtures H_2/D_2– air 119
§6. Catalytic ignition of mixtures of deuterium and hydrogen with carbon monoxide and air over the surface of palladium metal at pressures of 1-2 atm 123
§7. Features of catalytic ignition of hydrogen-methane-air mixtures over metallic rhodium and palladium at pressure 1-2 atm 131
Conclusions to Chapter 4 139
References to Chapter 4 142

Chapter 5 149
The influence of external gas flows on the interaction of the flame front with obstacles
§1. Features of propagation of the front of a rarefied methane-oxygen flame in the direction of the counter flow of the initial combustible gas 150
§2. Determination of rarefied methane-oxygen flame propagation patterns in a cocurrent flow of combustible ga 159
§3. Interaction of a laminar flame of methane-oxygen mixtures with fine-meshed spherical obstacles in the counterflow of combustible gas produced by a fan in a closed cylindrical reactor 165
Conclusions to Chapter 5 171
References to Chapter 5 172

Chapter 6 175
Flame propagation of methane-oxygen mixtures in volumes of complex geometry
§1. Interaction of the combustion front of a methane-air mixture with cylindrical obstacles at subatmospheric pressures 176
§2. Features of the interaction of the flame front of dilute methane-oxygen mixtures with hollow cylindrical and conical obstacles at pressures below atmospheric 187

§3. Laminar flame propagation of natural gas-oxygen mixtures in volumes of complex geometry 194
§4. Interaction of counter flames in methane-oxygen mixtures in a closed reactor, 3D model 202
Conclusions to Chapter 6 213
References to Chapter 6 214

Conclusions 219

PREFACE

The book develops current lines of research in the field of combustion processes carried out by the authors in 2021-2024.

The book is aimed at the consideration of the essential problems of combustion science; it is complementary to the previously published books mentioned below and presents the results obtained by the authors in 2021-2024 In this book we did not intend to carry out a comprehensive review of the literature, since our previous books, mentioned below, contain sufficiently comprehensive reviews, which, in our opinion, have not yet become obsolete. The book presents the patterns of gas combustion processes discovered by the authors and new theoretical results obtained when considering these new patterns. These include the establishment of the mechanism of thermal and catalytic initiation of gas-phase combustion, which consists in the formation of one or more local combustion centers on a heated or catalytic surface, from which flame fronts propagate into the volume. This means that homogeneous ignition hardly ever takes place, but ignition by a heated chemically active surface is usually the case. *It is shown that taking into account the reaction of chain development on the surface makes it possible to carry out a qualitative modeling of the occurrence of local ignition centers using a system of Navier-Stokes equations for a compressible reacting medium in the small Mach number approximation on a uniformly chemically active wall of a cylindrical reactor. It is found that a qualitative study using the approximate theory of flame velocity leads to the conclusion that the equation obtained for the undistributed (spatially homogeneous) problem is qualitatively valid within the experimental error for ignition, which begins with the appearance of a local active ignition center on the most chemically active area of the surface and the subsequent propagation of the flame from this center.*

For the first time, the regularities of catalytic ignition of a mixture of deuterium with air, as well as with additives of methane over noble metals (rhodium and palladium) have been established. New experimental patterns of initiation and propagation of methane-oxygen flames, both in co-flow and counter-flow of combustible gas created by fans, and in spaces of complex geometry in the presence of ignition sources have been revealed. The experimental characteristics of methane-oxygen flame counterflow interaction have been established. It is shown that the Navier-Stokes equations for a compressible reacting medium in the acoustic approximation qualitatively satisfactorily describe the new experimental regularities obtained.

At present, remote sensing methods for studying various processes using different optoelectronic devices are becoming increasingly popular. In particular, multi-zone imaging using optoelectronic sensors for different wavelength ranges is of great interest. This book describes and analyzes some of the possibilities of optoelectronic devices for studying combustion processes in a wide range of wavelengths from ultraviolet to near infrared, methods for visualizing fast combustion processes, flame propagation and acceleration, and limiting phenomena during ignition and flame propagation. Optoelectronic devices convert an optical signal into an electrical signal that is processed by computers. Optoelectronic devices include digital cameras, digital video cameras, hyperspectrometers, UV sensors, etc. As a rule, the recorded radiation spectrum is limited for individual devices. Therefore, two or more sensors can be used for the so-called multispectral analysis - multisensor imaging. Numerous examples of the use of modern optoelectronic devices have demonstrated the effectiveness of multi-zone, multi-sensor imaging in the study of combustion and explosion processes. It is shown that the combined use of 4D hyperspectrometry and high-speed color imaging has made it possible to solve the following tasks Characteristics of combustion in flame cells caused by hydrodynamic instability are experimentally determined. It is shown that each flame cell is a separate "chemical reactor" in which the process of complete chemical transformation takes place. It is shown that the used experimental technique allows to separate the cold flame from the hot one in time and space in a single experiment. It was found that the cellular mode in H_2 combustion over Pt is determined by the catalytic combustion of hydrogen on Pt containing particles formed during the decomposition of unstable platinum oxide in the gas phase.

With the help of various methods of visualization of the hydrogen flame, it was experimentally established that the thermal ignition of the explosive mixture always starts on the walls of the reactor and then the combustion process moves into the volume, i.e. the stages of heating (in our experimental conditions the delay period exceeds 10 seconds), local ignition and flame propagation are realized. This means that there is no homogeneous ignition, but ignition by a heated chemically active surface. It is shown that taking into account the reaction of chain development on the surface makes it possible to carry out a qualitative modeling of the occurrence of local ignition centers using a system of Navier-Stokes equations for a compressible reacting medium in the small Mach number approximation on a uniformly chemically active wall of a cylindrical reactor. It is shown that a qualitative examination using the approximate theory of flame velocity leads to the conclusion that the governing equation obtained for the undistributed problem is qualitatively valid within the framework of the experimental error for ignition, which begins with the appearance of a local primary center at the most chemically active site of the surface and subsequent flame propagation. It can also be shown, using hydrogen oxidation as an example, that in the diffusion region of chain termination, where the lower ignition limit exceeds 10 Torr and inhomogeneous ignition occurs with noticeable heating, the limit equation obtained for homogeneous ignition is also valid within the experimental error.

The regularities of catalytic ignition of deuterium-air mixtures over the catalytic surface of metallic rhodium at pressures of 1-2 atm and temperatures of 20-250^{0}C have been established using hyperspectrometers in the range of 400-1650 nm and high-speed filming. It has been shown that catalytic ignition of deuterium-air mixtures in the studied temperature range is observed with a deuterium content of more than 12%; with a deuterium content of less than 12%, only intensive heating of the catalytic wire is observed. The results obtained using rhodium and palladium catalysts and the simplest combustible hydrogen and deuterium illustrate the rich variety of catalytic combustion modes.

It is also shown that the primary ignition center occurs on the surface of the catalyst. Under the same conditions in subsequent experiments, the location of the initial center changes. It has been shown that it is more accurate to speak of ignition via noble metal hydrides/deuterides formed on the noble metal surface. The upper and lower temperature limits of catalytic ignition have been found, which correspond to the ignition limits over noble metal, untreated and previously treated with ignitions. It was found that the upper limit of catalytic ignition of the D2+air mixture on rhodium deuteride is significantly lower than the lower limit of the H2-air mixture on rhodium hydride; thus, D2 is more flammable than H2 on rhodium at pressures above 1 atm; the catalytic ignition limits are even lower than 20 °C, although the flame velocity of the hydrogen-air flame and the flame temperature in mixtures of the same composition are significantly higher than those of deuterium-air mixtures. The nature of the detected kinetic reverse isotope effect is determined by the high activity of rhodium deuteride with respect to the deuterium oxidation reaction.

For the first time, experimental studies of the combustion of deuterium+carbon monoxide in air over Rh metal at a total pressure of 1-2 atm and initial temperatures in the range of 20-300°C were carried out to determine the temperature dependence of the limits of catalytic ignition on the surfaces of noble metals. The regularities of catalytic ignition of deuterium-carbon monoxide-air mixtures over the surface of metallic rhodium at pressures of 1-2 atm and temperatures of 25-300^{0}C have been established using hyperspectrometers in the range of 400-1650 nm and high-speed filming. It was found that the temperature dependences of the lower catalytic ignition limit of the mixtures D_2+CO+air and H_2+CO+air on the surface of metallic rhodium at pressures above 1 atm are close to each other. At the same time, the fact that the temperature dependences of the upper limit of catalytic ignition of deuterium and hydrogen in a mixture with CO are very different, and those of the lower limit are very close, may be due to the different adsorption capacity of carbon monoxide poisoning the untreated surface of noble metal hydride/deuteride at the upper limit of catalytic ignition. At the same time, at the lower catalytic ignition limit, the surface layer of adsorbed carbon monoxide is restored with each subsequent addition of the combustible mixture containing CO. It is shown that the primary ignition center of D_2+CO+air occurs on the surface of the catalyst; in subsequent experiments, under the same conditions, the place of origin of the primary center changes. It was found that the delay times of catalytic ignition increase only with decreasing temperature, which is due to the adsorption of carbon monoxide poisoning the catalyst on the surface of the noble metal hydride/deuteride at the upper catalytic limit, while the state of the noble metal surface changes only due to the disappearance of the CO layer during the first ignition. However, the surface layer of adsorbed carbon monoxide is restored with each subsequent addition of the combustible mixture as it approaches the lower catalytic limit. Visible and infrared spectra of the combustion of D_2-CO-air mixtures have been obtained for the first time. A comparison of the visible emission spectra of the combustion of the stoichiometric mixture of 30% D_2-70% CO-air and 17% D_2-air allowed us to establish that the heating in the presence of CO is significantly higher than in the combustion of deuterium. Heavy water bands are detected in the NIR spectrum.

It was found that the primary ignition center of the deuterium-air mixture over palladium metal occurs on the surface of the catalyst. It is shown that the temperature dependence of the catalytic ignition limits of hydrogen/deuterium-air mixtures over palladium is determined by the diffusion rates of deuterium and hydrogen in palladium and the different reactivity of phases in the palladium-deuterium system. For the first time, the catalytic ignition temperatures of mixtures (60÷90%D_2+

40÷10%CH_4)stoich+air over the surface of palladium metal (Pd) have been experimentally determined at pressures of 1-2 atm in the temperature range of 20÷300^{0}C under static conditions. The limits of the region of catalytic ignition of mixtures (60-90% D_2+30-10% $CH_4)_{stoich}$+air over metallic Pd have been established. In this case, there is a critical nature of the volumetric reaction: the volumetric process accompanied by ignition and a sharp increase in pressure occurs at 70% D_2, but is absent at ≥ 65% D_2. At a D_2 content of less than 5%, only a slow surface reaction occurs. Using the Navier-Stokes equations for a compressible reacting medium in the small Mach number approximation, the formation of chaotic structures of heated dispersed particles is qualitatively illustrated, which is determined by the peculiarities of heat release/losses and mass transfer in the reacting gas. The determination of the characteristics of the interaction of the flame front with obstacles is valuable for the development of both reliable numerical models and flame arresters in solving explosion safety problems.

It has been shown experimentally that the flame front of a dilute methane-oxygen mixture at 298K and 100-300 Torr does not form von Karman vortex shedding behind a cylindrical obstacle, including a perforated cylinder; however, under the same conditions, vortex instability occurs in the flow of hot products. In a perforated cylinder, local centers of primary ignition are formed on its inner surface. The modeling takes into account the main observed features of the propagation of the flame front past the obstacle: a branched chain combustion mechanism and the absence of vortex formation behind the obstacle during flame propagation. It is shown that a qualitative model based on the Navier-Stokes equations in the small Mach number approximation for a compressible inert/reacting medium allows obtaining both the mode of occurrence of the von Karman instability in chemically inert gas and the absence of a flame propagation regime in a reacting flow. This model also illustrates the occurrence of local primary ignition centers on the inner surface of the obstacle.

It has been shown experimentally that the flame front of a premixed dilute methane-oxygen mixture at 298K and 100-300 Torr propagating against hollow cylindrical and conical obstacles oriented along the axis of the reactor does not form a von Karman Vortex Street behind them; however, under the same conditions, vortex instability occurs behind the obstacle in the flow of hot products. The reason why vortices are not observed behind an obstacle during flame propagation, but appear during propagation of the reflected flow of hot products, is that heat transfer reduces the curvature of the flame and leads to its stabilization. Convex sections of the chemical reaction zone in a combustible mixture give off more heat relative to cold sections than in a flat flame: heat from them is transferred not only forward in the direction of flame propagation, but also laterally. The resulting cooling of the reaction zone leads to a delay in the forward flame regions. The opposite situation is observed in concave areas where the temperature rises for the same reasons. The rate of reactions increases and they spread faster as the flame spreads. Thus, the surface of the curved flame front is leveled. In other words, thermal conductivity has a stabilizing effect on a curved flame. This effect is absent in non-reactive gas.

Numerical estimates based on the acoustic approximation of the Navier-Stokes equations for a compressible reacting medium have made it possible to account for the main observed feature of the flame front hitting a cylindrical obstacle: when the flame spreads behind the obstacle, the von Karman Vortex Street is absent. Thus, a qualitative model allows to obtain both the mode of occurrence of the von Karman instability in a chemically inert gas and its absence during flame propagation.

It has been found that the model flame propagation process (methane combustion) in a conventional room with an inner space with two holes and flammable material inside exhibits a wide variety of combustion modes depending on the geometry of this complex volume. The preliminary numerical calculation of the expected flame propagation patterns may not always be successful. Therefore, a real experiment under laboratory conditions, assuming the possibility of scaling the process, seems to be the most informative.

The main regularities of the interaction of methane-oxygen counterflames in a closed cylindrical reactor, initiated by a spark discharge at the ends, have been established using high-speed filming. It has been shown that gas-dynamic factors predominate in the interaction of the counterflames, both in the hot combustion products and in the initial non-stratified mixture. Under conditions of density stratification, two-dimensional vortices can spread beyond the zone of counterflame interaction. It is found that the three-dimensional model used in the work provides a satisfactory qualitative description of the characteristics of the counterflame interaction in both homogeneous and stratified media.

ACKNOWLEDGMENTS

The authors are grateful to Ph.D. Boris S.Seplyarsky, Ph.D. Roman A. Kochetkov, Ph.D. Victor I.Chernysh, leading engineer Georgii I.Tsvetkov (A.G.Merzhanov Institute of Structural Macrokinetics and Problems of Materials Science of the Russian Academy of Sciences); Academician, Prof. Oleg F.Petrov, Prof.Victor V.Golub, Prof. Eugene F. Lebedev, Dr of Sci Vladimir A. Zeigarnik, (Joint Institute of High Temperatures of Russian Academy of Sciences), engineer Alexey B. Ankudinov (A.A. Baikov Institute of Metallurgy and Materials Science, RAS) for their constant help and invaluable support, and jeweler Eugene A. Baturin for the samples of high quality.

INTRODUCTION

Gaseous fuels, especially hydrogen or natural gas, have a number of advantages over liquid fuels. These include good anti-detonation properties of gaseous fuels, favorable mixing conditions and wide ignition limits in mixtures with air. In terms of specific power and fuel economy, the best modern gas and gas-liquid engines are close to liquid-fueled engines, and in terms of exhaust toxicity they have significant advantages over liquid engines. The patterns of chemical reactions, including those underlying combustion processes, are primarily determined by the mechanism and laws of chemical kinetics. Reaction kinetics also determines the rate of heat release, the non-thermal modes of the process, and plays an important role in heat and mass transfer as well as the gas dynamics of the explosion.

The rapidly increasing demand for energy worldwide, the increasing fuel consumption, the progressive depletion of fossil fuels and the emissions into the atmosphere such as CO, CO_2 and NO generated by the combustion of fossil fuels have led to an intensive search for alternative fuels such as natural gas and hydrogen. Natural gas is considered to be one of the most promising alternative fuels for internal combustion engines. Natural gas has an effective potential as an engine fuel. Hydrogen is a sustainable fuel that can replace fossil fuels. Hydrogen can improve the performance of automobiles and aircraft while enhancing environmental quality and energy security.

Any combustion or explosion process is first of all a chemical reaction between the components of the combustible mixture, accompanied by the release of heat and various types of motion in gases, i.e. gas dynamics phenomena. For this reason, all phenomena occurring in the combustion process are closely related to the ideas and laws of chemical kinetics and gas dynamics, and especially to the rates of chemical reaction steps under non-isothermal conditions. To illustrate, even according to the simple Arrhenius law, the heat generated by the reaction itself increases the rate of the reaction. The existence of such feedback is characteristic of most combustion phenomena. As a result of the influence of the reaction on the generation of heat in the mixture, on the one hand, and the increase in the reaction velocity due to this greater heat, as already mentioned, on the other hand, a self-accelerating wave of heat is set up. The dissipation of heat on the walls of the reactor allows the development of a heat shock only under certain conditions, which are therefore decisive for the temperature of this ignition. This temperature, which is a relative value, is a function of kinetic and thermal parameters, namely the order of the reaction, the activation energy, the density, the viscosity, the mass and heat transfer coefficients, the Mach number and the composition of the combustible mixture, the heat of reaction and the heat dissipation on the vessel walls.

This book discusses the effects of gas dynamic processes and chemical kinetics on the modes of hydrocarbon oxidation processes, including catalytic oxidation on noble metals; catalytic oxidation of hydrogen and deuterium on palladium and rhodium at pressures above 1 atm. Catalysis by noble metals is usually studied when the metal is deposited on a substrate, while the action of the catalyst itself should be separated from the processes of interaction of the metal and the reaction being studied with the substrate. Nevertheless, relatively few studies have been devoted to catalysis on the surface of pure metals. This book is one such study. The book addresses issues in catalytically stabilized (CS) combustion technology, including the stimulation of combustion of deuterium-mixed carbon monoxide and methane, and the determination of catalytic ignition limits in noble metal-deuterium-carbon monoxide or methane systems.

When the catalyst is introduced into a combustible mixture, new critical phenomena arise, namely the temperature and pressure limits of catalytic ignition, which are determined by the state and history of the catalyst surface. This is another phenomenon that has not yet received sufficient attention: the dependence of the catalyst surface state on the surface treatment by ignitions of a combustible gas mixture, which is manifested in the fact that the catalytic activity of the untreated surface is significantly different from that of the surface over which ignitions have been carried out. This phenomenon and its related effects are considered in this book.

Catalytic combustion has received considerable experimental and theoretical attention in the last decades. The potential of heterogeneous processes to reduce pollutant emissions, improve ignition, and enhance flame stability has been investigated. The modeling and simulation of heterogeneous systems requires the coupling of reactive flows with gas-surface interactions to achieve at least a quantitative understanding of catalytic combustion. Catalytic ignition is an abrupt transition from a kinetically controlled system to one controlled by mass transport. Therefore, the complex interactions of chemical and transport processes in the gas phase as well as at the surface have to be taken into account. Therefore, numerical simulations of catalytic ignition and the comparison of calculated and experimental results are a suitable tool to qualitatively validate the proposed models and reaction mechanisms.

To study the details of chemical interactions, "non-destructive" methods that do not affect the course of the process are preferred. These are optical methods. Optical methods have two undeniable advantages: they are non-contact and panoramic. In other words, they do not affect the "object-medium" system and, in many cases, allow obtaining data in the form of an image directly within the entire flow field or, for example, the flame front. Among the optical methods, we can highlight the methods of flow visualization, which are no less important than the measurement of its parameters, because they provide a visual representation of the general view of the flow process in a given medium or the propagation of the combustion front.

It is clear that it is important to visualize the flows and fronts of chemical reactions in liquids or gases that occur spontaneously or under the influence of external sources initiated by various physical factors (ultrasound, laser radiation, magnetic and electric fields, etc.). Velocity, pressure and temperature fields are usually visualized in flows of liquids and gases. Visualization of chemical processes in flow conditions using a variety of methods and means is used to determine their qualitative characteristics: observation of the optical spectrum of a chemical reaction, current lines, boundary layer separation areas, vortices and pressure shocks, flow conditions (laminar or turbulent, stationary or unsteady, etc.). Visualization of chemical reaction fronts and flows is possible by both non-optical and optical methods. Non-optical (direct) visualization of gas and liquid flows includes the method of introducing smoke streams (for gas) or colored liquid (for hydrodynamic flows) into the flow, the method of tracing particles, the method of applying droplets or films of a specific liquid (colored, with solid impurities or fluorescent) to the surface of a streamlined body, the use of a thin light plane (laser sheet) for highlighting particles, etc. Optical methods make it possible to visualize flows using optical devices and equipment. These methods provide visualization of inhomogeneous flows of reacting gases and liquids, qualitative analysis of the state and structure of the flow, non-contact and inertia-free simultaneous measurement within the entire visualized flow section of the flow density. The first experiments with chronophotography, which allowed to record the movement of an object by photographing its phases at short and regular intervals and which became the prototype of cinematography, were carried out with the same objectives, allowing to study phenomena inaccessible to human perception. Modern equipment makes it possible to record from a few thousand to tens of millions of images per second, allowing the observation of very fast processes. High-speed digital equipment is used to analyze many fast-moving phenomena, especially the processes of flame propagation, the transition from combustion to detonation, spark discharges, and other phenomena. The images obtained under laboratory conditions allow to measure the parameters of the medium flows, the speed and structure of the combustion fronts, and finally to present the visualization results in a form that is easy to understand and simulate.

Modern recording electronic devices, as a rule, do not contain moving parts that limit performance. CCD arrays allow one to register fast processes with a frequency of up to millions frames per second. The advent of CMOS matrices made it possible to shoot millions of frames per second and completely replace film. The level of 0.6 trillion frames per second achieved at the beginning of the decade made it possible to record the movement of the light front of a pulsed laser. Even some digital compact cameras, such as Casio Exilim series, are equipped with a high-speed video recording function with a frequency of up to 1200 frames per second with reduced frame sizes. Special digital movie cameras are used for accelerated filming, among which the most famous are "Phantom" devices capable of shooting up to a million frames per second. Infrared video cameras (for example, Xeva-2.35-320) are already able to register radiation with an acceptable resolution of up to 400 frames per second.

Currently, along with the above mentioned visualization methods, remote methods for studying various processes using the latest optoelectronic devices are becoming increasingly widespread. In this book, we will talk about the use of hyperspectrometers, the domestic line of which is being intensively developed, as well as the joint use of hyperspectrometers and high-speed color cinematography. Hyperspectrometers are devices that allow the remote registration of reflected, scattered, and ascending radiation to obtain its spectrum in a wide range of wavelengths. Hyperspectral measurements are performed in the range of several hundred to a thousand spectral channels, and a hyperspectrometer (hyperspectral imaging sensor) is a device that simultaneously measures spectral and spatial coordinates. This book examines some home-use hyperspectrometers that register a narrow band of a radiating, reflecting, or scattering surface at one time (the so-called push-broom systems). The registration is performed on a two-dimensional matrix, on one coordinate of which the spatial coordinate x is fixed (along a narrow strip of the recorded surface), and on the other - the spectral one. As a rule, the third y-coordinate is formed by the movement of the hyperspectrometer by any carrier (airplane, helicopter, car, satellite), or this movement is carried out by means of a rotating device. In addition to the two standard x and y coordinates, the spectral coordinate and the intensity of the spectral line are added, providing a 4D dimension of the data space. If the hyperspectrometer is kept at rest, then since the data is taken from the hyperspectrometer's recorder by frames accumulated on the recorder over a certain time, in this case (instead of the y-coordinate) the t-time coordinate appears, i.e. it becomes possible to study the time characteristics of processes occurring on a narrow strip of the surface. Thus, the 4D dimension is formed by the x coordinate; the spectral coordinate is the wavelength λ, the intensity of the spectral line I and the time t.

Let us now consider the main topics covered in this book.

The first Chapter introduces the reader to the basics of understanding combustion processes and certain approaches to the mathematical description of the processes used in this book.

The second Chapter is devoted to the classification and description of the operating principles of the hyperspectrometers used in this study. Examples of the combined use of 4D hyperspectrometry and high-speed color filming are given. The characteristics of combustion in flame cells caused by hydrodynamic instability are experimentally determined. It is shown that each flame cell is a separate "chemical reactor" in which the process of complete chemical transformation takes place. It is shown that the used experimental technique allows to separate the cold flame from the hot one in time and space in a single experiment. It was found that the cellular mode of hydrogen combustion over Pt is determined by the catalytic combustion of hydrogen on Pt containing particles formed during the decomposition of unstable platinum oxide in the gas phase.

In the third Chapter it has been established that there is no homogeneous ignition, but ignition through a heated chemically active surface. It is shown that taking into account the reaction of chain development on the surface makes it possible to carry out a qualitative modeling of the occurrence of local ignition centers using a system of Navier-Stokes equations for a compressible reacting medium in the approximation of a small Mach number on a uniformly chemically active wall of a cylindrical reactor. Using the example of the model reaction of hydrogen oxidation, it is found that a qualitative study using the approximate theory of flame velocity leads to the conclusion that the key equation for combustion limits obtained for the undistributed problem is qualitatively valid within the framework of the experimental error for ignition, which begins with the appearance of a local active center at the most chemically active site of the surface and subsequent flame propagation. It is also shown that in the diffusion region of chain termination, where the lower limit exceeds 10

Torr and inhomogeneous ignition with significant heating occurs, the limit equation obtained for homogeneous ignition is also valid within the experimental error.

The fourth chapter is devoted to the determination of combustion patterns of mixtures of deuterium with air and deuterium with carbon monoxide or methane and air. When the noble metal catalyst is introduced into the combustible mixture, new critical phenomena appear, namely the temperature limits of catalytic ignition, which are determined by the state and history of the catalyst surface. This is the phenomenon that has not yet received enough attention: the dependence of the state of the catalyst surface on the surface treatment by ignitions of a combustible gas mixture, which is manifested in the fact that the catalytic activity of the untreated surface is significantly different from that of the surface over which ignitions were carried out. This is expressed in the existence of upper and lower limits of catalytic ignition that we have discovered, which correspond to the ignition limits over noble metal, untreated and previously treated with ignitions. This phenomenon and its implications are discussed in this chapter. It was found that the upper temperature limit of catalytic ignition of the D_2-air mixture on rhodium deuteride is significantly lower than the lower limit of the H_2-air mixture on rhodium hydride; thus, D_2 is more flammable than H_2 on rhodium at pressures above 1 atm; the limits of catalytic ignition are even lower than 20°C, although the flame velocity in the hydrogen-air mixture and the flame temperature in mixtures of the same composition are significantly higher than those in deuterium-air mixtures. The nature of the detected kinetic reverse isotope effect is determined by the high activity of rhodium deuteride with respect to the deuterium oxidation reaction. For the first time, experimental studies of the combustion of deuterium+carbon monoxide in air mixtures over rhodium metal at total pressures of 1-2 atm and initial temperatures in the range of 20-200°C were carried out in order to establish the temperature dependence of the limits of catalytic ignition on the surfaces of noble metals. The regularities of catalytic ignition of deuterium-carbon monoxide-air mixtures over the surface of metallic rhodium at pressures of 1-2 atm and temperatures of 25-300^{0}C have been established using hyperspectrometers in the range of 400-1650 nm and high-speed filming. It is shown that the primary ignition center in D_2+CO+air combustion occurs on the surface of the catalyst; in subsequent experiments under the same conditions, the place of origin of the primary center changes. It is found that the delay times of the catalytic ignition increase only with decreasing temperature, which is due to the adsorption of carbon monoxide poisoning the catalyst on the surface of the noble metal hydride/deuteride at the upper catalytic limit, while the state of the noble metal surface changes only due to the disappearance of the CO layer during the first ignition. However, the surface layer of adsorbed carbon monoxide is restored with each subsequent admission of the combustible mixture containing CO as it approaches the lower catalytic limit. For the first time, visible and infrared spectra of the combustion of D_2-CO-air mixtures have been obtained. It is shown that the temperature dependence of the limits of catalytic ignition of hydrogen/deuterium-air mixtures over palladium is determined by the diffusion rates of deuterium and hydrogen in palladium and by the different reactivities of the phases in the palladium-deuterium system.

For the first time, catalytic ignition temperatures of mixtures $(60\div90\%\ D_2+40\div10\%\ CH_4)_{stoich}$+air over the surface of palladium metal (Pd) at pressures of 1-2 atm in the temperature range of $20\div300^0$C under static conditions have been experimentally determined. The limits of the region of catalytic ignition of mixtures $(70\text{-}90\%\ D_2+30\text{-}10\%\ CH_4)_{stoich}$+air over metallic Pd have been established. In this case, a critical nature of the volumetric reaction was detected: the volumetric process, accompanied by ignition and a sharp increase in pressure, occurs at 70% D_2, but is absent at $\geq$ 65% D_2. At less than 5% D_2, only a slow surface reaction occurs. Using the Navier-Stokes equations for a compressible reacting medium in the low Mach number approximation, the formation of chaotic structures of heated dispersed particles is qualitatively illustrated, which is determined by the peculiarities of heat release/loss and mass transfer in the reacting gas. The change of the surface morphology of noble metals under the influence of ignition of H_2/D_2 -air mixtures has been studied by the method of electron microscopy in combination with XRD. For the first time, experimental studies of the combustion of mixtures of deuterium and hydrogen with carbon monoxide in air over palladium metal at total pressures of 1-2 atm and initial temperatures in the range of 20-200°C were carried out to determine the temperature dependence of catalytic ignition limits over the noble metal surface. A comparison of the patterns of catalytic ignition of mixtures of deuterium and hydrogen with carbon monoxide in air over the surfaces of metallic palladium and rhodium at pressures of 1-2 atm and temperatures of $25\text{-}300^0$C using simultaneous recording of pressure, resistance of a metal sample, and high-speed filming has been made. It was found that the temperature dependences of CO content on temperature at the catalytic ignition limits of mixtures D_2+CO+air and H_2+CO+air over the surface of metallic rhodium at pressures above 1 atm are close to each other. At the same time, the temperature dependence of the CO content on the temperature at the catalytic ignition limits of mixtures D_2+CO+air and H_2+CO+air over the surface of palladium metal is qualitatively different; CO additives have a stronger effect on the combustion of deuterium. It has been found that near the lower limit of catalytic ignition mixtures of H_2+CO+air on the surface of palladium metal in the temperature range of 60-100^{0}C, a double ignition mode is observed. In this case, the delay times of the first ignition are less than 0.1 s, and the delay times of the second ignition are about several seconds. The factors responsible for this phenomenon are discussed.

In the fifth Chapter, the experiments on the propagation of the flame front of a dilute methane-oxygen mixture at 200-300 Torr against the flow of combustible gas generated by a fan are described and interpreted. We have shown that both the average flame velocity and the length of the "flame jump" through a hole in a flat obstacle increase with increasing velocity of the counterflow of unreacted combustible gas, i.e., the counterflow of combustible gas from the fan accelerates the flame. Experiments on the propagation of the flame front of a dilute methane-oxygen mixture at 200-300 Torr in a co-current flow of combustible gas generated by a fan have shown that the average flame velocity also increases in the presence of the co-current flow of the initial combustible gas. Flame propagation through holes in flat obstacles is accompanied by the appearance of swirling flames and large vortices. It has been experimentally determined that a hemispherical mesh obstacle, with its convex part facing the direction of a spreading flame, has a "focusing" effect on the length of the "flame jump". The obstacle facing in the opposite direction does not show this effect. These features have been modeled qualitatively, taking into account the distribution of gas density and velocity over the diameter of the reactor created by the fan. The results obtained are important for solving explosion safety issues for volumes of complex geometry.

In the sixth chapter, the characteristics of the interaction of the flame front with obstacles in volumes of complex geometry are considered. It has been experimentally shown that the flame front of a dilute methane-oxygen mixture at 298 K and 100-300 Torr does not form a von Karman Vortex Street behind a cylindrical obstacle, including a perforated cylinder; however, under the same conditions the vortex instability occurs in the flow of hot products. In a perforated cylinder, local centers of primary ignition are formed on its inner surface. The modeling takes into account the main observed features of the propagation of the flame front against the obstacle: a branched chain combustion mechanism and the absence of vortex formation behind the obstacle during flame propagation. It is shown that a qualitative model based on the Navier-Stokes equations in the small Mach number approximation for a compressible inert/reacting medium allows obtaining both the mode of occurrence of the von Karman instability in a chemically inert gas and the absence of a flame propagation regime in a reacting flow. This model also illustrates the occurrence of local primary ignition centers on the inner surface of the obstacle. It has been shown experimentally that the flame front of a premixed dilute methane-oxygen mixture at 298K and 100-300 Torr propagating against hollow cylindrical and conical obstacles oriented along the axis of the reactor does not form von Karman vortex shedding behind them; however, under the same conditions, vortex instability occurs behind the obstacles in the flow of hot products. Numerical estimates based on the acoustic approximation of the Navier-Stokes equations for a compressible reacting medium have made it possible to take into account the main observed feature of the flame front hitting a cylindrical obstacle: when the flame penetrates the obstacle, the von Karman Vortex Street is absent. Thus, a qualitative model allows obtaining both the mode of occurrence of von Karman instability in a chemically inert gas and its absence during flame propagation.

In this Chapter, it has been established that the model of the flame propagation process (methane combustion) in a conventional room containing an inner space with two holes and flammable material inside shows a wide variety of combustion modes depending on the geometry of this complex volume. It is shown that the preliminary numerical calculation of the expected flame propagation patterns cannot a priori predict all possible combustion modes. Thus, a real experiment under laboratory conditions, assuming the possibility of scaling the process, seems to be the most optimal way for experimental investigation of combustion modes in order to solve certain fire safety problems. The main regularities of the interaction of methane-oxygen counterflames in a closed cylindrical reactor, when initiated by a spark discharge at the ends using high-speed filming, have been established. It was found that gas-dynamic factors predominate in the interaction of the counterflames both in the hot combustion products and in the initial non-stratified mixture; under conditions of uneven density stratification, two-dimensional vortices can spread beyond the zone of interaction of the counterflames. It is shown that the three-dimensional model used in the work provides a satisfactory qualitative description of the characteristics of the counterflame interaction in both homogeneous and stratified media.

The authors would also like to acquaint the readers with virtually inaccessible works of Russian authors published in Russian until 2024.

CHAPTER 1

THEORY AND QUALITATIVE MATHEMATICAL INTERPRETATION OF COMBUSTION AND CATALYTIC COMBUSTION PROCESSES

The basic principles of combustion processes are presented below, with emphasis on the most important aspects of the presentation of this material, as it was carried out earlier in our books [1-3].

Keywords: chain branching, ignition, combustion, heating, instability, reacting flow, Navier-Stokes equations, acoustic approximation

It should be noted that the vast majority of gas-phase combustion reactions have a branched chain nature, and the authors will constantly draw the reader's attention to this fact. It is determined by fundamental chemical laws. The branched chain reaction produces active particles, free atoms and radicals, the number of which increases in an avalanche-like manner. Therefore, it is enough for a single free radical to be produced (e.g. thermally) for the radicals to multiply, which leads to an acceleration of the processes of the branched chain type. Heat evaluation accelerates chain branching and vice versa, this feedback also plays a significant role, even close to the concentration combustion limits [4].

In the case of branched chain combustion, there are two possibilities

- the branching rate exceeds the active particle termination rate, resulting in a very rapid development of the reaction chains and leading to an explosion;
- the rate of termination is higher than that of branching, so that the chains cannot develop and the reaction cannot take place at all (if, as usual, the rate of free radical formation is quite low). For example, hydrogen gas or phosphorus vapor in contact with oxygen can remain below the limit for weeks without even a trace of reaction being observed. The transition from a completely inert state to a rapid reaction (explosion) can easily be caused, for example, by increasing the pressure of the oxygen or the dimensions of the reactor, etc. [4]. Similar limit phenomena

have been observed by Hinshelwood [5] in the case of pressures exceeding a certain "second upper limit" (e.g. in the case of the hydrogen oxidation reaction). The second upper limit was explained on the basis of the ideas of Semenov and Hinshelwood concerning the competition between the process of chain termination in the volume in the case of termolecular collisions and the process of chain branching.

We draw the reader's attention to the fact that free atoms and radicals are highly chemically active particles, and they react with molecules much more readily than molecules react with each other. Obviously, the free valence cannot disappear in the course of the reaction between a free atom/radical and a molecule. This means that at least one product of the reaction is a free atom/radical. This atom/radical then reacts with the nearest molecule, creating another free atom/radical, and so on in a long chain of changes. So there are three possible cases:

- during the reaction between the radical and the molecule, a monoradical can be formed, leading to the formation of an unbranched chain, e.g.

$$.\mathrm{CH_3} + \mathrm{CH_3CHO} \rightarrow \mathrm{CH_4} + .\mathrm{CH_3CO}$$
$$.\mathrm{CH_3CO} \rightarrow .\mathrm{CH_3} + \mathrm{CO}$$

- if the main chain of the reaction is unbranched, but the monomolecular decomposition of the reaction products can lead to the formation of free radicals and thus to the formation of new chains, it is usually called degenerate branching. As an example, we can consider the formation of alkyl hydroperoxides:

$$.\mathrm{R} + \mathrm{O_2} \rightarrow .\mathrm{RO_2}$$
$$\mathrm{RO_2} + \mathrm{RH} \rightarrow \mathrm{ROOH} + .\mathrm{R}$$
$$\mathrm{ROOH} \rightarrow .\mathrm{RO} + .\mathrm{OH}$$

- during the reaction, instead of one free valence, three are formed; each valence starts a new chain. The result is the occurrence of a (rather simplified) branched chain reaction [6]:

$.\mathrm{OH} + \mathrm{H_2} \rightarrow \mathrm{H_2O} + \mathrm{H}(k_1)$;
$.\mathrm{H} + \mathrm{O_2} \rightarrow .\mathrm{OH} + .\mathrm{O}.(k_2)$;
$.\mathrm{O}. + \mathrm{H_2} \rightarrow \mathrm{OH} + \mathrm{H}(k_3)$;
$\mathrm{H} + \text{wall} \rightarrow \mathrm{H_s}(k_4)$ chain termination;
$.\mathrm{H} + \mathrm{O_2} + \mathrm{M} \rightarrow \mathrm{HO_2} + \mathrm{M}\,(k_5)$;
$\mathrm{HO_2} + \mathrm{H_2} \rightarrow \mathrm{H_2O_2} + .\mathrm{H}\,(k_6)$,

Reactions (1)-(3) correspond to the following overall process:

$$.\mathrm{H} + \mathrm{O_2} + 3\mathrm{H_2} \rightarrow 2\mathrm{H_2O} + 3.\mathrm{H}$$

Note that the hydrogen-oxygen system is considered a model object because its detailed reaction mechanism is well understood (in contrast, for example, to hydrocarbon oxidation), since it involves the simplest fuel in the realistic combustion system.

In reaction (5), M is the particle that removes excess energy from the relatively low-active HO_2 radical, whose reactions at low temperatures and pressures mainly lead to the termination of reaction chains. Under these conditions, the proportion of HO_2 entering reaction (6) is small. At conventional combustion temperatures of H_2 above 1000K, the branching rate of the chains realized in reactions (1) - (3) exceeds the rate of reaction (5), and even more exceeds the rate of termolecular chain termination.

Due to the branched-chain nature of H_2 oxidation, the developing combustion can occur in different kinetic modes with different critical conditions. The branched-chain character of the process also determines its exposure to impurities of substances that react with active intermediates to form products that are not able to participate in the development of chains, and thus even small amounts of impurities lead to suppression of combustion.

One of the characteristics of hydrogen oxidation is the existence of three critical ignition pressures (so-called ignition limits), which form a self-ignition region in P-T coordinates (Fig.1.1a). The chain nature of the two lower limits is generally obvious (corresponding to reactions 4 and 5). The nature of the third limit, which covers pressures above 0.5 atm and increases with decreasing initial temperature, is still under discussion. As can be seen from the reaction scheme, the rates of branching and chain development (1) - (3) are proportional to the first order concentration of the initial reagents. The rapid reaction (5) is proportional to the square of their concentration. Therefore, at these temperatures, above a certain pressure, the termolecular termination reaction (5) predominates over the branching reaction, and ignition is not possible. This is the second limit of auto-ignition. Above 850K, the second and third limits are not observed, since the reaction (6) begins to play a significant role, regenerating atomic hydrogen and thus compensating for the chain termination caused by the termolecular reaction (5).

Let us illustrate the above with a simplified example.

As we have seen, chain reactions occur through the formation of active particles. During the reaction, the number of these particles can increase. First, active particles can be formed as a result of thermal motion independent of the chain reaction, since reagent molecules can dissociate when they collide; the rate of this process can be high enough only at high temperatures. Second, an elementary process of chain branching can occur, in which an active atom or radical gives rise to two or more atoms (or free radicals). Branching always occurs because of the reaction energy. For example, the reaction $H+H_2 \rightarrow 3H$ is possible from a material balance point of view. However, from the energy point of view this reaction is not possible, but the reaction $H+3H_2+O_2 \rightarrow 3H+2H_2O$ is possible. The rate of formation of active particles in this way is proportional to their concentration. The presence of a source of active particles is extremely important and determines the main features of the chain kinetics. The appearance of active particles can initiate branching, i.e. the formation of multiple numbers of active particles, if thermodynamically possible. In addition, there are always processes that cause their loss. The rate of removal of active centers from the reaction by collision with stable molecules or by diffusion to the vessel walls is also proportional to the concentration of active centers. When the rate of chain branching becomes greater than the rate of chain termination, we get explosion conditions; when these conditions do not exist, explosion is impossible. Essentially, the same type of concept applies to thermal explosion (or thermal ignition). If the rate of thermal energy release is greater than the rate of thermal energy loss, the condition of explosion will occur. However, this is not a case of chemical catalysis. The increase in temperature of the catalytic wire in the hydrogen-containing combustible mixture leads primarily to the formation of primary active centers on the wire, which initiate combustion and then propagate into the volume. A number of experimental evidences in favor of this statement are given later in this book (see also [3]).

Thus, for our simplified model, the equation for the time variation of the concentration of active centers can be written in the form$\frac{d[H]}{dt} = w_0 + f[H] - g[h]$

w_0 is the very small rate of origination of active centers from molecular reagents and $f = k_2[O_2]$ and $g = k_4$ for heterogeneous chain termination or $k_5[O_2][M]$ for homogeneous chain termination on the second ignition limit [4]. Writing $f - g = \varphi$ we obtain $\frac{d[H]}{dt} = w_0 + \varphi[H]$. Note that the rate of origination of active centers w_0 is very small, so that in experiment we can hardly measure either the change in the concentration of active centers or the heat of the reaction. A change in the external conditions (temperature, pressure) causes changes in both f and g. Since no activation energy is required for heterogeneous loss of an active hydrogen atom H, the kinetic constant characterizing the formation of new active centers by chain branching typically has stronger temperature dependence than the rate of chain termination. Thus, the difference f - g changes sign as the temperature is raised. At low temperatures, it is negative and at high temperatures, it is positive. Thus, depending on the sign of f - g the type of solution changes fundamentally. The temperature, at which φ equals zero,