

COMBUSTION

Irvin Glassman

SECOND EDITION

Combustion

Second Edition

IRVIN GLASSMAN

*Department of Mechanical and Aerospace Engineering
Princeton University
School of Engineering and Applied Science
Princeton, New Jersey*

1987



ACADEMIC PRESS, INC.

Harcourt Brace Jovanovich, Publishers
Orlando San Diego New York Austin
Boston London Sydney Tokyo Toronto

COPYRIGHT © 1987 BY ACADEMIC PRESS, INC.
ALL RIGHTS RESERVED.
NO PART OF THIS PUBLICATION MAY BE REPRODUCED OR
TRANSMITTED IN ANY FORM OR BY ANY MEANS, ELECTRONIC
OR MECHANICAL, INCLUDING PHOTOCOPY, RECORDING, OR
ANY INFORMATION STORAGE AND RETRIEVAL SYSTEM, WITHOUT
PERMISSION IN WRITING FROM THE PUBLISHER.

ACADEMIC PRESS, INC.
Orlando, Florida 32887

United Kingdom Edition published by
ACADEMIC PRESS INC. (LONDON) LTD.
24-28 Oval Road, London NW1 7DX

Library of Congress Cataloging in Publication Data

Glassman, Irvin.
Combustion.

Includes index.

1. Combustion. I. Title.
QD516.G55 1986 541.3'61 86-13975
ISBN 0-12-285851-4 (alk. paper)

PRINTED IN THE UNITED STATES OF AMERICA

86 87 88 89 9 8 7 6 5 4 3 2 1

Combustion

Second Edition

*To
My Graduate Students
Past and Present
for the continual joy and pride they have given me*

“No man can reveal to you aught but that which already lies half asleep in the dawning of your knowledge.

If he (the teacher) is wise he does not bid you to enter the house of his wisdom, but leads you to the threshold of your own mind.

The astronomer may speak to you of his understanding of space, but he cannot give you his understanding.

And he who is versed in the science of numbers can tell of the regions of weight and measures, but he cannot conduct you thither.

For the vision of one man lends not its wings to another man.”

Gibran, THE PROPHET

Preface to the Second Edition

Motivations to write a second edition of *Combustion* were numerous. Great progress has been made in many areas of this field, and the original edition was being used as a text and therefore required problem sets and improved methods of explaining many of the basic concepts that had evolved over another decade of teaching. Every chapter of the original edition has been enlarged and, it is hoped, improved with new material, concepts, or methods of presentation.

Chapter One has been expanded with more detailed developments with respect to the relationship of the equilibrium constant to the basic thermodynamic properties. In addition, a method of rapidly estimating the flame temperature of any CH hydrocarbon in air is presented. Chapter Two now contains a more detailed discussion of chemical kinetics, particularly as it relates to transition state theory, chain reaction concepts, and the “fall-off” pressure effect. Chapter Three now provides a more extensive discussion of aliphatic and aromatic hydrocarbon oxidation processes at both low and high temperatures. The structure of a laminar flame and effects of turbulence on chemical systems such as flames are now considered in great detail in Chapter Four. The major modifications to Chapter Five consist of a completely revised discussion of the structure of the detonation front and the introduction of some discussion of the dynamic detonation parameters.

Buoyancy effects in gaseous diffusion flames, transient heating effects in droplet burning, and conceptual ideas in developing the Spalding B variables comprise the new material introduced in Chapter Six. Chapter Seven has been completely revised to integrate the concepts of both chain and thermal spontaneous ignition concepts. Discussion of forced ignition and, particularly, the minimum ignition energy concept has been added as well. Chapter Eight

contains extensive new material on SO_x , NO_x , and soot formation processes. Chapter Nine now considers the combustion of low volatile metals as well as carbon char. Also included is new material on the controlling elements in pulverized coal and soot oxidation.

The idea of adding appendixes first evolved in order to provide data required for the problem sets added to each chapter. However, various data collections have accumulated in the author's laboratory. Such data have proven to be of enormous convenience for many research purposes. Since no complete compilation of combustion data was known to exist, it was decided to expand the initial idea of the appendixes to meet a more general need and to include a large number which would provide a wide source of various data needed in combustion considerations. The author hopes this material will be as useful to the reader as it has been to the author in the past.

Acknowledgments to the Second Edition

Many people have contributed directly and indirectly to the content of this second edition. In particular, I must recognize the numerous stimulating discussions I have had with my colleagues F. A. Williams, F. L. Dryer, and K. Brezinsky. Professor Williams was very generous in making a draft of the second edition of his book *Combustion Theory* available to me during my writing. This draft was a stimulus to my thinking about many revisions I have made.

In much of the material added in the text, I drew heavily from the work of Westbrook and Dryer, Libby and Williams, Mulcahy and Smith, Bray and Lee. For the appendixes the major sources of data were from the compilers of the JANAF tables and the compilations of Westbrook and Dryer, McMillen and Golden, Gibbs and Calcote, Zebatakis, Mullins, Calcote, Gregory, and Barnett and Gilmer. I wish to express my appreciation to all these authors. K. Brezinsky, R. Yetter, C. Fernandez-Pello, M. Sichel, F. A. Williams, E. Dibora, D. Seery, and A. Sarofim each read a draft chapter of this revised edition and offered many helpful comments. To them, thanks are due as well.

One's research environment provides the stimulus and background for such an endeavor as writing a book. I must thank the Air Force Office of Scientific Research and the Mobil Research and Development Corporation for their continued support of my research program and J. A. Sivo, D. Peoples, and the late T. A. Bozowski for making that research program work.

Thanks are also due to Mrs. Memory J. Leleszi who typed the many drafts of this effort, and to Mrs. Norma-Jean Proscia who typed some of the first chapters. Mrs. Betty Adam ably assisted with the appendixes. As to be expected, my wife Beverly's support was always there.

Preface to the First Edition

During my twenty years of teaching combustion at Princeton, I had accumulated extensive lecture notes and developed my own approach to the subject matter. For years former students and associates have encouraged me to publish these notes. This book is the result.

My whole concept of teaching has been to stimulate the student to think, to learn the material on his own, and to understand how to use it in his own research and development endeavors. It is difficult to assess whether this concept will prevail in this book. Combustion is a most complex subject that involves primarily the disciplines of chemistry, physics, and fluid mechanics. However, it is important to understand that approaches to a complex subject can be made in a fundamental manner. One must gain the physical insight into underlying principles. Although many subjects are presented, I have tried to strip away the complexities and elaborate upon the physical insights essential to understanding. Chapter Nine on coal combustion epitomizes this approach. When I thought it necessary to cover this topic in class, I was surprised that there was not readily available in the literature some of the simple results developed in this chapter.

The subject matter which comprises the field of combustion is diverse. No attempt has been made to develop a unified approach to all material. Indeed, in my opinion, in order to gain the best insight the approach should vary with the subject matter.

Acknowledgments to the First Edition

My understanding of combustion came about from many associations. The one that I cherished the most has been with my own graduate students. Their contributions to this book are many. In particular, I must recognize and thank Dr. F. L. Dryer who chose to remain at Princeton and assume numerous responsibilities in our laboratory while I undertook other endeavors—such as writing this book.

The foundation for much of what I have written was developed during 25 years of research in the field. I had no previous experience or training in this prior to coming to Princeton. Practically all my Princeton research was sponsored by the U.S. government. Thus I would also like to recognize the confidence expressed in me by the technical monitors of my research contracts and grants. They deserve the thanks of many of us. In particular, I owe much to Dr. J. F. Masi of the Air Force Office of Scientific Research for his particular interest in the contributions he thought I could make by my approach to combustion. I hope this book is another such contribution.

Special thanks are due to my wife and children who gave me the love and happiness necessary to pursue this arduous, but enjoyable, career.

Contents

<i>Preface to Second Edition</i>	xv
<i>Acknowledgments to the Second Edition</i>	xvii
<i>Preface to First Edition</i>	xix
<i>Acknowledgments to the First Edition</i>	xxi

Chapter One **Chemical Thermodynamics and Flame Temperatures**

A. Introduction	1
B. Heats of Reaction and Formation	1
C. Free Energy and the Equilibrium Constants	6
D. Flame Temperature Calculations	15
Problems	27
References	30

Chapter Two **Chemical Kinetics**

A. Introduction	31
B. The Rates of Reactions and Their Temperature Dependency	32
1. The Arrhenius Rate Expression	33
2. Transition State and Recombination Rate Theories	36
C. Simultaneous Interdependent Reactions	40
D. Chain Reactions	41
E. Pseudo-First-Order Reactions and the "Fall-Off" Range	44
F. The Partial Equilibrium Assumption	47
G. Pressure Effect in Fractional Conversion	48
Problems	48
References	50

Chapter Three Explosive and General Oxidative Characteristics of Fuels

A. Introduction	51
B. Chain Branching Reactions and Criteria for Explosion	51
C. Explosion Limits and Oxidation Characteristics of Hydrogen	56
D. Explosion Limits and Oxidation Characteristics of Carbon Monoxide	63
E. Explosion Limits and Oxidation Characteristics of Hydrocarbons	67
1. Organic Nomenclature	68
2. Explosion Limits	72
a. The Negative Coefficients of Reaction Rate	73
b. Cool Flames	74
3. "Low-Temperature" Hydrocarbon Oxidation Mechanisms	75
a. Competition Between Chain Branching and Steady Reaction Steps	76
b. Importance of Isomerization in Large Hydrocarbon Radicals	78
F. The Oxidation of Aldehydes	81
G. The Oxidation of Methane	81
H. The Oxidation of Higher-Order Hydrocarbons	85
1. Aliphatic Hydrocarbons	85
a. Overall View	85
b. Paraffin Oxidation	87
c. Olefin and Acetylene Oxidation	90
2. Alcohols	94
3. Aromatic Hydrocarbons	96
a. Benzene Oxidation	96
b. Oxidation of Alkylated Aromatics	102
Problems	104
References	105

Chapter Four Flame Phenomena in Premixed Combustible Gases

A. Introduction	107
B. Laminar Flame Structure	111
C. The Laminar Flame Speed	114
1. The Theory of Mallard and Le Chatelier	117
2. The Theory of Zeldovich, Frank-Kamenetskii, and Semenov	119
3. The Laminar Flame and the Energy Equation	126
4. Flame Speed Measurements	126
a. Burner Method	130
b. Cylindrical Tube Method	131
c. Soap Bubble Method	132
d. Closed Spherical Bomb Method	132
e. Flat Flame Burner Method	133
5. Experimental Results—Physical and Chemical Effects	134
D. Stability Limits of Laminar Flames	141
1. Flammability Limits	142
2. Quenching Distance	148
3. Flame Stabilization (Low Velocity)	150

a. Flashback and Blowoff	151
b. Analysis and Results	151
4. Stability Limits and Design	156
E. Turbulent Reacting Flows and Turbulent Flames	159
1. The Rate of Reaction in a Turbulent Field	161
2. Regimes of Turbulent Reacting Flows	163
3. The Turbulent Flame Speed	175
F. Stirred Reactor Theory	178
G. Flame Stabilization in High-Velocity Streams	182
Problems	192
References	194

Chapter Five Detonation

A. Introduction	197
1. Premixed and Diffusion Flames	197
2. Explosion, Deflagration, and Detonation	198
3. The Onset of Detonation	198
B. Detonation Phenomena	201
C. Hugoniot Relations and the Hydrodynamic Theory of Detonations	202
1. Characterization of the Hugoniot Curve and the Uniqueness of the Chapman–Jouguet Point	203
2. Determination of the Speed of Sound in the Burned Gases for Conditions above the Chapman–Jouguet Point	211
a. Behavior of the Entropy along the Hugoniot Curve	211
b. The Concavity of the Hugoniot Curve	212
c. The Burned Gas Speed	214
3. Calculation of the Detonation Velocity	216
D. Comparison of Detonation Velocity Calculations with Experimental Results	220
E. The ZND Structure of Detonation Waves	223
F. The Structure of the Cellular Detonation Front and other Detonation Phenomena Parameters	226
1. The Cellular Detonation Front	226
2. The Dynamic Detonation Parameters	230
3. Detonation Limits	231
G. Detonations in Nongaseous Media	235
Problems	235
References	236

Chapter Six Diffusion Flames

A. Introduction	238
B. Gaseous Fuel Jets	239
1. Appearance	239
2. Structure	242
3. Theoretical Considerations	245
4. The Burke–Schumann Development	248
5. Turbulent Fuel Jets	254
C. Burning of Condensed Phases	255
1. General Mass Burning Considerations and the Evaporation Coefficient	256

2. Single Fuel Droplets in Quiescent Atmospheres	260
a. Heat and Mass Transfer without Chemical Reaction (Evaporation)— the Transfer Number B	262
b. Heat and Mass Transfer with Chemical Reaction (Droplet Burning Rates)	268
c. Refinements of the Mass Burning Rate Expression	275
D. Burning of Droplet Clouds	280
E. Burning in Convective Atmospheres	281
1. The Stagnant Film Case	281
2. The Longitudinally Burning Surface	283
3. The Flowing Droplet Case	285
4. Burning Rates of Plastics; The Small B Assumption and Radiation Effects	288
Problems	288
References	290

Chapter Seven Ignition

A. Concepts	292
B. Chain Spontaneous Ignition	295
C. Thermal Spontaneous Ignition	297
1. Semenov Approach to Thermal Ignition	298
2. Frank-Kamenetskii Theory of Thermal Ignition	303
a. The Stationary Solution—The Critical Mass and Spontaneous Ignition Problems	303
b. The Nonstationary Solution	305
D. Forced Ignition	308
1. Spark Ignition and Minimum Ignition Energy	309
2. Ignition by Adiabatic Compression and Shock Waves	315
Problems	316
References	316

Chapter Eight Environmental Combustion Considerations

A. Introduction	318
B. The Nature of Photochemical Smog	319
1. Primary and Secondary Pollutants	320
2. The Effect of NO_x	321
3. The Effect of SO_x	324
C. NO_x Formation and Reduction	326
1. The Structure of the Nitrogen Oxides	327
2. The Effect of Flame Structure	328
3. Atmospheric Nitrogen Kinetics	329
4. Fuel-Bound Nitrogen Kinetics	337
5. The Formation of NO_2	340
6. The Reduction of NO_x	342
D. SO_x Emissions	345
1. The Product Composition and Structure of Sulfur Compounds	346
2. Oxidative Mechanisms of Sulfur Fuels	348
a. H_2S	349

b. COS and CS ₂	353
c. Elemental Sulfur	354
d. Organic Sulfur Compounds	355
e. Sulfur Trioxide and Sulfates	357
f. SO _x -NO _x Interactions	360
E. Particulate Formation	360
1. Characteristics of Soot	361
2. Soot Formation Processes	362
3. The Use of Flames in Soot Formation Analyses	365
a. Premixed Flames	366
b. Diffusion Flames	369
4. The Influence of Physical and Chemical Parameters on Soot Formation	373
5. Particulates from Liquid Hydrocarbon Pyrolysis	375
F. Stratospheric Ozone	376
1. The HO _x Catalytic Cycle	376
2. The NO _x Catalytic Cycle	377
3. The ClO _x Catalytic Cycle	380
Problems	382
References	382

Chapter Nine The Combustion of Nonvolatile Fuels

A. Carbon Char and Metal Combustion	386
B. Diffusion Kinetics	388
C. Diffusion Controlled Burning Rate	390
1. The Burning of Carbon Char Particles	391
2. The Burning of Boron Particles	394
3. The Role of Gaseous Inerts in Heterogeneous Diffusion Burning	396
4. Oxidation of Very Small Particles—Pulverized Coal and Soot	397
D. The Burning of Porous Chars	404
E. The Burning Rate of Ash-Forming Coal	407
Problems	409
References	410

Appendix	411
Appendix A. Thermochemical Data and Conversion Factors	413
Appendix B. Specific Reaction Rate Constants	448
Appendix C. Bond Dissociation Energies of Hydrocarbons	454
Appendix D. Laminar Flame Speeds	460
Appendix E. Flammability Limits in Air	465
Appendix F. Spontaneous Ignition Temperature Data	472
Appendix G. Minimum Spark Ignition Energies and Quenching Distances	486

<i>Indexes</i>	491
----------------	-----

Chemical Thermodynamics and Flame Temperatures

A. INTRODUCTION

The most essential parameters necessary for the evaluation of combustion systems are the equilibrium product temperature and composition. If all the heat evolved in the reaction is employed solely to raise the product temperature, then this temperature is called the adiabatic flame temperature. Because of the importance of the temperature and gas composition in combustion considerations, it is useful to review those aspects of the field of chemical thermodynamics which deal with these subjects.

B. HEATS OF REACTION AND FORMATION

All chemical reactions are accompanied either by an absorption or evolution of energy, which usually manifests itself as heat. It is possible to determine this amount of heat and thus the temperature and product composition from very basic principles. Spectroscopic data and statistical calculations permit one to determine the internal energy of a substance. The internal energy of a given substance is found to be dependent upon its temperature, pressure, and state and is independent of the means by which