COMBUSTION

FOURTH EDITION

IRVIN GLASSMAN
RICHARD A. YETTER

Combustion

Fourth Edition

Irvin Glassman
Richard A. Yetter

ELSEVIER

AMSTERDAM • BOSTON • HEIDELBERG • LONDON
NEW YORK • OXFORD • PARIS • SAN DIEGO
SAN FRANCISCO • SINGAPORE • SYDNEY • TOKYO

Academic Press is an imprint of Elsevier
30 Corporate Drive, Suite 400, Burlington, MA 01803, USA
525 B Street, Suite 1900, San Diego, California 92101-4495, USA
84 Theobald's Road, London WC1X 8RR, UK

Library of Congress Cataloging-in-Publication Data

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

ISBN: 978-0-12-088573-2

Typeset by Charon Tec Ltd., A Macmillan Company. (www.macmillansolutions.com)

Printed in the United States of America
08 09 10 9 8 7 6 5 4 3 2 1

This Fourth Edition is dedicated to the graduate students, post docs, visiting academicians, undergraduates, and the research and technical staff who contributed so much to the atmosphere for learning and the technical contributions that emanated from Princeton's Combustion Research Laboratory.

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 hither.

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

Gibran, *The Prophet*

The reward to the educator lies in his pride in his students' accomplishments. The richness of that reward is the satisfaction in knowing the frontiers of knowledge have been extended.

D. F. Othmer

Prologue

This 4th Edition of "Combustion" was initiated at the request of the publisher, but it was the willingness of Prof. Richard Yetter to assume the responsibility of co-author that generated the undertaking. Further, the challenge brought to mind the oversight of an acknowledgment that should have appeared in the earlier editions.

After teaching the combustion course I developed at Princeton for 25 years, I received a telephone call in 1975 from Prof. Bill Reynolds, who at the time was Chairman of the Mechanical Engineering Department at Stanford. Because Stanford was considering developing combustion research, he invited me to present my Princeton combustion course during Stanford's summer semester that year. He asked me to take in consideration that at the present time their graduate students had little background in combustion, and, further, he wished to have the opportunity to teleconference my presentation to Berkeley, Ames, and Sandia Livermore. It was an interesting challenge and I accepted the invitation as the Standard Oil of California Visiting Professor of Combustion.

My early lectures seemed to receive a very favorable response from those participating in the course. Their only complaint was that there were no notes to help follow the material presented. Prof. Reynolds approached me with the request that a copy of lecture notes be given to all the attendees. He agreed it was not appropriate when he saw the handwritten copies from which I presented the lectures. He then proposed that I stop all other interactions with my Stanford colleagues during my stay and devote all my time to writing these notes in the proper grammatical and structural form. Further, to encourage my writing he would assign a secretary to me who would devote her time organizing and typing my newly written notes. Of course, the topic of a book became evident in the discussion. Indeed, eight of the nine chapters of the first edition were completed during this stay at Stanford and it took another 2 years to finish the last chapter, indexes, problems, etc., of this first edition. Thus I regret that I never acknowledged with many thanks to Prof. Reynolds while he was alive for being the spark that began the editions of "Combustion" that have already been published.

"Combustion, 4th Edition" may appear very similar in format to the 3rd Edition. There are new sections and additions, and many brief insertions that are the core of important modifications. It is interesting that the content of these insertions emanated from an instance that occurred during my Stanford presentation. At one lecture, an attendee who obviously had some experience

in the combustion field claimed that I had left out certain terms that usually appear in one of the simple analytical developments I was discussing. Surprisingly, I subconscientiously immediately responded "You don't swing at the baseball until you get to the baseball park!" The response, of course, drew laughter, but everyone appeared to understand the point I was trying to make. The reason of bringing up this incident is that it is important to develop the understanding of a phenomenon, rather than all its detailed aspects. I have always stressed to my students that there is a great difference between knowing something and understanding it. The relevant point is that in various sections there have been inserted many small, important modifications to give greater understanding to many elements of combustion that appear in the text. This type of material did not require extensive paragraphs in each chapter section. Most chapters in this edition contain, where appropriate, this type of important improvement. This new material and other major additions are self-evident in the listings in the Table of Contents.

My particular thanks go to Prof. Yetter for joining me as co-author, for his analyzing and making small poignant modifications of the chapters that appeared in the earlier additions, for contributing new material not covered in these earlier additions and for further developing all the appendixes. Thanks also go to Dr. Chris Shaddix of Sandia Livermore who made a major contribution to Chapter 9 with respect to coal combustion considerations. Our gracious thanks go to Mary Newby of Penn State who saw to the final typing of the complete book and who offered a great deal of general help. We would never have made it without her. We also wish to thank our initial editor at Elsevier, Joel Stein, for convincing us to undertake this edition of "Combustion" and our final Editor, Matthew Hart, for seeing this endeavor through.

The last acknowledgments go to all who are recognized in the Dedication. I initiated what I called Princeton's Combustion Research Laboratory when I was first appointed to the faculty there and I am pleased that Prof. Fred Dryer now continues the philosophy of this laboratory. It is interesting to note that Profs. Dryer and Yetter and Dr. Shaddix were always partners of this laboratory from the time that they entered Princeton as graduate students. I thank them again for being excellent, thoughtful, and helpful colleagues through the years.

Speaking for Prof. Yetter as well, our hope is that "Combustion, 4th Edition" will be a worthwhile contributing and useful endeavor.

Irvin Glassman
December 2007

Preface

When approached by the publisher Elsevier to consider writing a 4th Edition of Combustion, we considered the challenge was to produce a book that would extend the worthiness of the previous editions. Since the previous editions served as a basis of understanding of the combustion field, and as a text to be used in many class courses, we realized that, although the fundamentals do not change, there were three factors worthy of consideration: to add and extend all chapters so that the fundamentals could be clearly seen to provide the background for helping solve challenging combustion problems; to enlarge the Appendix section to provide even more convenient data tables and computational programs; and to enlarge the number of typical problem sets. More important is the attempt to have these three factors interact so that there is a deeper understanding of the fundamentals and applications of each chapter. Whether this concept has been successful is up to the judgment of the reader. Some partial examples of this approach in each chapter are given by what follows.

Thus, Chapter 1, Chemical Thermodynamics and Flame Temperatures, is now shown to be important in understanding scramjets. Chapter 2, Chemical Kinetics, now explains how sensitivity analyses permit easier understanding in the analysis of complex reaction mechanisms that endeavor to explain environmental problems. There are additions and changes in Chapter 3, Explosive and General Oxidative Characteristics of Fuels, such as consideration of wet CO combustion analysis, the development procedure of reaction sensitivity analysis and the effect of supercritical conditions. Similarly the presentation in Chapter 4, Flame Phenomena in Premixed Combustible Gases, now considers flame propagation of stratified fuel–air mixtures and flame spread over liquid fuel spills. A point relevant to detonation engines has been inserted in Chapter 5. Chapter 6, Diffusion Flames, more carefully analyzes the differences between momentum and buoyant fuel jets. Ignition by pyrophoric materials, catalysts, and hypergolic fuels is now described in Chapter 7. The soot section in Chapter 8, Environmental Combustion Considerations, has been completely changed and also points out that most opposed jet diffusion flame experiments must be carefully analyzed since there is a difference between the temperature fields in opposed jet diffusion flames and simple fuel jets. Lastly, Chapter 9, Combustion of Nonvolatile Fuels, has a completely new approach to carbon combustion.

The use of the new material added to the Appendices should help students as the various new problem sets challenge them. Indeed, this approach has changed the character of the chapters that appeared in earlier editions regardless of apparent similarity in many cases. It is the hope of the authors that the objectives of this edition have been met.

Irvin Glassman
Richard A. Yetter

Contents

Chapter 1

Chemical Thermodynamics and Flame Temperatures

A. INTRODUCTION

The parameters essential 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, this temperature is called the adiabatic flame temperature. Because of the importance of the temperature and gas composition in combustion considerations, it is appropriate to review those aspects of the field of chemical thermodynamics that deal with these subjects.

B. HEATS OF REACTION AND FORMATION

All chemical reactions are accompanied by either an absorption or evolution of energy, which usually manifests itself as heat. It is possible to determine this amount of heat—and hence 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 the state is attained. Likewise, the change in internal energy, ΔE, of a system that results from any physical change or chemical reaction depends only on the initial and final state of the system. Regardless of whether the energy is evolved as heat, energy, or work, the total change in internal energy will be the same.

If a flow reaction proceeds with negligible changes in kinetic energy and potential energy and involves no form of work beyond that required for the flow, the heat added is equal to the increase of enthalpy of the system

$$Q = \Delta H$$

where Q is the heat added and H is the enthalpy. For a nonflow reaction proceeding at constant pressure, the heat added is also equal to the gain in enthalpy

$$Q = \Delta H$$