COMBUSTION

Irvin Glassman

SECOND EDITION

Combustion
Second Edition

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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

Chapter Three Explosive and General Oxidative Characteristics of Fuels

Chapter Four Flame Phenomena in Premixed Combustible Gases

Chapter One

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