

Combustion

IRVIN GLASSMAN

Combustion

IRVIN GLASSMAN

*Department of Aerospace and Mechanical Sciences
and Center for Environmental Studies
Princeton University
Princeton, New Jersey*



ACADEMIC PRESS

New York San Francisco London 1977

A Subsidiary of Harcourt Brace Jovanovich, Publishers

COPYRIGHT © 1977, 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.
111 Fifth Avenue, New York, New York 10003

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

Library of Congress Cataloging in Publication Data

Glassman, Irvin.
Combustion.

Includes bibliographies.

I.	Combustion.	I.	Title.
QD516.G55	541'.361		76-27442
ISBN: 0-12-285850-6			

PRINTED IN THE UNITED STATES OF AMERICA

*"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

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 the 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 IX 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 the material. Indeed, in my opinion, in order to gain the best insight the approach should vary with the subject matter.

Acknowledgments

My understanding of combustion came about from many associations. The one that I have 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 area 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</i>	xiii
<i>Acknowledgments</i>	xv

Chapter One Chemical Thermodynamics

A. Heats of Reaction and Formation	1
B. Free Energy, the Equilibrium Constant, and Flame Temperature Calculations	5
References	15

Chapter Two Chemical Kinetics

A. The Rates of Reactions and Their Temperature Dependency	16
B. Simultaneous Interdependent and Chain Reactions	20
C. Pseudo-First-Order Reactions	23
D. Pressure Effect in Fractional Conversion	24
References	25

Chapter Three Explosive and General Oxidation Characteristics of Fuels

A. The Criterion for Explosion	26
B. Explosion Limits and Oxidation Characteristics of Hydrogen	29
C. Explosion Limits and Oxidation Characteristics of Carbon Monoxide	34
D. Explosion Limits and Oxidation Characteristics of Hydrocarbons	37
1. Organic Nomenclature	38
2. Explosion Limits, Cool Flames, and General Mechanisms	41
3. Detailed Oxidation Mechanisms of Hydrocarbons	49
a. Methane	49
b. Aldehydes	51
c. Higher Paraffin Hydrocarbons	52

d. Olefins	55
e. Aromatics	56
References	57

Chapter Four Flame Phenomena in Premixed Combustible Gases

A. The Laminar Flame Speed	64
1. The Theory of Mallard and Le Chatelier	66
2. The Theory of Zeldovich, Frank-Kamenetskii, and Semenov	68
3. The Laminar Flame and the Energy Equation	75
4. Flame Speed Measurements	75
a. Bunsen Burner Method	79
b. Cylindrical Tube Method	80
c. Soap Bubble Method	81
d. Closed Spherical Bomb Method	82
e. Flat Flame Burner Method	82
5. Experimental Results and Physical and Chemical Effects	84
B. Stability Limits of Laminar Flames	87
1. Flammability Limits	87
a. Experimental Results and Physical and Chemical Effects	88
b. A Theoretical Approach	91
2. Quenching Distance	99
3. Flame Stabilization (Low Velocity)	101
a. Flashback	102
b. Blowoff	102
c. Analysis and Results	103
4. Stability Limits and Design	105
C. Turbulent Flames	107
1. Work of Damköhler and Schelkin	110
2. The Characteristic Time Approach	113
3. Experimental Results and Physical and Chemical Effects	115
D. Stirred Reactor Theory	116
E. Flame Stabilization in High Velocity Streams	119
References	125

Chapter Five Detonation

A. Introduction	127
1. Premixed and Diffusion Flames	127
2. Explosion, Deflagration, and Detonation	128
3. The Onset of Detonation	129
B. The Detonation Velocity	130
1. Characterization of the Hugoniot Curve and the Uniqueness of the Chapman-Jouguet Point	130
2. Determination of the Speed of Sound in the Burned Gases for Conditions above the Chapman-Jouguet Point	139
a. Behavior of the Entropy along the Hugoniot Curve	139

CONTENTS

xi

b. The Burned Gas Speed	142
3. Calculation of the Detonation Velocity	144
C. The Structure of the Detonation Wave	147
D. Comparison of Detonation Calculations with Experimental Results	150
E. Detonation Limits	153
References	157

Chapter Six Diffusion Flames

A. Gaseous Fuel Jets	158
1. Appearance	159
2. Structure	159
3. Theoretical Considerations	161
a. The Burke-Schumann Development	164
b. Phenomenological Analysis and the Turbulent Fuel Jet	166
B. Burning of Condensed Phases	168
1. General Mass Burning Considerations and the Evaporation Coefficient	169
2. Single Fuel Droplets in Quiescent Atmospheres	174
a. Heat and Mass Transfer without Chemical Reaction (Evaporation)—the Transfer Number B	176
b. Heat and Mass Transfer with Chemical Reaction (Burning Rates)	181
C. Burning in Convective Atmospheres	185
1. The Stagnant Film Case	185
2. The Longitudinally Burning Surface	187
3. The Flowing Droplet Case	189
4. Burning Rates of Plastics; The Small B Assumption and Radiation Effects	191
References	193

Chapter Seven Ignition

A. Concepts	194
B. The Theory of Thermal Ignition	195
1. The Stationary Solution—The Critical Mass and Spontaneous Ignition Problems	196
2. The Nonstationary Solution	198
References	201

Chapter Eight Environmental Combustion Considerations

A. The Nature of Photochemical Smog	203
1. Primary and Secondary Pollutants	204
2. The Effect of NO_x	204
3. The Effect of SO_x	208
B. NO_x Formation and Reduction	210
1. The Structure of the Nitrogen Oxides	211
2. The Effect of Flame Structure	211
3. Atmospheric Nitrogen Kinetics	213
4. Fuel-Bound Nitrogen Kinetics	219

5. The Formation of NO_2	223
6. The Reduction of NO_x	224
7. The Partial Equilibrium Assumption	225
C. SO_x Emissions	227
1. The Product Composition and Structure of Sulfur Compounds	228
2. Oxidative Mechanisms of Sulfur Fuels	230
a. H_2S	231
b. COS and CS_2	233
c. Elemental Sulfur	235
d. Organic Sulfur Compounds	236
e. Sulfur Trioxide and Sulfates	237
D. Particulate Formation	240
1. Characteristics of Soot	241
2. Mechanisms of Soot Formation in Flames	243
3. Influence of Physical and Chemical Parameters on Soot Formation	246
4. Particulates from Liquid Hydrocarbon Pyrolysis	249
E. Stratospheric Ozone	249
1. The HO_x Catalytic Cycle	250
2. The NO_x Catalytic Cycle	251
3. The ClO_x Catalytic Cycle	254
References	255

Chapter Nine The Combustion of Coal

A. Diffusional Kinetics	258
B. The Burning Rate of Carbon	260
C. The Burning of Porous Chars	264
D. The Burning Rate of Ash-Forming Coal	267
References	269

Index

271

Chemical Thermodynamics

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.

A. HEATS OF REACTION AND FORMATION

All chemical reactions are accompanied either by an absorption or an 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. 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 was attained. Likewise the change in internal energy ΔE of a system which results from any physical change or chemical reaction depends only on the initial and final state of the system. The total change in internal energy will be the same, whether or not the energy is evolved in any form of heat, energy, or work.

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

$$Q = \Delta H$$

For a nonflow reaction proceeding at constant pressure, the heat added is also equal to the gain in enthalpy

$$Q_p = \Delta H$$

and if heat is evolved

$$Q_p = -\Delta H$$

Most thermochemical calculations are made for closed thermodynamic systems; the stoichiometry is most conveniently represented in terms of the molar quantities as determined from statistical calculations. In compressible flow problems in which open thermodynamic systems are essential, it is best to deal with mass quantities. Upper case symbols will be used for molar quantities, and lower case systems will be used for mass quantities.

One of the most important thermodynamic facts to be known about a given chemical reaction is the change in energy or heat content associated with the reaction at some specified temperature with each of the reactants and products in an appropriate standard state. This change is known either as the energy or heat of reaction at the specified temperature.

The standard state means that for each state a reference state of the aggregate exists. For gases, the thermodynamic standard reference state is taken to be equal to that of the ideal gaseous state at atmospheric pressure at each temperature. The ideal gaseous state is the case of isolated molecules which give no interactions and which obey the equation of state of a perfect gas. The standard reference state for pure liquids and solids at a given temperature is the real state of the substance at a pressure of one atmosphere.

The thermodynamic symbol which represents the property of the substance in the standard state at a given temperature is written, for example, as H_T° , E_T° , etc., where the superscript $^\circ$ specifies the standard state and the subscript T the specific temperature. Statistical calculations actually permit the determination of $E_T - E_0$, which is the energy content at a given temperature referred to the energy content at 0°K . For one mole in the ideal gaseous state,

$$PV = RT \quad (1)$$

$$H^\circ = E^\circ + (PV)^\circ = E^\circ + RT \quad (2)$$

which at 0°K reduces to

$$H_0^\circ = E_0^\circ \quad (3)$$

Thus the heat content at any temperature referred to the heat or energy content at 0°K is known and is

$$(H^\circ - H_0^\circ) = (E^\circ - E_0^\circ) + RT \quad (4)$$

From the definition of the heat of reaction, Q_p will depend on the temperature T at which the reaction and product enthalpies are evaluated. The heat of reaction at one temperature T_0 can be related to that at another temperature T_1 . Consider the reaction configuration shown in Fig. 1.

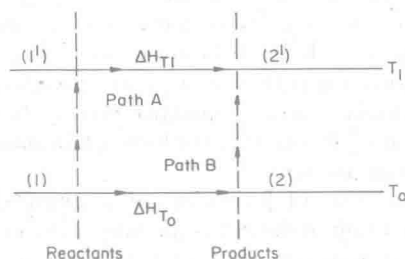


Fig. 1. Temperature-reaction paths.

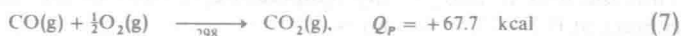
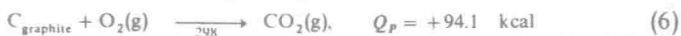
According to the First Law, the heat changes which proceed from reactants at temperature T_0 to products at temperature T_1 by either Path A or Path B shown must be the same. Path A raises the reactants from temperature T_0 to T_1 and reacts at T_1 . Path B reacts at T_0 and raises the products from T_0 to T_1 . The energy equality which relates the heats of reaction at the two different temperatures is written as

$$\begin{aligned} \sum_{j \text{ react}} n_j [(H_{T_1}^\circ - H_0^\circ) - (H_{T_0}^\circ - H_0^\circ)]_j + \Delta H_{T_1} \\ = \Delta H_{T_0} + \sum_{i \text{ prod}} n_i [(H_{T_1}^\circ - H_0^\circ) - (H_{T_0}^\circ - H_0^\circ)]_i \end{aligned} \quad (5)$$

Any changes of phase can be included in the heat content terms. Thus by knowing the difference in energy content at the different temperatures for the products and reactants, it is possible to determine the heat of reaction at one temperature from the heat of reaction at another.

If the heats of reaction at a given temperature are known for two separate reactions, the heat of reaction of a third reaction at the same temperature may be determined by simple algebraic addition. This statement is

the Law of Heat Summation. For example, two reactions which can be carried out conveniently in a calorimeter at constant pressure are



Subtracting these two reactions, one obtains



Since some of the carbon would burn to CO_2 and not just CO , it is difficult to determine calorimetrically the heat released by reaction (8).

It is, of course, not necessary to have an extensive list of heats of reaction to determine the heat absorbed or evolved in every possible chemical reaction. A more convenient and logical procedure is to list what are known as the standard heats of formation of chemical substances. The standard heat of formation is the enthalpy of a substance in its standard state referred to its elements in their standard states at the same temperature. From this definition it is obvious that the heats of formation of the elements in their standard states are zero.

The value of the heat of formation of a given substance from its elements may be the result of the determination of the heat of one reaction. Thus from the calorimetric reaction for burning carbon to CO_2 (Eq. (6)), it is possible to write the heat of formation of carbon dioxide at 298°K as

$$(\Delta H_f^\circ)_{298, \text{CO}_2} = -94.1 \text{ kcal/mole}$$

The superscript to the heat of formation symbol ΔH_f represents the standard state and the subscript number the base or reference temperature. From the example for the Law of Heat Summation, it is apparent that the heat of formation of carbon monoxide from Eq. (8) is

$$(\Delta H_f^\circ)_{298, \text{CO}} = -26.4 \text{ kcal/mole}$$

It is evident that, by judicious choice, the number of reactions which must be measured calorimetrically will be about the same as the number of substances whose heats of formation are to be determined.

The logical consequence of the above is that given the heats of formation of the substances which make up any particular reaction, one can determine directly the heat of reaction or heat evolved at the reference temperature as follows

$$\Delta H_T = \sum_{i \text{ prod}} n_i(\Delta H_f^\circ)_{T, i} - \sum_{j \text{ react}} n_j(\Delta H_f^\circ)_{T, j} = -Q_P \quad (9)$$

There exist extensive tables of standard heats of formation; however, all are not at the same reference temperature. The most convenient are the

TABLE 1

Heats of formation at 298.1°K

Chemical symbol	Name	State	ΔH_f° (kcal/mole)
C	Carbon	Vapor	126.36
N	Nitrogen atom	Gas	112.75
O	Oxygen atom	Gas	59.16
C ₂ H ₂	Acetylene	Gas	54.19
H	Hydrogen atom	Gas	52.09
O ₃	Ozone	Gas	34.00
NO	Nitric oxide	Gas	21.60
C ₆ H ₆	Benzene	Gas	19.80
C ₆ H ₆	Benzene	Liquid	11.71
C ₂ H ₄	Ethane	Gas	12.50
N ₂ H ₄	Hydrazine	Liquid	12.05
OH	Hydroxyl radical	Gas	10.06
O ₂	Oxygen	Gas	0
N ₂	Nitrogen	Gas	0
H ₂	Hydrogen	Gas	0
C	Carbon	Solid	0
NH ₃	Ammonia	Gas	-11.04
C ₂ H ₄ O	Ethylene oxide	Gas	-12.19
CH ₄	Methane	Gas	-17.89
C ₂ H ₄	Ethane	Gas	-20.24
CO	Carbon monoxide	Gas	-26.42
C ₄ H ₁₀	Butane	Gas	-29.81
CH ₃ OH	Methanol	Gas	-48.10
CH ₃ OH	Methanol	Liquid	-57.04
H ₂ O	Water	Gas	-57.80
C ₈ H ₁₈	Octane	Liquid	-59.74
H ₂ O	Water	Liquid	-68.32
SO ₂	Sulfur dioxide	Gas	-71.00
C ₁₂ H ₁₆	Dodecane	Liquid	-83.00
CO ₂	Carbon dioxide	Gas	-94.05
SO ₃	Sulfur trioxide	Gas	-94.45

compilations known as the JANNAF and NBS Tables, both of which use 298°K as the reference temperature. Table 1 lists some values of the heat of formation taken from Penner (1957), NBS Circular C461 (1947), and other sources.

B. FREE ENERGY, THE EQUILIBRIUM CONSTANT, AND FLAME TEMPERATURE CALCULATIONS

For those cases in which the products are measured at a different temperature T_2 than the reference temperature T_0 , and the reactants enter

the system at a different temperature T_1 than the reference temperature, the heat of reaction becomes

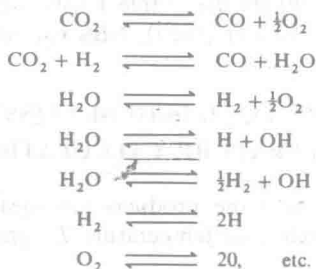
$$\begin{aligned}\Delta H_R &= \sum_{i \text{ prod}} n_i [(H_{T_2}^\circ - H_0^\circ) - (H_{T_0}^\circ - H_0^\circ)] + (\Delta H_f^\circ)_{T_0}]_i \\ &\quad - \sum_{j \text{ react}} n_j [(H_{T_1}^\circ - H_0^\circ) - (H_{T_0}^\circ - H_0^\circ)] + (\Delta H_f^\circ)_{T_0}]_j \\ &= -Q_P \quad (\text{evolved})\end{aligned}\quad (10)$$

Most systems are considered to have the reactants enter at the standard reference temperature 298°K. Consequently the enthalpy terms in the braces for the reactants disappear. The JANNAF Tables tabulate, as a supposed convenience, $(H_{T^\circ} - H_{298}^\circ)$ instead of $(H_{T^\circ} - H_0^\circ)$. This type of tabulation is unfortunate since for systems using cryogenic fuels and oxidizers, such as rockets, the reactants can enter the system at temperatures lower than the reference temperature. Indeed the fuel and oxidizer could enter at different temperatures, and the summation in Eq. (10) can be handled conveniently by first realizing that T_1 may vary with the substance j .

When all the heat evolved is used to heat the product gases, the product temperature T_2 is called the adiabatic flame temperature. In this case $\Delta H_R = 0$ and Eq. (10) becomes

$$\begin{aligned}\sum_{i \text{ prod}} n_i [(H_{T_2}^\circ - H_0^\circ) - (H_{T_0}^\circ - H_0^\circ)] + (\Delta H_f^\circ)_{T_0}]_i \\ = \sum_{j \text{ react}} n_j [(H_{T_1}^\circ - H_0^\circ) - (H_{T_0}^\circ - H_0^\circ)] + (\Delta H_f^\circ)_{T_0}]_j\end{aligned}\quad (11)$$

If the products n_i of this reaction are known, then Eq. (11) can be solved for the flame temperature. For a reacting system whose product temperature is less than 1250°K, the products are the normal stable species CO_2 , H_2O , N_2 , and O_2 , whose molar quantities can be determined from simple mass balances. However, most combustion systems reach temperatures appreciably greater than 1250°K and dissociation of the stable species occurs. Since the dissociation reactions are quite endothermic, a few percent dissociation can lower the flame temperature substantially. The stable products from a C-H-O reaction system can dissociate by any of the following reactions:



Each of these reactions helps specify a definite equilibrium concentration of each product at a given temperature. Whereas in heat of reaction experiments or low temperature combustion experiments, the products could be specified from the chemical stoichiometry, one sees now that with dissociation the specification of the product concentrations becomes much more complex and the n_i 's in the flame temperature equation [Eq. (11)] are as unknown as the flame temperature itself. In order to solve the equation for the n_i 's and T_2 , it is apparent that more than mass balance equations are needed. The necessary equations are found in the equilibrium relationships which exist among the product composition in the equilibrium system.

Recall from elementary thermodynamics that the condition for equilibrium of a chemical system comes from the following form of the Second Law

$$T dS = dE + P dV \quad (12)$$

At constant temperature and pressure, Eq. (12) takes the form

$$d(E + PV - TS)_{T, P} = 0 \quad (13)$$

or

$$d(H - TS)_{T, P} = 0 \quad (14)$$

By definition, the free energy F is written as

$$F \equiv E + PV - TS = H - TS \quad (15)$$

Thus the condition for equilibrium at constant temperature and pressure is that the change in free energy be zero, i.e.,

$$(dF)_{T, P} = 0 \quad (16)$$

If one considers an arbitrary equilibrium reaction



it can be shown that for ideal gases,

$$\Delta F^\circ = -RT \ln(p_R^r p_S^s / p_A^a p_B^b) \quad (18)$$

where the pressures are measured in atmospheres. The logarithm of the pressures arises from the relationship of the entropy to the pressure. One can define

$$K_P \equiv p_R^r p_S^s / p_A^a p_B^b \quad (19)$$

as the proper quotient of partial pressure at equilibrium. K_P is called the equilibrium constant at constant pressure and K_P is not a function of total pressure but of temperature alone. This statement is clear since ΔF° is a