

FIFTH EDITION

# Combustion

Irvin Glassman, Richard A. Yetter,  
and Nick G. Glumac



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Fifth Edition

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*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 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

# Preface

For the fifth edition of Combustion, the approach taken of providing students and practicing professionals with the fundamental physical and chemical principles of combustion has not changed from the previous editions of the book. The emphasis remains on clarity of concepts and on elaborating upon the physical insights essential to understanding. It is hoped that the fifth edition of Combustion continues to stimulate the reader to think, learn on their own, and empower them to make use of the material and understandings gained in their future research and development endeavors.

The fifth edition of Combustion is similar in format to the fourth edition. However, there are new sections and additions, and many brief insertions that are the core of important modifications. New to this edition are sections on the combustion kinetics and low-temperature chemistry of biofuels, catalytic combustion, the combustion of nanomaterials, chemical looping, and the mixture fraction concept. Updated appendices and additional problems are at the end of chapters. In addition, small, important modifications have been inserted throughout the text to give greater understanding to many elements of combustion. This new material and other major additions are self-evident in the listings in the Table of Contents.

As with the fourth edition of Combustion, special thanks go to Dr. Chris Shaddix of Sandia Livermore, who made major contributions to Chapter 9 with respect to coal combustion considerations. Our thanks go to Mary Newby of Penn State, who performed the typing of the complete book and who with insight offered a great deal of general help. We also wish to thank our Acquisitions Editor, Tiffany Gasbarrini, and Senior Editorial Project Manager, Kattie Washington, for convincing us to undertake this edition of Combustion and for seeing this endeavor through.

Irvin Glassman  
Richard A. Yetter  
Nick G. Glumac

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# Chemical thermodynamics and flame temperatures

# 1

## 1.1 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.

## 1.2 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 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,  $\Delta E$ , 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 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

$$Q_p = \Delta H$$

and if heat is evolved,

$$Q_p = -\Delta H$$

Most thermochemical calculations are made for closed thermodynamic systems, and the stoichiometry is most conveniently represented in terms of the molar quantities. In dealing with compressible flow problems in which it is essential to work with open thermodynamic systems, it is best to employ mass quantities. Throughout this text uppercase symbols will be used for molar quantities and lowercase symbols for mass quantities.

One of the most important thermodynamic facts to know about a given chemical reaction is the change in energy or heat content associated with the reaction at some specified temperature, where each of the reactants and products is in an appropriate standard state. This change is known either as the enthalpy of reaction or as the 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 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 1 atm. As discussed in Chapter 9, understanding this definition of the standard reference state is very important when considering the case of high-temperature combustion in which the product composition contains a substantial mole fraction of a condensed phase, such as a metal oxide.

The thermodynamic symbol that represents the property of the substance in the standard state at a given temperature is written, for example, as  $H_T^\circ$ ,  $E_T^\circ$ , etc., where the 'degree sign' superscript  $^\circ$  specifies the standard state and the subscript  $T$ , the specific temperature. Statistical mechanics calculations actually permit the determination of  $E_T - E_0$ , which is the energy content at a given temperature referenced to the energy content at 0 K. For one mole in the ideal gaseous state

$$PV = RT \quad (1.1)$$

$$H^\circ = E^\circ + (PV)^\circ = E^\circ + RT \quad (1.2)$$

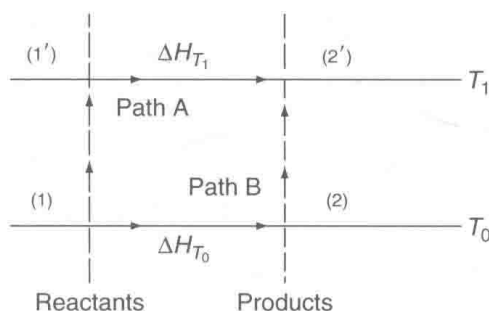
which at 0 K reduces to

$$H_0^\circ = E_0^\circ \quad (1.3)$$

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

$$(H^\circ - H_0^\circ) = (E^\circ - E_0^\circ) + RT = (E^\circ - E_0^\circ) + PV \quad (1.4)$$

The value  $(E^\circ - E_0^\circ)$  is determined from spectroscopic information and is actually the energy in the internal (rotational, vibrational, and electronic) and

**FIGURE 1.1**

Heats of reactions at different base temperatures.

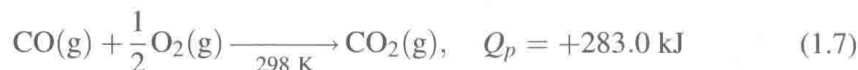
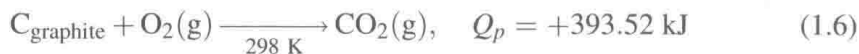
external (translational) degrees of freedom of the molecule. Enthalpy ( $H^\circ - H_0^\circ$ ) has meaning only when there is a group of molecules, a mole for instance; it is thus the ability of a group of molecules with internal energy to do  $PV$  work. In this sense, then, a single molecule can have internal energy, but not enthalpy. As stated, the use of the lowercase symbol will signify values on a mass basis. Since flame temperatures are calculated for a closed thermodynamic system of fixed mass, and molar conservation is not required, working on a molar basis is most convenient. In flame propagation or reacting flows through nozzles, mass is conserved as it crosses system boundaries; thus when these systems are considered, the per-unit mass basis of the thermochemical properties is used for a convenient solution.

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 Figure 1.1. According to the First Law of Thermodynamics, the changes in energy that proceed from reactants at temperature  $T_0$  to products at temperature  $T_1$ , by either path A or path B 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  $T_1$ . This energy equality, which relates the heats of reaction at the two different temperatures, is written as

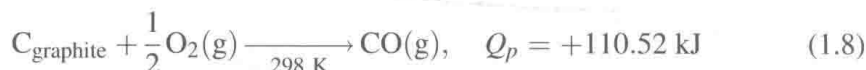
$$\left\{ \sum_{j \text{ react}} n_j \left[ (H_{T_1}^\circ - H_0^\circ) - (H_{T_0}^\circ - H_0^\circ) \right]_j \right\} + \Delta H_{T_1} = \Delta H_{T_0} + \left\{ \sum_{i \text{ prod}} n_i \left[ (H_{T_1}^\circ - H_0^\circ) - (H_{T_0}^\circ - H_0^\circ) \right]_i \right\} \quad (1.5)$$

where  $n$  specifies the number of moles of the  $i$ th product or  $j$ th reactant. Any phase changes 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, reactions (1.6) and (1.7) can be carried out conveniently in a calorimeter at constant pressure:



Subtracting these two reactions, one obtains



Since some of the carbon would burn to  $\text{CO}_2$  and not solely to  $\text{CO}$ , it is difficult to determine calorimetrically the heat released by reaction (1.8).

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 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 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  $\text{CO}_2$  (Eqn (1.6)), it is possible to write the heat of formation of carbon dioxide at 298 K as

$$(\Delta H_f^\circ)_{298, \text{CO}_2} = -393.52 \text{ kJ/mol}$$

The superscript to the heat of formation symbol  $\Delta H_f^\circ$  represents the standard state, and the subscript number represents 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 Eqn (1.8) is

$$(\Delta H_f^\circ)_{298, \text{CO}} = -110.52 \text{ kJ/mol}$$

It is evident that, by judicious choice, the number of reactions that 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 preceding discussion is that, given the heats of formation of the substances comprising any particular reaction, one can directly determine the heat of reaction or heat evolved at the reference temperature  $T_0$ , most generally  $T_{298}$ , as follows:

$$\Delta H_{T_0} = \sum_{i \text{ prod}} n_i (\Delta H_f^\circ)_{T_0, i} - \sum_{j \text{ react}} n_j (\Delta H_f^\circ)_{T_0, j} = -Q_p \quad (1.9)$$



Extensive tables of standard heats of formation are available, but they are not all at the same reference temperature. The most convenient are the compilations known as the JANAF [1] and NBS Tables [2], both of which use 298 K as the reference temperature and are now available as the NIST-JANAF Thermochemical Tables (<http://kinetics.nist.gov/janaf/>). Table 1.1 lists some values of the heat of formation taken from the JANAF Thermochemical Tables. Actual JANAF tables are reproduced in Appendix A. These tables, which represent only a small selection from the JANAF volume, were chosen as those commonly used in combustion and to aid in solving the problem sets throughout this book. Note that, although the developments throughout this book take the reference state as 298 K, the JANAF Tables also list  $\Delta H_f^\circ$  for all temperatures.

When the products are measured at a temperature  $T_2$  different from the reference temperature  $T_0$ , and the reactants enter the reaction system at a temperature  $T'_0$  different from the reference temperature, the heat of reaction becomes

$$\begin{aligned}\Delta H &= \sum_{i \text{ prod}} n_i \left[ \{ (H_{T_2}^\circ - H_0^\circ) - (H_{T_0}^\circ - H_0^\circ) \} + (\Delta H_f^\circ)_{T_0} \right]_i \\ &\quad - \sum_{j \text{ react}} n_j \left[ \{ (H_{T'_0}^\circ - H_0^\circ) - (H_{T_0}^\circ - H_0^\circ) \} + (\Delta H_f^\circ)_{T_0} \right]_j \\ &= -Q_p(\text{evolved})\end{aligned}\quad (1.10)$$

The reactants in most systems are considered to enter at the standard reference temperature 298 K. Consequently, the enthalpy terms in the braces for the reactants disappear. The JANAF Tables tabulate, as a putative convenience,  $(H_T^\circ - H_{298}^\circ)$  instead of  $(H_T^\circ - H_0^\circ)$ . This type of tabulation is unfortunate since the reactants for systems using cryogenic fuels and oxidizers, such as those used in rockets, can enter the system at temperatures lower than the reference temperature. Indeed, the fuel and oxidizer individually could enter at different temperatures. Thus the summation in Eqn (1.10) is handled most conveniently by realizing that  $T'_0$  may vary with the substance  $j$ .

The values of heats of formation reported in Table 1.1 are ordered so that the largest positive values of the heats of formation per mole are the highest, and those with negative heats of formation are the lowest. In fact, this table is similar to a potential energy chart. As species at the top react to form species at the bottom, heat is released, and an exothermic system exists. Even a species that has a negative heat of formation can react to form products of still lower negative heats of formation species, thereby releasing heat. Since some fuels that have negative heats of formation form many moles of product species having negative heats of formation, the heat release in such cases can be large. Equation (1.9) shows this result clearly. Indeed, the first summation in Eqn (1.9) is generally much greater than the second. Thus the characteristic of the reacting species or the fuel that significantly determines the heat release is its chemical composition and not necessarily its molar heat of formation.