J. Warnatz, U. Maas, R.W. Dibble

# Combustion

## Physical and Chemical Fundamentals, Modeling and Simulation, Experiments, Pollutant Formation

4th Edition

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With 227 Figures and 22 Tables

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# Preface

This book has evolved from a lecture series (of *J. Wa.*) on combustion at Stuttgart University. The lectures were intended to provide first-year graduate students (and advanced undergraduates) with a basic background in combustion. Such a course was needed since students of combustion arrive with a wide variety of backgrounds, including physics, physical chemistry, mechanical engineering, computer science and mathematics, aerodynamics, and atmospheric science. After a few years of improving printed matter distributed to the students, the lecture notes have been organized into a book, first in German, and later translated and augmented in an English version.

We intend that the book provides a common basis from which research begins. Thus, the treatment of the many topics is compact with much citation to the research literature and presents numerous exercises. Beyond this, the book expects that combustion engineers and researchers will increasingly rely on mathematical modeling and numerical simulation for guidance toward greater understanding, in general, and, specifically, toward producing combustion devices with ever higher efficiencies and with lower pollutant emissions. Spatially homogeneous combustion and laminar flame computer codes and selected sample data to run them are available on the internet at *http://reaflow.iwr.uni-heidelberg.de/software/*.

The actual fourth edition presents a completely restructured book: Mathematical formulae and derivations and the space-consuming reaction mechanisms have been removed from the text to appendices, a new chapter has been added to discuss the impact of combustion processes on the earth atmosphere, the chapter on auto-ignition is moved and has been extended to deal with combustion in Otto and Diesel engines, and the chapters on heterogeneous combustion and on soot formation have been heavily revised. The rest of the chapters is polished and extended to account for recent developments and new results.

Because this book is a research launching point, we expect it to be updated in a timely fashion. For this reason, we invite the readers to contact our e-mail address (*juergen@warnatz.de*) for additional comments and constructive critical remarks that may be part of the next edition.

Heidelberg, Karlsruhe, Berkeley, in April 2006 *J. Warnatz, U. Maas, R. W. Dibble*

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# 1 Introduction, Fundamental Definitions and Phenomena

## 1.1 Introduction

Combustion is the oldest technology of mankind; it has been used for more than one million years. At present, about 90% of our worldwide energy support (e. g., in traffic, electrical power generation, heating) is provided by combustion; therefore it is really worthwhile studying this process.

Combustion research in the past was directed to fluid mechanics that included global heat release by chemical reaction. This heat release was often described simply with the help of thermodynamics, which assumes infinitely fast chemical reaction. This approach was useful to some extent for designing stationary combustion processes; it is not sufficient for treating transient processes like ignition and quenching or if pollutant formation shall be treated. However, pollutant formation during combustion of fossil fuels is, and will continue to be, a central topic in the future.

The focus of this book is therefore to treat the coupling of chemical reaction and fluid flow; in addition, combustion-specific topics of chemistry (hydrocarbon oxidation, large reaction mechanisms, simplification of reaction mechanisms) and combustion-specific topics of fluid mechanics (turbulent flow with density change by heat release, potential generation of turbulence by heat release) shall be considered.

Thus, this book will not consider in great detail the theory of chemical reaction rates and experimental methods for the determination of reaction rate coefficients (this is the task of reaction kinetics). Nor will this book discuss the details of turbulence theory and the handling of complex geometries (this is the task of fluid mechanics), although all of these topics are needed in understanding combustion.

## 1.2 Some Fundamental Definitions

The quantitative treatment of combustion processes requires some understanding of fundamental concepts and definitions, which shall be described in this section.

A *chemical reaction* is the exchange and/or rearrangement of atoms between colliding molecules. In the course of a chemical reaction, e. g.,

$$HCN + OH \rightarrow CN + H_2O\,,$$

the atoms (relevant in combustion: C, H, O, and N) are conserved; i. e., they are not created or destroyed. On the other hand, molecules (e. g., HCN, OH, CN, and $H_2O$) are not conserved. A partial list of molecules relevant in combustion is given in Table 1.1. Reactant molecules are rearranged to become product molecules, with simultaneous release of heat. A primary interest in the heat of reaction sets combustion engineering apart from chemical engineering.

Atoms and molecules are conveniently counted in terms of *amount of substance* or (worse, but used everywhere) *mole numbers* (unit: mol). 1 mol of a compound corresponds to $6.023 \cdot 10^{23}$ particles (atoms, molecules, etc.). Accordingly, the *Avogadro* constant (also called *Avogadro's* constant ) is $N_A = 6.023 \cdot 10^{23}$ mol$^{-1}$. The *mole fraction* $x_i$ of the species $i$ denotes the ratio of the *mole number* $n_i$ of species $i$ to the total *mole number* $n = \Sigma n_i$ of the mixture ($x_i = n_i / n$).

The *mass* $m$ is a fundamental property of matter (units of kg in the SI system). The *mass fraction* $w_i$ is the ratio of the mass $m_i$ of the species $i$ and the total mass $m = \Sigma m_i$ of the mixture ($w_i = m_i / m$).

The *molar mass* (obsolete: *molecular weight*) $M_i$ (units of, e. g., g/mol) of species $i$ is the mass of 1 mol of this species. Some examples (for atomic carbon, molecular hydrogen, molecular oxygen, and methane) are $M_C = 12$ g/mol, $M_{H_2} = 2$ g/mol, $M_{O_2} = 32$ g/mol, $M_{CH_4} = 16$ g/mol. The mixture *mean molar mass* $\overline{M}$ (in g/mol, e. g.) denotes an average molar mass, using the mole fractions as weighting ( $\overline{M} = \Sigma x_i M_i$ ).

Frequently mass fractions $w_i$ and mole fractions $x_i$ are expressed in terms of percentages (*mole-%* or *mass-%*). The following relations hold, which can be verified by simple calculations ($S$ denotes the number of different compounds):

$$w_i = \frac{M_i\, n_i}{\sum_{j=1}^{S} M_j\, n_j} = \frac{M_i\, x_i}{\sum_{j=1}^{S} M_j\, x_j}, \tag{1.1}$$

$$x_i = \frac{w_i}{M_i}\,\overline{M} = \frac{w_i / M_i}{\sum_{j=1}^{S} w_j / M_j}. \tag{1.2}$$

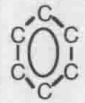
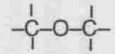
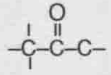
*Densities* do not depend on the size (extent) of a system. Such variables are called *intensive* properties, and are defined as the ratio of the corresponding *extensive* properties (which depend on the extent of the system) and the system volume $V$. Examples of intensive properties are

| | | |
|---|---|---|
| *mass density* (*density*) | $\rho = m/V$ | (in, e. g., kg/m$^3$) , |
| *molar density* (called *concentration*) | $c = n/V$ | (in, e. g., mol/m$^3$) . |

It follows (very easy to verify) that the mean molar mass is given by the expression

$$\frac{\rho}{c} = \frac{m}{n} = \overline{M}\,. \tag{1.3}$$

**Tab. 1.1.** List of molecules relevant for combustion processes

| | FAMILY | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | Alkane | Alkene | Alkyne | Arene | Haloalkane | Alcohol | Ether | Amine | Aldehyde | Ketone | Carboxylic Acid |
| Specific Example | $CH_3$-$CH_3$ | $CH_2$=$CH_2$ | HC≡CH |  | $CH_3CH_2Cl$ | $CH_3CH_2OH$ | $CH_3OCH_3$ | $CH_3NH_2$ | $CH_3\overset{O}{\overset{\|}{C}}H$ | $CH_3\overset{O}{\overset{\|}{C}}CH_3$ | $CH_3\overset{O}{\overset{\|}{C}}OH$ |
| IUPAC Name | Ethane | Ethene | Ethyne | Benzene | Chloroethane | Ethanol | Methoxy Methane | Methyl Amine | Ethanal | Propanone | Ethanoic Acid |
| Common Name | Ethane | Ethylene | Acetylene | Benzene | Ethyl Chloride | Ethyl Alcohol | Dimethyl Ether | Methyl Amine | Acetaldehyde | Acetone | Acetic Acid |
| General Formula | RH | $H_2C$=$CH_2$<br>RCH=$CH_2$<br>RCH=CHR<br>$R_2C$=CHR<br>$R_2C$=$CR_2$ | RC≡CH<br>RC≡CR | ArH, ArR | RX | ROH | ROR | $RNH_2$<br>$R_2NH$<br>$R_3N$ | $\overset{O}{\overset{\|}{C}}$RH | $\overset{O}{\overset{\|}{C}}$RR | $\overset{O}{\overset{\|}{C}}$ROH |
| Functional Group | C–H bonds<br>C–C bonds |  | –C≡C– | Aromatic Ring |  |  |  |  |  |  |  |

In chemistry, concentrations $c$ of chemical species defined in this way are usually denoted by species symbols in square brackets (e. g., $c_{H_2O} = [H_2O]$).

For the gases and gas mixtures in combustion processes, an equation of state relates temperature, pressure, and density of the gas. For many conditions it is satisfactory to use the *ideal gas equation of state*,

$$p\,V = n\,R\,T\,, \tag{1.4}$$

where $p$ denotes the pressure (in units of Pa), $V$ the volume (in $m^3$), $n$ the mole number (in mol), $T$ the absolute temperature (in K), and $R$ the *universal gas constant* ($R$ = 8.314 J·mol$^{-1}$·K$^{-1}$). It follows that

$$c = \frac{p}{RT} \quad \text{and} \quad \rho = \frac{p\overline{M}}{RT} = \frac{p}{RT\sum_{i=1}^{S}\frac{w_i}{M_i}}\,. \tag{1.5}$$

When temperatures are near or less than the critical temperature, or when pressures are near or above the critical pressures, the concentration or density is inadequately predicted using the ideal gas equation of state, i. e., (1.5). The system is better approximated as a *real gas*. One example of a real gas equation of state is that of *van der Waals*. Details of this and other equations of state for real gas conditions can be found in textbooks on physical chemistry (e. g., Atkins 1990).

## 1.3 Basic Flame Types

**Tab. 1.2.** Example of combustion systems ordered with respect to premixedness and flow type

| Fuel/Oxidizer Mixing | Fluid Motion | Examples |
|---|---|---|
| premixed | turbulent | spark-ignited gasoline engine |
| | | low $NO_x$ stationary gas turbine |
| | laminar | flat flame |
| | | Bunsen flame (followed by a nonpremixed candle for $\Phi > 1$) |
| nonpremixed | turbulent | pulverized coal combustion |
| | | aircraft turbine |
| | | Diesel engine |
| | | $H_2/O_2$ rocket motor |
| | laminar | wood fire |
| | | radiant burners for heating |
| | | candle |

In combustion processes, fuel and oxidizer (typically air) are mixed and burned. It is useful to identify several combustion categories based upon whether the fuel and oxidizer is mixed first and burned later (*premixed*) or whether combustion and mixing occur simultaneously (*nonpremixed*). Each of these categories is further subdivided based on whether the fluid flow is laminar or turbulent. Table 1.2 shows examples of combustion systems that belong to each of these categories, which will be discussed in the following sections.

**Laminar Premixed Flames:** In *laminar premixed flames*, fuel and oxidizer are premixed before combustion and the flow is laminar. Examples are laminar *flat flames* and (under fuel-lean conditions) *Bunsen flames* (see Fig. 1.1).

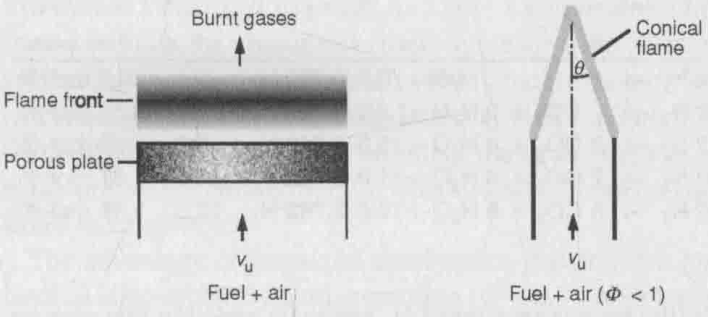



**Fig. 1.1.** Schematic illustration of a laminar flat flame (left) and of a Bunsen flame (right), both premixed

A premixed flame is said to be *stoichiometric*, if fuel (e. g., a hydrocarbon) and oxidizer (e. g., oxygen $O_2$) consume each other completely, forming only carbon dioxide ($CO_2$) and water ($H_2O$). If there is an excess of fuel, the system is called *fuel-rich*, and if there is an excess of oxygen, it is called *fuel-lean*. Examples are

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $2\,H_2$ | + | $O_2$ | $\rightarrow$ | $2\,H_2O$ | | | | | | | stoichiometric |
| $3\,H_2$ | + | $O_2$ | $\rightarrow$ | $2\,H_2O$ | + | $H_2$ | | | | | rich ($H_2$ left over) |
| $CH_4$ | + | $3\,O_2$ | $\rightarrow$ | $2\,H_2O$ | + | $CO_2$ | + | $O_2$ | | | lean ($O_2$ left over). |

Each species symbol in such a chemical reaction equation represents 1 mol. Thus, the first equation means: 2 mol $H_2$ react with 1 mole $O_2$ to form 2 mole $H_2O$.

If the reaction equation is written such that it describes exactly the reaction of 1 mol fuel, the mole fraction of the fuel in a stoichiometric mixture can be calculated easily to be

$$x_{\text{fuel,stoich.}} = \frac{1}{1+\nu} \,. \tag{1.6}$$

Here $\nu$ denotes the number of moles of $O_2$ in the reaction equation for a complete reaction to $CO_2$ and $H_2O$. An example is

$$H_2 + 0.5\,O_2 \rightarrow H_2O \qquad \nu = 0.5 \qquad x_{H_2,\text{stoich.}} = 2/3.$$

If air is used as an oxidizer, it has to be taken into account that dry air contains only about 21 % oxygen (78% nitrogen, 1% noble gases). Thus, for air $x_{N_2} = 3.762\, x_{O_2}$. It follows that the mole fractions in a stoichiometric mixture with air are

$$x_{\text{fuel,stoich.}} = \frac{1}{1+\nu\cdot 4.762},\quad x_{O_2,\text{stoich.}} = \nu\cdot x_{\text{fuel,stoich.}},\quad x_{N_2,\text{stoich.}} = 3.762\cdot x_{O_2,\text{stoich.}} \quad (1.7)$$

$\nu$ denotes, again, the mole number of $O_2$ in the reaction equation for a complete reaction of 1 mol of fuel to $CO_2$ and $H_2O$. Some examples are given in Table 1.3.

**Tab. 1.3.** Examples of stoichiometric numbers $\nu$ and of fuel mole fractions at stoichiometric conditions $x_{\text{fuel, stoich}}$ in fuel/air mixtures

| Reaction | $\nu$ | $x_{\text{fuel, stoich.}}$ |
|---|---|---|
| $H_2 + 0.5\ O_2 + 0.5\cdot 3.762\ N_2 \rightarrow H_2O + 0.5\cdot 3.762\ N_2$ | 0.5 | 29.6 mol-% |
| $CH_4 + 2.0\ O_2 + 2.0\cdot 3.762\ N_2 \rightarrow CO_2 + 2\ H_2O + 2.0\cdot 3.762\ N_2$ | 2.0 | 9.50 mol-% |
| $C_3H_8 + 5.0\ O_2 + 5.0\cdot 3.762\ N_2 \rightarrow 3\ CO_2 + 4\ H_2O + 5.0\cdot 3.762\ N_2$ | 5.0 | 4.03 mol-% |
| $C_7H_{16} + 11.0\ O_2 + 11.0\cdot 3.762\ N_2 \rightarrow 7\ CO_2 + 8\ H_2O + 11.0\cdot 3.762\ N_2$ | 11.0 | 1.87 mol-% |
| $C_8H_{18} + 12.5\ O_2 + 12.5\cdot 3.762\ N_2 \rightarrow 8\ CO_2 + 9\ H_2O + 12.5\cdot 3.762\ N_2$ | 12.5 | 1.65 mol-% |

Premixtures of fuel and air (the proper amount of $N_2$ has to be added in this case on both sides of the reaction equation; see Table 1.3) are characterized by the *air equivalence ratio* (sometimes *air number*) or the reciprocal value, the *fuel equivalence ratio* $\Phi = 1/\lambda$ with

$$\lambda = (x_{\text{air}}/x_{\text{fuel}}) / (x_{\text{air,stoich.}}/x_{\text{fuel, stoich.}}) = (w_{\text{air}}/w_{\text{fuel}}) / (w_{\text{air,stoich.}}/w_{\text{fuel, stoich.}})\,.$$

This formula can be rewritten to allow the evaluation of mole fractions in a mixture from $\Phi$ by

$$x_{\text{fuel}} = \frac{1}{1+\dfrac{4.762\cdot\nu}{\Phi}},\quad x_{\text{air}} = 1 - x_{\text{fuel}},\quad x_{O_2} = x_{\text{air}}/4.762,\quad x_{N_2} = x_{O_2}\cdot 3.762\,.$$

Accordingly, premixed combustion processes can now be divided into three groups,

| | | |
|---|---|---|
| rich combustion: | $\Phi > 1$ | , $\lambda < 1$ |
| stoichiometric combustion: | $\Phi = 1$ | , $\lambda = 1$ |
| lean combustion: | $\Phi < 1$ | , $\lambda > 1$ . |

The burning of freely burning premixed laminar flat flames into the unburnt mixture can be characterized by the *laminar burning velocity* $v_L$ (e. g., in m/s); other names in the literature are *flame velocity* or *flame speed*. It will be shown in Chapter 8 that the burning velocity depends only on the mixture composition ($\Phi$ or $\lambda$), the pressure $p$, and the initial temperature $T_u$.

If the laminar burning velocity of a flat flame is less than the velocity $v_u$ of the unburnt gases (see Fig. 1.1), the flame blows off. Therefore, the inequality $v_L > v_u$