

# 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.

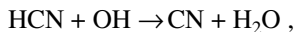
The focus of this book is therefore to treat the coupling of chemical reaction and fluid flow; in addition, combustion-specific topics of chemistry (hydrocarbon oxidation, large reaction mechanisms, simplification of reaction mechanisms) and combustion-specific topics of fluid mechanics (turbulent flow 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.,



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<sub>2</sub>O) 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  $N_A = 6.023 \cdot 10^{23} \text{ mol}^{-1}$ . 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*  $n = \sum n_i$  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  $m = \sum m_i$  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  $M_C = 12 \text{ g/mol}$ ,  $M_{\text{H}_2} = 2 \text{ g/mol}$ ,  $M_{\text{O}_2} = 32 \text{ g/mol}$ ,  $M_{\text{CH}_4} = 16 \text{ g/mol}$ . The mixture *mean molar mass*  $\bar{M}$  (in g/mol, e. g.) denotes an average molar mass, using the mole fractions as weighting ( $\bar{M} = \sum x_i M_i$ ).

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):

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

$$x_i = \frac{w_i \bar{M}}{M_i} = \frac{w_i / M_i}{\sum_{j=1}^S w_j / M_j} . \quad (1.2)$$


*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

$$\begin{array}{lll} \text{mass density (density)} & \rho = m/V & (\text{in, e. g., kg/m}^3) , \\ \text{molar density (called concentration)} & c = n/V & (\text{in, e. g., mol/m}^3) . \end{array}$$

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

$$\frac{\rho}{c} = \frac{m}{n} = \bar{M} . \quad (1.3)$$

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	$\text{CH}_3\text{-CH}_3$	$\text{CH}_2=\text{CH}_2$	$\text{HC}\equiv\text{CH}$		$\text{CH}_3\text{CH}_2\text{Cl}$	$\text{CH}_3\text{CH}_2\text{OH}$	$\text{CH}_3\text{OCH}_3$	$\text{CH}_3\text{NH}_2$	$\text{CH}_3\text{CHO}$	$\text{CH}_3\text{C(=O)CH}_3$	$\text{CH}_3\text{COOH}$
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	$\text{H}_2\text{C}=\text{CH}_2$ $\text{RCH}=\text{CH}_2$ $\text{RCH}=\text{CHR}$ $\text{R}_2\text{C}=\text{CHR}$ $\text{R}_2\text{C}=\text{CR}_2$	$\text{RC}\equiv\text{CH}$ $\text{RC}\equiv\text{CR}$	$\text{ArH}$ , $\text{ArR}$	RX	ROH	ROR	$\text{RNH}_2$ $\text{R}_2\text{NH}$ $\text{R}_3\text{N}$	$\text{RCHO}$	$\text{RC(=O)R}$	$\text{RC(=O)OH}$
Functional Group	C-H bonds C-C bonds	$\text{>C=C<}$	$\text{-C}\equiv\text{C-}$	Aromatic Ring	$\text{-C-X}$	$\text{-C-OH}$	$\text{-C-O-C-}$	$\text{-C-N-}$	$\text{O=C-H}$	$\text{O=C-C-}$	$\text{O=C-OH}$

In chemistry, concentrations  $c$  of chemical species defined in this way are usually denoted by species symbols in square brackets (e. g.,  $c_{\text{H}_2\text{O}} = [\text{H}_2\text{O}]$ ).

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*,

$$pV = nRT, \quad (1.4)$$

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

$$c = \frac{p}{RT} \quad \text{and} \quad \rho = \frac{p\bar{M}}{RT} = \frac{p}{RT} \sum_{i=1}^S \frac{w_i}{M_i}. \quad (1.5)$$

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).

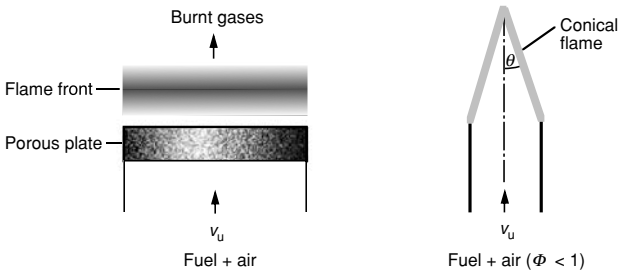
### 1.3 Basic Flame Types

**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 $\text{NO}_x$ 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 $\text{H}_2/\text{O}_2$ rocket motor
	laminar	wood fire radiant burners for heating candle

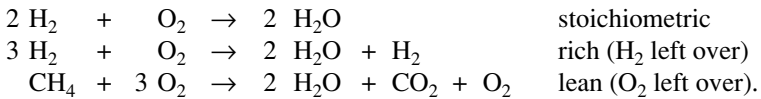
In combustion processes, fuel and oxidizer (typically air) are mixed and burned. It is useful to identify several combustion categories based upon whether the fuel and oxidizer is mixed first and burned later (*premixed*) or whether combustion and mixing occur simultaneously (*nonpremixed*). Each of 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



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

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

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



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  $x_{\text{N}_2} = 3.762 \cdot x_{\text{O}_2}$ . It follows that the mole fractions in a stoichiometric mixture with air are

$$x_{\text{fuel, stoich.}} = \frac{1}{1 + \nu \cdot 4.762}, \quad x_{\text{O}_2, \text{ stoich.}} = \nu \cdot x_{\text{fuel, stoich.}}, \quad x_{\text{N}_2, \text{ stoich.}} = 3.762 \cdot x_{\text{O}_2, \text{ stoich.}} \quad (1.7)$$

$\nu$  denotes, again, the mole number of  $\text{O}_2$  in the reaction equation for a complete reaction of 1 mol of fuel to  $\text{CO}_2$  and  $\text{H}_2\text{O}$ . 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	$\nu$	$x_{\text{fuel, stoich.}}$
$\text{H}_2 + 0.5 \text{O}_2 + 0.5 \cdot 3.762 \text{N}_2 \rightarrow \text{H}_2\text{O} + 0.5 \cdot 3.762 \text{N}_2$	0.5	29.6 mol-%
$\text{CH}_4 + 2.0 \text{O}_2 + 2.0 \cdot 3.762 \text{N}_2 \rightarrow \text{CO}_2 + 2 \text{H}_2\text{O} + 2.0 \cdot 3.762 \text{N}_2$	2.0	9.50 mol-%
$\text{C}_3\text{H}_8 + 5.0 \text{O}_2 + 5.0 \cdot 3.762 \text{N}_2 \rightarrow 3 \text{CO}_2 + 4 \text{H}_2\text{O} + 5.0 \cdot 3.762 \text{N}_2$	5.0	4.03 mol-%
$\text{C}_7\text{H}_{16} + 11.0 \text{O}_2 + 11.0 \cdot 3.762 \text{N}_2 \rightarrow 7 \text{CO}_2 + 8 \text{H}_2\text{O} + 11.0 \cdot 3.762 \text{N}_2$	11.0	1.87 mol-%
$\text{C}_8\text{H}_{18} + 12.5 \text{O}_2 + 12.5 \cdot 3.762 \text{N}_2 \rightarrow 8 \text{CO}_2 + 9 \text{H}_2\text{O} + 12.5 \cdot 3.762 \text{N}_2$	12.5	1.65 mol-%

Premixtures of fuel and air (the proper amount of  $\text{N}_2$  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

$$x_{\text{fuel}} = \frac{1}{1 + \frac{4.762 \cdot \nu}{\Phi}}, \quad x_{\text{air}} = 1 - x_{\text{fuel}}, \quad x_{\text{O}_2} = x_{\text{air}}/4.762, \quad x_{\text{N}_2} = x_{\text{O}_2} \cdot 3.762$$

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  $v_L > v_u$

has to be fulfilled for flat flames. Right before the blowoff  $v_L \approx v_u$ . Thus, the inlet gas velocity at flame lift-off is a measure of the laminar burning velocity.

Higher inlet velocities are possible when the flat flame is at an angle  $\theta$  to the flow. In the case of a premixed Bunsen flame attached to the exit of a round pipe, the flame front is approximately flat (the flame thickness is small compared to the curvature). It follows (see Fig. 1.1) that

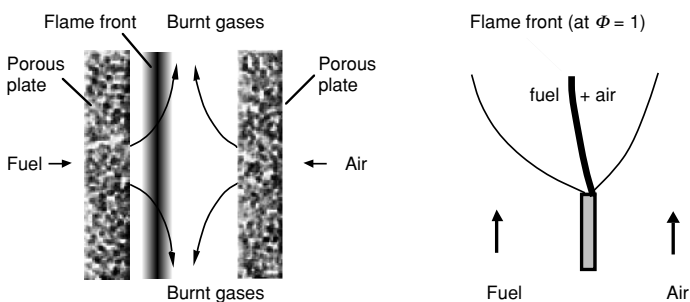
$$v_L = v_u \sin \theta. \quad (1.8)$$

Thus, a measurement of  $\theta$ , perhaps from a photograph, and of the inlet gas velocity  $v_u$  will lead to a measure of  $v_L$ . Problems connected with the determination of  $v_L$  and better experimental methods are discussed by Vagelopoulos and Egolfopoulos (1998).

**Turbulent Premixed Flames:** As Table 1.2 indicates, other examples of premixed flames include the ubiquitous spark-ignited engine (Otto engine) where the flow is seldom laminar. In this case, premixed flame fronts burn and propagate into a turbulent fluid flow. If the turbulence intensity is not too high, curved laminar premixed flame fronts are formed. The turbulent flame can then be viewed as an ensemble of many premixed laminar flames. This so-called *flamelet* concept will be discussed in detail in Chapter 15.

The advantage of premixed combustion is that much greater control of the combustion is possible. By lean premixing ( $\Phi < 0.7$ ), high temperatures are avoided and hence combustion with low production of the pollutant nitric oxide (NO) is accomplished. In addition, only a very small amount of soot is formed at these circumstances as soot is largely a product of rich combustion (see Chapters 17 and 18).

Despite the advantages, premixed combustion is not widely used because of the potential for accidental collection of large volumes of premixed reactants, which could burn in an uncontrolled explosion.



**Fig. 1.2.** Schematic illustration of a laminar counterflow nonpremixed flame (left) and a laminar coflow nonpremixed flame (right)

**Laminar Nonpremixed Flames:** In *laminar nonpremixed flames* (obsolete: *laminar diffusion flames*), fuel and oxidizer are mixed during the combustion process itself. The flow is laminar. As Table 1.2 indicates, examples include candles, oil lamps,

and campfires. For research purposes, two important configurations are used: *laminar counterflow* and *laminar coflow nonpremixed flames* as shown in Fig. 1.2.

Nonpremixed flames include more complex chemistry than premixed ones, because the equivalence ratio  $\Phi$  covers the whole range from 0 (air) to  $\infty$  (pure fuel). Rich combustion occurs on the fuel side, lean combustion on the air side. The flame front, which is usually characterized by intense luminescence, is fixed to regions near the location of the stoichiometric composition  $\Phi = 1$ , since (see later) this is where the temperature is highest. Thus, unlike premixed flames, nonpremixed flames do not propagate and, therefore, cannot be characterized by a laminar flame speed.

**Turbulent Nonpremixed Flames:** In this case, nonpremixed flames burn in a turbulent flow field, and for low turbulence intensities the so-called flamelet concept can be used again (see Chapter 14). Because of the safety considerations mentioned before, nonpremixed flames are mostly used in industrial furnaces and burners. Unless very sophisticated mixing techniques are used, nonpremixed flames show a yellow luminescence, caused by glowing soot particles formed by fuel-rich chemical reactions in the rich domains of the nonpremixed flames.

**Hybrid Premixed-Nonpremixed Laminar Flames:** Home heating and heating of water is often done with flames of this type. Fuel and air are premixed slightly rich to  $\Phi = 1.4$  so that sooting is suppressed. The products of this rich flame subsequently burn in a nonpremixed flame with the surrounding air. There are millions of such burners in service, collectively accounting for 30 % of natural gas consumption.

## 1.4 Exercises

**Exercise 1.1.** (a) How much  $O_2$  is needed for a stoichiometric combustion of methane  $CH_4$  and octane  $C_8H_{18}$  respectively (molar ratio and mass ratio)? (b) Which values of mole and mass fractions do stoichiometric mixtures of  $CH_4$  and of  $C_8H_{18}$  have with air? (c) How much air is needed for the preparation of a  $C_8H_{18}$ -air mixture with an equivalence ratio of  $\Phi = 2/3$ , assuming 1 mol of mixture?

**Exercise 1.2.** A safe is to be blown up. The safe, which has a volume of  $100 \text{ dm}^3$ , is filled with  $5 \text{ dm}^3$  of hydrogen in air ( $T = 298 \text{ K}$ ). In order to avoid noise, the safe is sunk in a cold ( $T = 280 \text{ K}$ ) lake and then the mixture is ignited. The pressure in the safe is 1 bar prior to ignition. The reaction can be taken to be isochoric (constant volume); assume that the safe did not burst. (a) How many moles of gas are in the safe prior to ignition? What are the values of the mole fractions of hydrogen, oxygen and nitrogen? What is the value of the mean molar mass? (b) How many moles of gas are left after the combustion, if the hydrogen is consumed completely and the resulting water condenses? (c) What is the pressure long after the ignition? What is the mean molar mass of the gas now? Is the safe heavier or lighter after the ignition?