

Lecture 1

Thermodynamics of Combustion Systems

Combustion

- mass and energy conversion process
- chemical bond energy → thermal energy

Fuel reacts with the oxygen of the air

→ products (mainly carbon dioxide and water) with lower **enthalpy of formation** or **reference enthalpy** than the reactants

The final state of a homogeneous system is governed by the

classical balance laws of thermodynamics.

Prerequisites:

- definitions of concentrations and thermodynamic variables
- mass and energy balance for multicomponent systems

Mole Fractions and Mass Fractions

In chemical reactions chemical elements are conserved.

For example:

the particular atom defining the element C within a CH_4 molecule will be found within the CO_2 molecule if combustion is completed.

In order to describe the chemical transformation between species quantitatively, we need to introduce definitions for **concentrations**.

The Mole Fraction

Multi-component system with k different chemical species

Mole: $6.0236 \cdot 10^{23}$ molecules are defined as one mole.

Number of moles of species i : n_i

Total number of moles:

$$n_s = \sum_{i=1}^k n_i$$

Mole fraction of species i : $X_i \equiv \frac{n_i}{n_s}, \quad i = 1, 2, \dots, k$

The Mass Fraction

Mass m_i of all molecules of species i is related to its number of moles by

$$m_i = W_i n_i, \quad i = 1, 2, \dots, k$$

where W_i is the molecular weight of species i .

Total mass of all molecules in the mixture:

$$m = \sum_{i=1}^k m_i$$

Mass fraction of species i :

$$Y_i = \frac{m_i}{m}, \quad i = 1, 2, \dots, k$$

Mean molecular weight W

$$W = \sum_{i=1}^k W_i X_i = \left[\sum_{i=1}^k \frac{Y_i}{W_i} \right]^{-1}$$

The mass fraction of elements

The mass fraction of elements is very useful in combustion.

Mass of the species changes due to chemical reactions,
the mass of the elements is conserved.

Mass and molecular weight of all atoms of element j contained in all molecules: m_j, W_j

Number of atoms of element j in a molecule of species i : a_{ij}

Mass of all atoms j in the system:
$$m_j = \sum_{i=1}^k \frac{a_{ij} W_j}{W_i} m_i, \quad j = 1, 2, \dots, k_e$$

where k_e is the total number of elements in the system.

Notice that no meaningful definition for the mole fraction of elements can be given because only the mass of the elements is conserved.

The mass fraction of element j is then

$$Z_j = \frac{m_j}{m} = \sum_{i=1}^k \frac{a_{ij}W_j}{W_i} Y_i = \frac{W_j}{W} \sum_{i=1}^k a_{ij} X_i, \quad j = 1, 2, \dots, k_e,$$

From the definitions above it follows

$$\sum_{i=1}^k X_i = 1, \quad \sum_{i=1}^k Y_i = 1, \quad \sum_{j=1}^{k_e} Z_j = 1$$

The partial molar density

Number of moles per volume V or partial molar density, the concentration:

$$[X_i] = \frac{n_i}{V}, \quad i = 1, 2, \dots, k$$

The molar density of the system is then

$$\frac{n_s}{V} = \sum_{i=1}^k [X_i]$$

The Partial Density

The density and the partial density are defined

$$\rho = \frac{m}{V}, \quad \rho_i = \frac{m_i}{V} = \rho Y_i, \quad i = 1, 2, \dots, k$$

The partial molar density is related to the partial density and the mass fraction by

$$[X_i] = \frac{\rho_i}{W_i} = \frac{\rho Y_i}{W_i}, \quad i = 1, 2, \dots, k$$

The thermal equation of state

In most combustion systems of technical interest the law of ideal gases is valid.

Even for high pressure combustion this is a sufficiently accurate approximation because the temperatures are typically also very high.

In a mixture of ideal gases the molecules of species i exert on the surrounding walls of the vessel the partial pressure

$$p_i = \frac{n_i \mathcal{R}T}{V} = [X_i] \mathcal{R}T = \frac{\rho Y_i}{W_i} \mathcal{R}T, \quad i = 1, 2, \dots, k$$

Universal gas constant equal to

$$\mathcal{R} = 8.3143 \text{ J/mol/K} = 82.05 \text{ atm cm}^3/\text{mol/K}$$

Dalton's law

For an ideal gas the total pressure is equal to the sum of the partial pressures.

Thermal equation of state for a mixture of ideal gases

$$p = \sum_{i=1}^k p_i = n_s \frac{\mathcal{R}T}{V} = \frac{\rho \mathcal{R}T}{W}$$

The partial pressure is equal to the total pressure times the mole fraction

$$p_i = pX_i, \quad i = 1, 2, \dots, k$$

Defining the partial volume by $V_i = \frac{n_i \mathcal{R}T}{p}, \quad i = 1, 2, \dots, k$

it follows that an equivalent relation exists for the partial volume

$$V_i = VX_i, \quad i = 1, 2, \dots, k$$

Stoichiometry

Equations describing chemical reactions

Global reactions like
$$\text{H}_2 + \frac{1}{2}\text{O}_2 = \text{H}_2\text{O}$$

or elementary reactions like
$$\text{H} + \text{O}_2 \xrightleftharpoons[k_b]{k_f} \text{OH} + \text{O}$$

are based on the principle of element conservation during reaction.

The stoichiometric coefficients of the reactant i : ν_i'

The stoichiometric coefficients of the product i : ν_i''

If M_i stands for the chemical symbol of species i a reaction equation may be cast into the form

$$\sum_{i=1}^k \nu_i' M_i = \sum_{i=1}^k \nu_i'' M_i$$

Net stoichiometric coefficient

$$\nu_i = \nu_i'' - \nu_i', \quad i = 1, 2, \dots, k$$

is positive for products and negative for reactants.

A system of r elementary reactions may be written

$$\sum_{i=1}^k \nu_{il} M_i = 0, \quad l = 1, 2, \dots, r$$

where the net stoichiometric coefficient of species i in reaction l is: ν_{il}

The stoichiometry defined by the reaction equation relates the molar production or consumption of species to each other.

The change of the number of moles of species i to that of species 1 is

$$\frac{dn_i}{\nu_i} = \frac{dn_1}{\nu_1}, \quad i = 2, \dots, k$$

The relation between the partial masses is

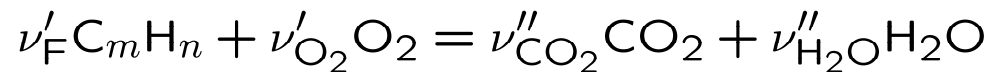
$$\frac{dm_i}{\nu_i W_i} = \frac{dm_1}{\nu_1 W_1}, \quad i = 2, \dots, k$$

Since the total mass in the system is independent of the chemical reaction (while the total number of moles is not), the relation between mass fractions is

$$\frac{dY_i}{\nu_i W_i} = \frac{dY_1}{\nu_1 W_1}, \quad i = 2, \dots, k$$

A fuel-air mixture is called stoichiometric, if the fuel-to-oxygen ratio is such that both are entirely consumed when combustion to CO_2 and H_2O is completed.

For example, the global reaction describing the combustion of a single component hydrocarbon fuel C_mH_n (subscript F for fuel)



the stoichiometric coefficients are

$$\nu'_F = 1, \quad \nu'_{\text{O}_2} = m + \frac{n}{4}, \quad \nu''_{\text{CO}_2} = m \quad \nu''_{\text{H}_2\text{O}} = \frac{n}{2}$$

where $\nu'_F = 1$ may be chosen arbitrarily to unity.

Stoichiometric mixture requires that the

ratio of the number of moles of fuel and oxidizer in the unburnt mixture

is equal to the

ratio of the stoichiometric coefficients

$$\frac{n_{\text{O}_2,u}}{n_{\text{F},u}} \Big|_{st} = \frac{\nu'_{\text{O}_2}}{\nu'_{\text{F}}}$$

or in terms of mass fractions

$$\frac{Y_{\text{O}_2,u}}{Y_{\text{F},u}} \Big|_{st} = \frac{\nu'_{\text{O}_2} W_{\text{O}_2}}{\nu'_{\text{F}} W_{\text{F}}} = \nu$$

where ν is called the stoichiometric mass ratio.

Then fuel and oxidizer are both consumed when combustion is completed.

Integrating

$$\frac{dY_i}{\nu_i W_i} = \frac{dY_1}{\nu_1 W_1}, \quad i = 2, \dots, k$$

with $i = \text{O}_2$, $1 = \text{F}$ between the initial unburnt state (subscript u) and any later state leads to

$$\frac{Y_{\text{O}_2} - Y_{\text{O}_2,u}}{\nu'_{\text{O}_2} W_{\text{O}_2}} = \frac{Y_{\text{F}} - Y_{\text{F},u}}{\nu'_{\text{F}} W_{\text{F}}}$$

This may be written as

$$\nu Y_{\text{F}} - Y_{\text{O}_2} = \nu Y_{\text{F},u} - Y_{\text{O}_2,u}$$

For a stoichiometric mixture fuel and oxygen are completely consumed at the end of combustion:

$$Y_F = Y_{O_2} = 0$$

Introducing this into

$$\nu Y_F - Y_{O_2} = \nu Y_{F,u} - Y_{O_2,u}$$

we recover

$$\frac{Y_{O_2,u}}{Y_{F,u}} \Big|_{st} = \frac{\nu'_{O_2} W_{O_2}}{\nu'_F W_F} = \nu$$

The Mixture Fraction

The mixture fraction is an extremely useful variable in combustion in particular for diffusion flames.

Here we present it first for a homogeneous system.

In a two-feed system a fuel stream (subscript 1) with mass flux m_1 is mixed with an oxidizer stream (subscript 2) with mass flux m_2 .

The mixture fraction represents the mass fraction of the fuel stream in the mixture:

$$Z = \frac{m_1}{m_1 + m_2}$$

Both fuel and oxidizer streams may contain inerts such as nitrogen.

The mass fraction $Y_{F,u}$ of the fuel in the mixture is proportional to the mass fraction in the original fuel stream, so

$$Y_{F,u} = Y_{F,1}Z$$

where $Y_{F,1}$ denotes the mass fraction of fuel in the fuel stream.

Similarly, since $1-Z$ represents the mass fraction of the oxidizer stream in the mixture, one obtains for the mass fraction of oxygen in the mixture

$$Y_{O_2,u} = Y_{O_2,2}(1 - Z)$$

where $Y_{O_2,2}$ represents the mass fraction of oxygen in the oxidizer stream ($Y_{O_2,2} = 0.232$ for air).

Introducing

$$Y_{F,u} = Y_{F,1}Z$$

and

$$Y_{O_2,u} = Y_{O_2,2}(1 - Z)$$

into

$$\nu Y_F - Y_{O_2} = \nu Y_{F,u} - Y_{O_2,u}$$

one obtains the mixture fraction as a variable that couples the mass fractions of the fuel and the oxygen

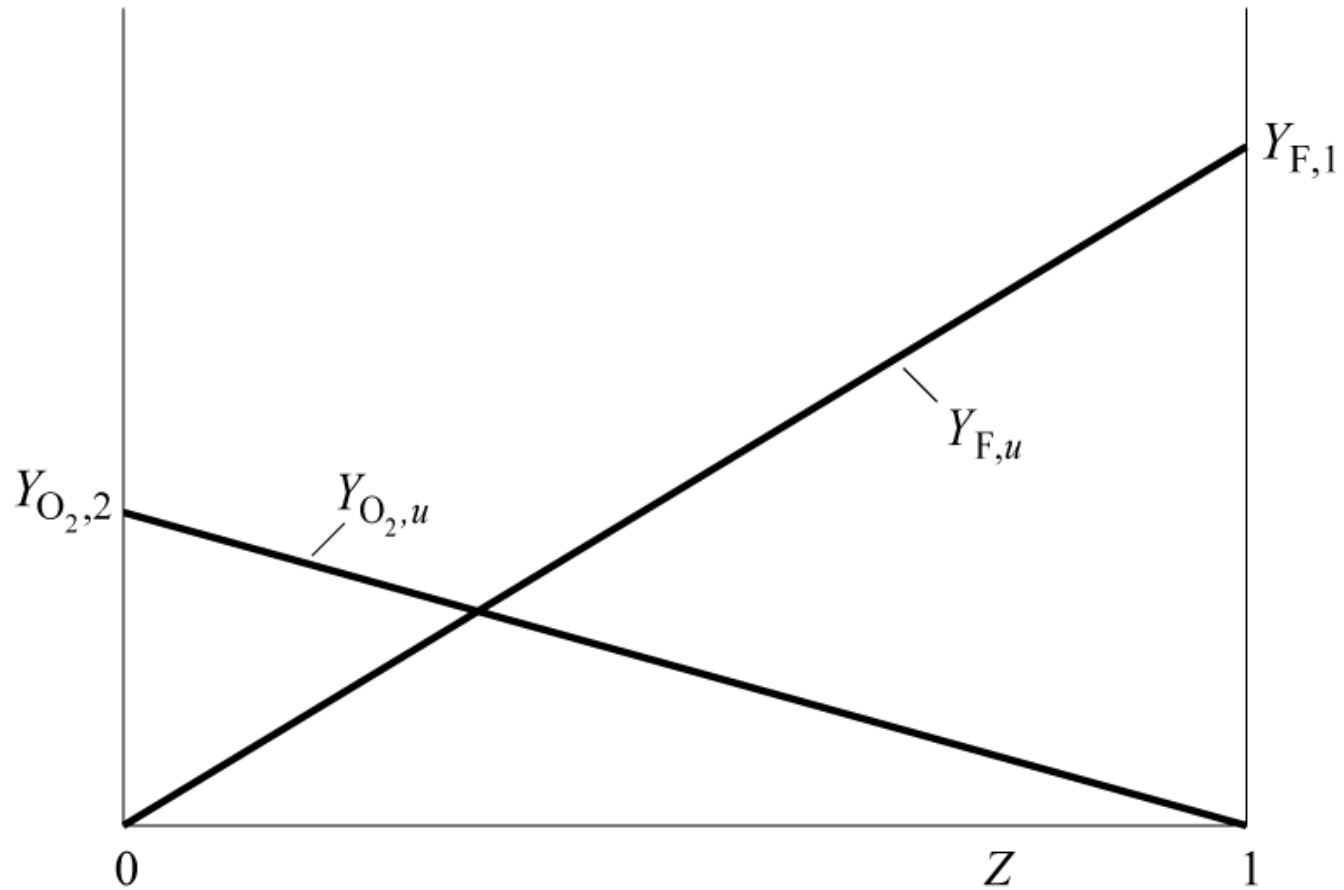
$$Z = \frac{\nu Y_F - Y_{O_2} + Y_{O_2,2}}{\nu Y_{F,1} + Y_{O_2,2}} = -\frac{Y_{O_2,b}}{\nu Y_{F,1} + Y_{O_2,2}} + Z_{st}$$

For a stoichiometric mixture one obtains with $\nu Y_F = Y_{O_2}$

the **stoichiometric mixture fraction** $Z_{st} = \frac{Y_{O_2,2}}{\nu Y_{F,1} + Y_{O_2,2}}$

Profiles of Y_F and Y_{O_2} in the unburnt gas

unburnt mixture



If $Z < Z_{st}$ fuel is deficient and the mixture is called **fuel lean**.

Then, combustion terminates when all the fuel is consumed: $Y_{F,b} = 0$
(burnt gas, subscript b).

The remaining oxygen mass fraction in the burnt gas is calculated from

$$Z = \frac{\nu Y_F - Y_{O_2} + Y_{O_2,2}}{\nu Y_{F,1} + Y_{O_2,2}}$$

as

$$Y_{O_2,b} = Y_{O_2,2} \left(1 - \frac{Z}{Z_{st}}\right), \quad Z \leq Z_{st}$$

where

$$Z_{st} = \frac{Y_{O_2,2}}{\nu Y_{F,1} + Y_{O_2,2}}$$

was used.

Similarly, if $Z > Z_{st}$ oxygen is deficient and the mixture is called **fuel rich**.

Combustion then terminates when all the oxygen is consumed: $Y_{O_2,b} = 0$

Leading to
$$Y_{F,b} = Y_{F,1} \frac{Z - Z_{st}}{1 - Z_{st}}, \quad Z \geq Z_{st}$$

For the hydrocarbon fuel considered above the element mass fractions in the unburnt mixture are

$$Z_C = m \frac{W_C}{W_F} Y_{F,u}, \quad Z_H = n \frac{W_H}{W_F} Y_{F,u}, \quad Z_O = Y_{O_2,u}$$

or

$$\frac{Z_C}{mW_C} = \frac{Z_H}{nW_H} = \frac{Y_{F,u}}{\nu'_F W_F}$$

For a stoichiometric mixture where

$$\frac{Y_{O_2,u}}{\nu'_{O_2} W_{O_2}} = \frac{Y_{F,u}}{\nu'_F W_F}$$

it follows that the combination

$$\beta = \frac{Z_C}{mW_C} + \frac{Z_H}{nW_H} - 2 \frac{Z_O}{\nu'_{O_2} W_{O_2}}$$

vanishes.

Normalizing this such that $Z = 1$ in the fuel stream and $Z = 0$ in the oxidizer stream, one obtains Bilger's definition

$$Z = \frac{\beta - \beta_2}{\beta_1 - \beta_2}$$

or

$$Z = \frac{Z_C/(mW_C) + Z_H/(nW_H) + 2(Y_{O_2,u} - Z_O)/(\nu'_{O_2}W_{O_2})}{Z_{C,1}/(nW_C) + Z_{H,1}/(mW_H) + 2Y_{O_2,u}/(\nu'_{O_2}W_{O_2})}$$

Because elements are conserved during combustion, the element mass fractions calculated from

$$Z_j = \frac{m_j}{m} = \sum_{i=1}^k \frac{a_{ij}W_j}{W_i} Y_i = \frac{W_j}{W} \sum_{i=1}^k a_{ij} X_i, \quad j = 1, 2, \dots, k_e,$$

do not change.

For the burnt gas they are for the hydrocarbon fuel considered above

$$Z_C = m \frac{W_C}{W_F} Y_{F,b} + \frac{W_C}{W_{CO_2}} Y_{CO_2,b}$$

$$Z_H = n \frac{W_H}{W_F} Y_{F,b} + 2 \frac{W_H}{W_{H_2O}} Y_{H_2O,b}$$

$$Z_O = 2 \frac{W_O}{W_{O_2}} Y_{O_2,b} + 2 \frac{W_O}{W_{CO_2}} Y_{CO_2,b} + \frac{W_O}{W_{H_2O}} Y_{H_2O,b}$$

This leads with $Y_{F,u} = Y_{F,1}Z$ and $Y_{F,b} = 0$ for $Z \leq Z_{st}$

and
$$Z = \frac{\nu Y_F - Y_{O_2} + Y_{O_2,2}}{\nu Y_{F,1} + Y_{O_2,2}} \quad \text{for } Z \geq Z_{st}$$

to **piecewise linear relations** of the product mass fractions in terms of Z :

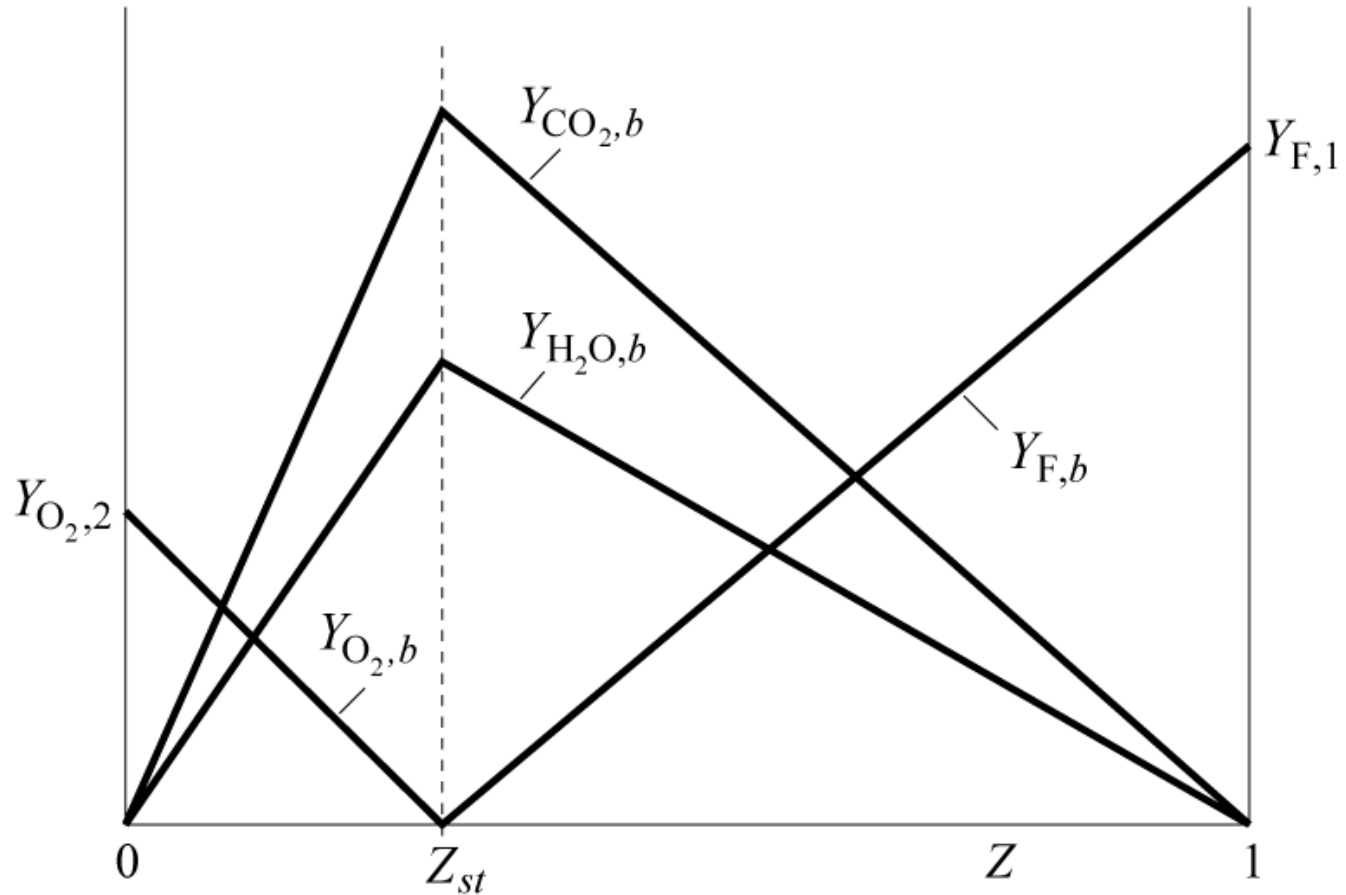
$$Z \leq Z_{st} : \quad Y_{CO_2,b} = Y_{CO_2,st} \frac{Z}{Z_{st}} \quad Y_{H_2O,b} = Y_{H_2O,st} \frac{Z}{Z_{st}}$$

$$Z \geq Z_{st} : \quad Y_{CO_2,b} = Y_{CO_2,st} \frac{1 - Z}{1 - Z_{st}}, \quad Y_{H_2O,b} = Y_{H_2O,st} \frac{1 - Z}{1 - Z_{st}}$$

where
$$Y_{CO_2,st} = Y_{F,1} Z_{st} \frac{mW_{CO_2}}{W_F}$$

Profiles in the burning mixture

burning mixture



The **fuel-air equivalence ratio** is the ratio of fuel-air ratio in the unburnt to that of a stoichiometric mixture

$$\phi = \frac{Y_{F,u}/Y_{O_2,u}}{(Y_{F,u}/Y_{O_2,u})_{st}} = \frac{\nu Y_{F,u}}{Y_{O_2,u}}$$

Introducing $Y_{F,u} = Y_{F,1}Z$ and $Y_{O_2,u} = Y_{O_2,2}(1 - Z)$

into $\nu Y_F - Y_{O_2} = \nu Y_{F,u} - Y_{O_2,u}$

leads with $\frac{\nu Y_{F,1}}{Y_{O_2,2}} = \frac{1 - Z_{st}}{Z_{st}}$

to a unique relation between the equivalence ratio and the mixture fraction

$$\phi = \frac{Z}{1 - Z} \frac{(1 - Z_{st})}{Z_{st}}$$

This relation is also valid for multicomponent fuels (*Exercise*).

It illustrates that the mixture fraction is simply another expression for the local equivalence ratio.

Exercise:

The element mass fractions $Z_{H,F}$, $Z_{C,F}$ of a mixture of hydrocarbons and its mean molecular weight W are assumed to be known.

Determine its stoichiometric mixture fraction in air.

A hint: $Z_{H,F} = n W_H/W$, $Z_{C,F} = m W_C/W$