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Combustion

Part I

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Preface

Combustion continues to be at the very core of energy conversion and power generation processes. Internal combustion engines, gas turbines, industrial furnaces, and propulsion systems, which are all based on combustion science, have the same principle. Hence the entire field of engineering keeps on depending heavily on combustion science to accomplish the goal of clean, efficient, and sustainable energy systems by way of the energy system design.

The first part of the lecture book, ***Combustion-Part I***, is a one-semester course that aims to provide the students of the master's program in Mechanical Engineering, with special emphasis on Energy Installations and Turbomachinery, a precise and organized introduction to combustion engineering practice and theory. The book covers the basics of thermochemistry, reaction kinetics, and reactive flow concepts, which enable the students to perform the analysis and the optimization of combustion systems.

This manuscript is divided into three major chapters.

The first chapter defines the basic concepts of combustion along with the properties of the fuel, stoichiometry, and the thermochemical laws that govern the combustion reactions.

Chapter 2 deals with thermochemistry, discussing adiabatic flame temperatures, combustion chamber energy balances, equilibrium, and kinetics.

Chapter 3 describes the conservation equations for fluid flow in which there are chemical reactions, hence linking fluid mechanics, thermodynamics, and chemical kinetics to the modeling of combustion phenomena in nature.

Chapters in the book are supplemented with examples, exercises, and problem solutions for students to apply theoretical knowledge in practice. The content of this course aligns with the program objectives in that it deepens students' analytical skills and prepares them for research along with professional practice in the field of energy and propulsion systems.

I thank my colleagues and students at the University of Tissemsilt for their interest and dedication which have been a great source of inspiration to me while preparing this material. I also acknowledge with gratitude the effort made by all the researchers in advancing clean and efficient combustion technologies which will provide a sustainable energy future.

Introduction:

Combustion is the main chemical change that combines the loss of heat with the release of light and is working a vital function in a variety of applications that include but are not limited to a range of cooking, industrial processes and car engines. The knowledge of combustion principles is the basis for the correct use of fuel, for the saving of energy and for the decrease of the pollutants' emissions. This chapter will introduce the basic concepts of combustion, dealing with the types of fuels and combustibles, their properties both physically and chemically, and the role of octane and cetane numbers.

1.1 Types of fuels and combustibles

Fuels and combustibles are materials that, by burning, give off heat and energy. They can be divided into six groups according to their physical state. Solid, liquid, and gas fuels are the first three groups based on physical state. Each type of fuel has specific physical and chemical properties that will greatly influence its combustion behavior.

1.1.1 Solid fuels

- **Coal:** A carbon-rich solid fuel, ultimately formed from prehistoric vegetable matters over the course of million years. In coal, those characteristics (anthracite, bituminous, sub-bituminous, and lignite) depend on carbon content and calorific value.
- **Wood:** A renewable biomass fuel that is basically made up of cellulose, hemicellulose, and lignin. It is the main source of heating and cooking in several areas of the globe.
- **Charcoal:** Charcoal, which has a higher carbon content and energy density than raw wood, is made by heating wood or other organic materials in the absence of oxygen.

a) Physical and chemical properties:

- **Density and porosity:** Compared to liquids and gases, solid fuels usually have higher density and lower porosity which significantly impact the rate of their combustion.
- **Moisture content:** If solid fuels have high moisture content the combustion efficiency will be low because a part of the energy is used to evaporate the water.
- **Volatile matter:** The release of volatile compounds that facilitate igniting and burning is the essence of volatile matter in the fuel.

1.1.2 Liquid fuels

- **Petroleum-based fuels:** Gasoline, diesel, kerosene, and jet fuel are the derivatives of crude oil and are the major fuels used in transport and industries.
- **Biofuels:** Ethanol and biodiesel are production of biomass and are good substitutes of petroleum fuel.

a) Physical and chemical properties:

- **Viscosity:** Viscosity is the property of a substance that defines resistance to flow and in the case of fuel it relates to atomization and mixing with air during combustion so it can be ignited.
- **Boiling point:** Vaporization will be quicker with lower boiling points, consequently, the gas with lower boiling point will ignite more easily.
- **Flash point:** The temperature of a liquid at which it produces enough vapor to form a flammable mixture with the surrounding air and ignite, given that there's an ignition source.

1.1.3 Gaseous fuels

- **Natural gas:** Methane (CH_4) is the main component of natural gas. It is utilized for heating, power generation, and as a fuel for vehicles.
- **Liquefied petroleum gas (LPG):** LPG is a combination of propane and butane that is used mostly for heating, cooking, and car fuel.
- **Hydrogen:** A pollutant-free fuel with good heating value, is considered a bright future of energy supply.

a) Physical and chemical properties:

- **Density:** Gaseous fuels are significantly less dense than their solid and liquid counterparts, thus their storage and transportation are affected.
- **Flammability range:** The range of concentration within which the gas can combust that is required for safety purposes.
- **Calorific value:** The amount of heat given off in the process of combustion, which shows the component's efficiency.

Famille	Formula	Structure	Saturé
Alcanes	C_nH_{2n+2}	Acyclique	✓
Alcènes	C_nH_{2n}	Acyclique	
Alcynes	C_nH_{2n-2}	Acyclique	
Cyclanes	C_nH_{2n}	Cyclique	✓
Aromatiques			
• Benzéniques	C_nH_{2n-6}	Cyclique	
• Naphtaléniques	C_nH_{2n-12}		

1.2 Octane and Cetane numbers

The performance of liquid fuels, particularly in internal combustion engines, is characterized by specific indices that measure their ignition properties and combustion quality.

1.2.1 Octane number

The octane number is a measure of a fuel's resistance to knocking or pre-ignition in spark-ignition engines. Higher octane numbers indicate greater resistance to knocking, allowing for higher compression ratios and improved engine performance.

a) Measurement and importance:

Research Octane Number (RON) and Motor Octane Number (MON): Two standard tests measure the octane number under different conditions. The average of RON and MON is often used to represent the fuel's overall octane rating.

b) Impact on Engine Performance:

Fuels with higher octane numbers enable more efficient engine operation, reducing the risk of engine damage and improving fuel economy.

1.2.2 Cetane number

The action of liquid fuels, most notably inside an internal combustion engine, is described using certain characteristics indices, which measure the fuels apos, ignition properties and combustion quality.

a) Measurement and importance:

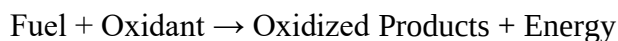
b) Ignition delay: The time between fuel injection and the start of combustion. Fuels with higher cetane numbers have shorter ignition delays.

c) Impact on engine performance: Higher cetane fuels improve cold starting, reduce engine noise, and lower emissions of unburned hydrocarbons and particulate matter.

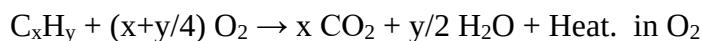
1.3 Combustion reactions

Combustion reactions are basic chemical changes that attract through a combination of a fuel with an oxidant (mostly oxygen) to obtain up to the reaction one unit of energy in the form of heat and light. Such reactions are the basis of numerous industrial utilizations, such as the production of energy, the internal combustion engine, or heating installation. We will start our course by learning the sources of combustion, stoichiometry, thermodynamics, and utilization.

The general form of a combustion reaction is:



For hydrocarbons of the C_xH_y form the reaction is written:



- **Example: Fuel Property Comparison**

Problem: Compare the volumetric energy density and stoichiometric air requirements for gasoline, diesel, and natural gas for transportation applications.

Solution:

Given data:

- Gasoline: $\rho = 740 \text{ kg/m}^3$, LHV = 44.0 MJ/kg, AFR = 15.1
- Diesel: $\rho = 850 \text{ kg/m}^3$, LHV = 42.5 MJ/kg, AFR = 14.5
- Natural gas: $\rho = 0.72 \text{ kg/m}^3$ (at STP), LHV = 50.0 MJ/kg, AFR = 17.2

Step 1: Calculate volumetric energy density

Gasoline: $E_v = \rho \times \text{LHV} = 740 \times 44.0 = 32,560 \text{ MJ/m}^3$

Diesel: $E_v = 850 \times 42.5 = 36,125 \text{ MJ/m}^3$

Natural gas: $E_v = 0.72 \times 50.0 = 36 \text{ MJ/m}^3$ (at STP)

Step 2: Calculate air volume requirements per unit fuel energy

For 1 MJ of fuel energy:

Gasoline: Air mass = $\text{AFR}/\text{LHV} = 15.1/44.0 = 0.343 \text{ kg air/MJ fuel}$

Air volume = $0.343/1.225 = 0.280 \text{ m}^3 \text{ air/MJ fuel}$

Diesel: Air mass = $14.5/42.5 = 0.341 \text{ kg air/MJ fuel}$

Air volume = $0.341/1.225 = 0.278 \text{ m}^3 \text{ air/MJ fuel}$

Natural gas: Air mass = $17.2/50.0 = 0.344 \text{ kg air/MJ fuel}$

Air volume = $0.344/1.225 = 0.281 \text{ m}^3 \text{ air/MJ fuel}$

Step 3: Analysis

- Diesel has the highest volumetric energy density (36,125 MJ/m³)
- Natural gas has extremely low volumetric energy density at atmospheric pressure
- All fuels require similar air volumes per unit energy ($\approx 0.28 \text{ m}^3/\text{MJ}$)

- Natural gas requires pressurization or liquefaction for practical vehicle applications

- **Example: Octane Number Determination**

Problem: A test fuel shows the same knocking characteristics as a mixture containing 92% iso-octane and 8% n-heptane by volume in a standard test engine. Determine the octane number and classify the fuel.

Solution:

Step 1: Apply octane number definition

Octane number = Volume percentage of iso-octane in the reference mixture

Step 2: Calculate octane number

Octane number = 92

Step 3: Fuel classification

- Octane number 92 indicates premium gasoline grade
- This fuel has knock resistance equivalent to 92% iso-octane
- Suitable for high-compression engines requiring premium fuel
- Would exhibit knocking in engines designed for higher octane fuels

Step 4: Practical implications

- Can be used in engines designed for 91+ octane fuel
- Provides better anti-knock performance than regular grade (87 octane)
- Higher cost but enables more aggressive engine timing for better performance

1.3.1 Enthalpy of reaction

The enthalpy of reaction (ΔH_r) measures the heat exchange that accompanies a chemical reaction occurring at constant pressure. It represents the total energy change when reactants transform into products. In combustion processes, where fuels react with oxidants like oxygen to produce combustion products such as carbon dioxide and water, the enthalpy of reaction reflects the energy released or absorbed during this transformation.



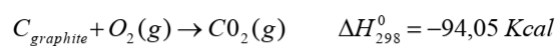
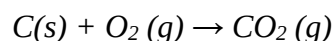
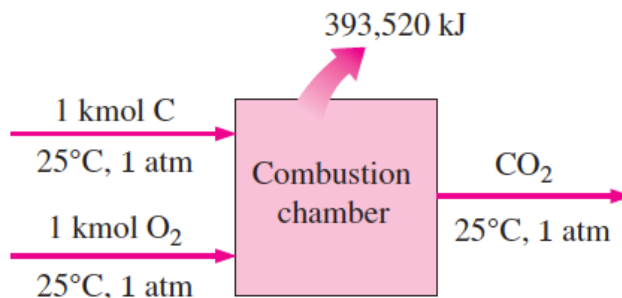
1.3.2 Exothermic and endothermic reactions:

- a. **Exothermic reactions:** These reactions release heat to the surroundings, resulting in a negative enthalpy change ($\Delta H_r < 0$). Combustion reactions, typical examples of exothermic processes, provide the heat necessary for various industrial and energy applications.
- b. **Endothermic reactions:** Conversely, these reactions absorb heat from the surroundings, leading to a positive enthalpy change ($\Delta H_r > 0$). While less common in combustion, endothermic reactions play vital roles in processes like gasification and certain chemical syntheses.

1.3.3 Types of Enthalpy changes

1.3.1.1 Standard enthalpy of formation (ΔH°_f):

The change in enthalpy when one mole of a substance is formed from its constituent elements in their standard states.

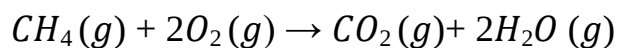


$$\Delta H_{298}^0 = (\Delta H_f^0)_{CO_2(g)} - \underbrace{(\Delta H_f^0)_{C_{\text{graphite}}(g)}}_{=0} - \underbrace{(\Delta H_f^0)_{O_2}}_{=0}$$

$$(\Delta H_f^0)_{CO_2(g)} = \Delta H_{298}^0 = -94,05 \text{ Kcal / Mole}$$

1.3.1.2 Standard enthalpy of combustion (ΔH_c):

The change in enthalpy is when one mole of a substance burns completely in oxygen under standard conditions.



1.4 Hess's Law:

States that the total enthalpy change of a reaction is the sum of the enthalpy changes of the steps into which the reaction can be divided.

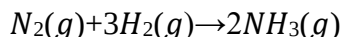
Example: If



Using Standard Enthalpies of Formation:

$$\Delta H_{\text{reaction}} = \sum \Delta H_f^0(\text{products}) - \sum \Delta H_f^0(\text{reactants}) \quad 1.1$$

For the reaction



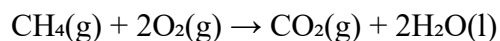
$$\Delta H_{reaction} = [2\Delta H^\circ_f(NH_3(g))] - [\Delta H^\circ_f(N_2(g)) + 3\Delta H^\circ_f(H_2(g))]$$

- **Example:** Calculating enthalpy of combustion

Question: Calculate the standard enthalpy of combustion (ΔH°_c) for one mole of methane (CH_4) gas at 298.15 K and 1 atm. Assume the products are $CO_2(g)$ and $H_2O(l)$.

Answer:

1. Write the balanced chemical equation:



2. Identify reactants and products and their mole numbers:

Reactants: 1 mole of $CH_4(g)$, 2 moles of $O_2(g)$ Products: 1 mole of $CO_2(g)$, 2 moles of $H_2O(l)$

3. Look up the standard enthalpies of formation (from the table above):

$$\Delta H^\circ_f, CH_4(g) = -74.81 \text{ kJ/mol} \quad \Delta H^\circ_f, O_2(g) = 0 \text{ kJ/mol}$$

$$\Delta H^\circ_f, CO_2(g) = -393.51 \text{ kJ/mol} \quad \Delta H^\circ_f, H_2O(l) = -285.83 \text{ kJ/mol}$$

Apply the formula for enthalpy of reaction:

$$\Delta H^\circ_c = [\sum n_p * \Delta H^\circ_{f,p}] - [\sum n_r * \Delta H^\circ_{f,r}]$$

$$\Delta H^\circ_c = [(1 * \Delta H^\circ_f, CO_2(g)) + (2 * \Delta H^\circ_f, H_2O(l))] - [(1 * \Delta H^\circ_f, CH_4(g)) + (2 * \Delta H^\circ_f, O_2(g))]$$

$$\Delta H^\circ_c = [(1 * -393.51) + (2 * -285.83)] - [(1 * -74.81) + (2 * 0)]$$

$$\Delta H^\circ_c = [-393.51 - 571.66] - [-74.81]$$

$$\Delta H^{\circ}c = [-965.17] + 74.81$$

$$\Delta H^{\circ}c = -890.36 \text{ kJ/mol}$$

The standard enthalpy of combustion for methane is -890.36 kJ per mole of methane burned. The negative sign confirms that the process is exothermic, releasing 890.36 kJ of energy as heat.

1.4.1 Sensible enthalpies

Sensible enthalpy refers to the heat absorbed or released by a substance during a temperature change without a phase change. It is called “sensible” because it results in a temperature change that can be sensed or measured.

1.4.2 Specific heat capacity

The amount of heat required to raise the temperature of one gram of a substance by one degree Celsius.

$$q = mc\Delta T \quad 1.2$$

q = heat absorbed or released

m = mass of the substance

c = specific heat capacity

ΔT = change in temperature

For water, the specific heat capacity is 4.18 J/g°C

Calculation of Sensible Enthalpies

Heating or Cooling a Substance:

$$q = mc\Delta T$$

Heating 100 grams of water from 25°C to 100°C,

$$q = (100\text{g}) \times (4.18 \text{ J/g}^{\circ}\text{C}) \times (100^{\circ}\text{C} - 25^{\circ}\text{C}) = 31350\text{J}$$

Here are the standard enthalpies of formation for some common substances involved in combustion. Note that the state (gas, liquid, solid) is important.

Substance	Formula	State	ΔH°_f (kJ/mol)
Oxygen	O ₂	gas	0
Nitrogen	N ₂	gas	0
Carbon Dioxide	CO ₂	gas	-393.51
Water	H ₂ O	gas	-241.82
Water	H ₂ O	liquid	-285.83
Methane	CH ₄	gas	-74.81
Propane	C ₃ H ₈	gas	-103.85
n-Octane	C ₈ H ₁₈	liquid	-249.9

1.5 Kirchhoff's Law

Thermochemical Kirchhoff's law allows the user to determine the value of enthalpy change for the reaction at different temperatures. It finds great use in processes of combustion where high-temperature reactions are the norm and standard enthalpy changes are given at reference temperatures (usually 298K). With the use of Kirchhoff's Law, we are able to convert these enthalpy values to the actual temperatures of the combustion process.

The law can be expressed as:

$$\Delta H_T = \Delta H_{T_0} + \int_{T_0}^T \Delta C_p dT \quad 1.3$$

Where:

ΔH_T = enthalpy change at temperature

ΔH_{T_0} = enthalpy change at reference temperature T_0 (usually 298 K)

ΔC_p = difference in heat capacities of products and reactants at constant pressure

T_0 = reference temperature

T = actual temperature

- **Example**

Consider the combustion of methane (CH_4):

Standard Enthalpy Change at 298 K:

$$\Delta H_{298} = -890.3 \text{ kJ/mol}$$

Heat Capacity Data:

Assume heat capacities of reactants and products are given by

$$C_{p,CH_4} = a_1 + b_1T + c_1T^2 + d_1T^3$$

$$C_{p,O_2} = a_2 + b_2T + c_2T^2 + d_2T^3$$

$$C_{p,CO_2} = a_3 + b_3T + c_3T^2 + d_3T^3$$

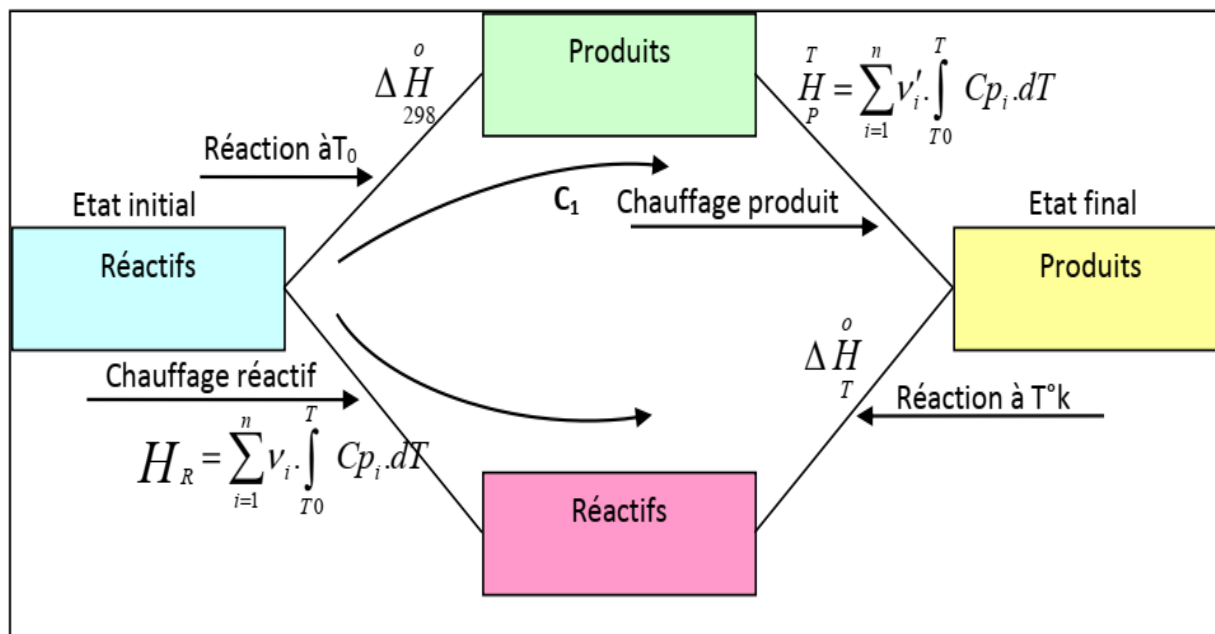
$$C_{p,H_2O} = a_4 + b_4T + c_4T^2 + d_4T^3$$

Heat Capacity Difference (ΔC_p):

$$\Delta C_p = (C_{p,CO_2} + 2C_{p,H_2O}) - (C_{p,CH_4} + 2C_{p,O_2})$$

Integrate ΔC_p over the temperature range. If the integration is complex, numerical methods or specific heat capacity **tables** can be used.

$$\Delta \overset{\circ}{H}_T = \Delta \overset{\circ}{H}_{298} + \sum_{i=1}^n \nu_i' \int_{T_0}^T (C_p)_{Xi} dT - \sum_{i=1}^n \nu_i \int_{T_0}^T (C_p)_{Xi} dT \quad 1.4$$



1.6 Gaseous Mixtures

Mixtures of gases can be found both in nature and in industries. The knowledge of gas mixtures behavior and their characteristics is the basis for the most different applications of science, from the atmospheric studies to the processing of chemicals. The topic will introduce the basic principles for gas mixtures which will include Dalton's Law of Partial Pressures, the Ideal Gas Law as it applies to mixtures, and the concepts of mole fraction and partial pressure.

1.6.1 Dalton's law of partial pressures

Dalton's Law states that the total pressure exerted by a mixture of non-reacting gases is equal to the sum of the partial pressures of each individual gas.

Mathematically, $P_{total} = P_1 + P_2 + P_3 + \dots$ etc

P_{total} = total pressure of the gas mixture

P_i = partial pressure of gas

The partial pressure of a gas in a mixture is the pressure it would exert if it occupied the entire volume alone at the same temperature.

$$P_i = X_i \cdot P_{total} \quad 1.5$$

$$P_{total} = \sum_{i=1}^n P_i \quad 1.6$$

X_i = mole fraction of gas i (defined as the ratio of the number of moles of gas i to the total number of moles in the mixture)

Example:

Consider a mixture of oxygen (O_2) and nitrogen (N_2) in a container. If the partial pressures are

$P_{O_2} = 0.2$ atm and $P_{N_2} = 0.8$ atm, then the total pressure $P_{total} = 0.2 + 0.8 = 1$ atm.

1.6.2 Ideal gas law for mixtures

The Ideal Gas Law can be applied to a mixture of gases by considering the total number of moles of gas present.

$$P_{total}V = n_{total}RT \quad 1.7$$

P_{total} = total pressure of the gas mixture

V = volume of the container

n_{total} = total number of moles of gas in the mixture

R = universal gas constant

T = temperature in Kelvin

1.6.1 Mole fraction:

- The mole fraction X_i of a component i in a mixture is given by

$$X_i = \frac{n_i}{n_{total}} \quad 1.8$$

- n_i = number of moles of gas i
- n_{total} = total number of moles of all gases in the mixture

1.6.3 Properties of gas mixtures

1.6.3.1 Density of gas mixtures:

The density ρ of a gas mixture can be determined using the ideal gas law and the molar masses of the individual gases.

$$\rho = \frac{P_{total} M_{mix}}{RT} \quad 1.9$$

M_{mix} = average molar mass of the gas mixture

$$M_{mix} = \sum X_i M_i \quad 1.10$$

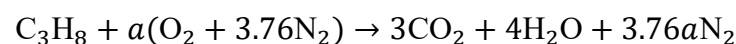
M_i = molar mass of gas i

• Example 1.3.1: Stoichiometric Analysis of Propane

Problem: Determine the stoichiometric air-fuel ratio, equivalence ratio, and product composition for propane (C_3H_8) combustion with 25% excess air.

Solution:

Step 1: Write the stoichiometric combustion equation



Step 2: Determine stoichiometric oxygen coefficient

$$a = \alpha + \frac{\beta}{4} - \frac{\gamma}{2} = 3 + \frac{8}{4} - \frac{0}{2} = 5$$

Step 3: Calculate stoichiometric AFR

Molecular weights: $\text{C}_3\text{H}_8 = 44.10 \text{ kg/kmol}$, air = 28.85 kg/kmol

$$\text{AFR}_s = \frac{5 \times 4.76 \times 28.85}{44.10} = \frac{686.47}{44.10} = 15.57$$

Step 4: Determine actual AFR with 25% excess air

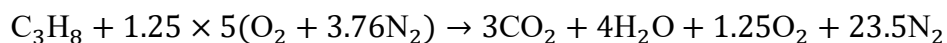
$$\lambda = 1.25$$

$$\text{AFR}_{\text{actual}} = \lambda \times \text{AFR}_s = 1.25 \times 15.57 = 19.46$$

Step 5: Calculate equivalence ratio

$$\phi = \frac{1}{\lambda} = \frac{1}{1.25} = 0.8$$

Step 6: Write the actual combustion equation with excess air



Step 7: Calculate product mole fractions

Total moles of products = 3 + 4 + 1.25 + 23.5 = 31.75 mol

Mole fractions:

- $y_{\text{CO}_2} = \frac{3}{31.75} = 0.0945 \text{ (9.45\%)}$
- $y_{\text{H}_2\text{O}} = \frac{4}{31.75} = 0.1260 \text{ (12.60\%)}$
- $y_{\text{O}_2} = \frac{1.25}{31.75} = 0.0394 \text{ (3.94\%)}$
- $y_{\text{N}_2} = \frac{23.5}{31.75} = 0.7402 \text{ (74.02\%)}$

- **Example 1.3.2: Natural Gas Mixture Analysis**

Problem: A natural gas has the following volumetric composition: 85% CH₄, 10% C₂H₆, 3% C₃H₈, 2% N₂. Calculate the average molecular weight, stoichiometric AFR, and heating value of this fuel mixture.

Solution:

Step 1: Calculate average molecular weight

$$\overline{MW} = \sum y_i MW_i$$

$$\overline{MW} = 0.85(16.04) + 0.10(30.07) + 0.03(44.10) + 0.02(28.01)$$

$$\overline{MW} = 13.63 + 3.01 + 1.32 + 0.56 = 18.52 \text{ kg/kmol}$$

Step 2: Determine stoichiometric oxygen requirements for each component

- CH₄: requires 2 mol O₂
- C₂H₆: requires 3.5 mol O₂
- C₃H₈: requires 5 mol O₂
- N₂: inert, requires 0 mol O₂

Step 3: Calculate weighted oxygen requirement

$$\begin{aligned} a_{\text{mix}} &= 0.85(2) + 0.10(3.5) + 0.03(5) + 0.02(0) = 1.7 + 0.35 + 0.15 + 0 \\ &= 2.2 \text{ mol O}_2/\text{mol fuel} \end{aligned}$$

Step 4: Calculate stoichiometric AFR

$$\text{AFR}_s = \frac{2.2 \times 4.76 \times 28.85}{18.52} = \frac{302.23}{18.52} = 16.32$$

Step 5: Calculate mixture heating value (LHV)

LHV values: CH₄ = 50.0, C₂H₆ = 47.6, C₃H₈ = 46.4 MJ/kg

$$\text{LHV}_{\text{mix}} = \frac{\sum y_i \times MW_i \times \text{LHV}_i}{\overline{MW}}$$

$$\text{LHV}_{\text{mix}} = \frac{0.85 \times 16.04 \times 50.0 + 0.10 \times 30.07 \times 47.6 + 0.03 \times 44.10 \times 46.4}{18.52}$$

$$\text{LHV}_{\text{mix}} = \frac{681.7 + 143.1 + 61.4}{18.52} = \frac{886.2}{18.52} = 47.8 \text{ MJ/kg}$$

1.6.4 Stoichiometry

Knowing the exact relationships between reactants and products in chemical reactions is a must-have skill for anyone willing to optimize processes in chemistry, engineering, and environmental science. Stoichiometry gives a quantitative foundation for these relationships. In combustion operations, the air-fuel ratio and the coefficient of the excess air are very important to getting a clean and complete combustion process.

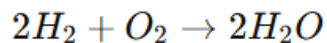
1.6.4.1 Definition

Stoichiometry is a part of chemistry that deals with the quantitative relationships between the reactants and products in a chemical reaction. It relies on the principle of conservation of mass and the idea that matter cannot be created or destroyed in a chemical reaction.

1.6.4.2 Stoichiometric calculations

a. Balanced chemical equation:

A balanced chemical equation has equal numbers of each type of atom on both sides of the equation.



The coefficients in a balanced chemical equation represent the mole ratios of the reactants and products.

In the above reaction the mole ratio of hydrogen to oxygen is 2:1, and the mole ratio of hydrogen to water is 1:1.

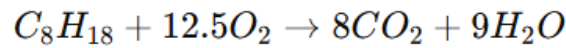
b. Air-Fuel ratio

The air-fuel ratio (AFR) is the ratio of the mass of air to the mass of fuel in a combustion process. It is a critical parameter in engines and combustion systems to ensure efficient and complete combustion.

c. Stoichiometric Air-Fuel Ratio:

The stoichiometric AFR is the ideal ratio at which all the fuel is burned using all the available oxygen in the air.

Example: For gasoline (octane, C_8H_{18}):



The stoichiometric AFR for gasoline is approximately 14.7:1 (14.7 parts air to 1 part fuel by mass).

$$AFR = m_a/m_f \quad 1.11$$

d. Lean and rich mixtures:

- A lean mixture has more air than the stoichiometric ratio, leading to excess oxygen after combustion.
- A rich mixture has less air than the stoichiometric ratio, leading to unburned fuel after combustion.

e. Coefficient of excess air

The coefficient of excess air (λ) is the ratio of the actual amount of air used in the combustion process to the stoichiometric amount of air required. It indicates whether the combustion process is running lean ($\lambda > 1$) or rich ($\lambda < 1$).

$$\lambda = \frac{1}{\phi} = \frac{AFR_{\text{actual}}}{AFR_s} \quad 1.12$$

$$\phi = \frac{(F/A)_{\text{actual}}}{(F/A)_{\text{stoichiometric}}} = \frac{AFR_s}{AFR_{\text{actual}}} \quad 1.13$$

• Implications:

Lean Combustion ($\lambda > 1$):

- More efficient fuel usage

- Lower emissions of unburned hydrocarbons and carbon monoxide
- Higher combustion temperatures, which can lead to higher Nox emissions

Rich Combustion ($\lambda < 1$):

- Higher fuel consumption
- Increased emissions of unburned hydrocarbons and carbon monoxide
- Lower combustion temperatures

Example: Stoichiometric calculation

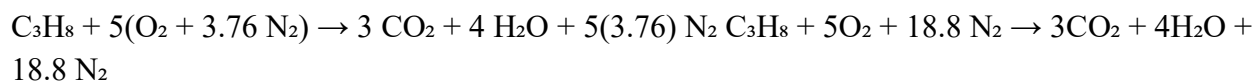
Question: Propane (C_3H_8) is burned with 50% excess air. Calculate:

- The stoichiometric mass AFR.
- The actual mass AFR.
- The equivalence ratio (Φ).

Solution:

1. Write the stoichiometric reaction for propane (C_3H_8):

Here, $x=3$, $y=8$, $z=0$. The stoichiometric moles of O_2 are $a = x + y/4 - z/2 = 3 + 8/4 - 0 = 5$. The balanced stoichiometric equation is:



a) Calculate the stoichiometric mass AFR:

Molar mass of fuel (C_3H_8) = $3 \times 12.01 + 8 \times 1.01 \approx 44.1$ g/mol. Molar mass of air ≈ 29 g/mol.

Moles of air (stoic) = $5 \times (1 + 3.76) = 23.8$ moles. Moles of fuel = 1 mole.

$$AFR_{stoic} = (\text{Mass of Air}) / (\text{Mass of Fuel}) = (\text{moles}_{air} \times M_{air}) / (\text{moles}_{fuel} \times M_{fuel})$$

$$AFR_{stoic} = (23.8 \times 29) / (1 \times 44.1) \approx 15.67$$

$$(AFR)_{stoic} \approx 15.7 : 1$$

b) Calculate the actual mass AFR:

50% excess air means we are supplying 1.5 times the stoichiometric amount of air.

$$AFR_{actual} = 1.5 \times AFR_{stoic} = 1.5 \times 15.67 \approx 23.5$$

$$(AFR)_{actual} \approx 23.5 : 1$$

c) Calculate the equivalence ratio (Φ):

$$\Phi = (\text{AFR})_{\text{stoic}} / (\text{AFR})_{\text{actual}} = 15.67 / 23.5 \approx 0.667$$

$$\Phi \approx 0.67$$

Since $\Phi < 1.0$, this confirms it is a lean mixture, as expected with 50% excess air.

1.7 Calorific Value

Calorific value is an indicator of how much energy is present from a unit of fuel. It plays a significant role in the evaluation of the effectiveness and the working of the systems that involve burning. One can determine the calorific value as a Higher Heating Value (HHV) or a Lower Heating Value (LHV), based on the assumption of the water generated during combustion being in the liquid or vapor phase. The knowledge and computation of these figures become necessary accompaniments for the successful implementation and the effective utilization of combustion processes.

1.7.1 Higher heating value (HHV)

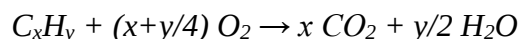
- HHV (or Gross Calorific Value, GCV) is the total heat released when a fuel is completely combusted, and the products are brought back to the starting temperature, thus, all the water vapor formed is condensed.
- The heat content measured is one that does not allow the release of the heat from water, which is why it includes the latent heat of vaporization of water.
- Typical unit: MJ/kg or kJ/mol.

1.7.2 Lower heating value (LHV)

- LHV (or Net Calorific Value, NCV) is the sum of heat released on complete combustion of a fuel, but the combustion products are not cooled to a temperature at which the water formed is condensed.
- The latent heat of vaporization of the water is not accounted for.
- Common units: MJ/kg or kJ/mol.

1.7.3 Calculation of Higher Heating Value (HHV)

To calculate the HHV, the energy released from the combustion of the fuel, including the condensation of water vapor, must be considered. For a hydrocarbon fuel C_xH_y , the combustion reaction is:



In order to find out the HHV, it is necessary to include the energy that is released when the fuel is burned and water vapor gets condensed. The combustion of hydrocarbon fuel is as follows:

$$HHV = -\Delta H_{\text{combustion}} = \sum \Delta H_f^\circ(\text{products}) - \sum \Delta H_f^\circ(\text{reactants}) \quad 1.14$$

1.7.4 Calculation of lower heating value (LHV)

The LHV is obtained from the HHV by subtracting the energy required to vaporize the water produced during combustion. The latent heat of vaporization of water ($\Delta H_{\text{vap}}, H_2O$) at 298 K is approximately 44 kJ/mol.

$$LHV = HHV - n \times \Delta H_{\text{vap}, H_2O} \quad 1.16$$

Where n is the number of moles of water produced per mole of fuel.

- **Example 1.5.1: LHV and HHV Calculation for Butane**

Problem: Calculate the HHV and LHV for butane (C_4H_{10}) and determine the percentage difference between them.

Solution:

Step 1: Identify fuel properties

Butane: C_4H_{10}

Molecular weight = $4(12.01) + 10(1.008) = 58.12 \text{ kg/kmol}$

Step 2: Determine water formation

Combustion: $C_4H_{10} + 6.5O_2 \rightarrow 4CO_2 + 5H_2O$

Moles of H₂O per mole of butane = 5

Mass of H₂O per kg of butane:

$$m_{\text{H}_2\text{O}} = \frac{5 \times 18.015}{58.12} = \frac{90.075}{58.12} = 1.550 \text{ kg H}_2\text{O/kg fuel}$$

Step 3: Calculate the HHV-LHV difference

$$\text{HHV} - \text{LHV} = 1.550 \times 2.44 = 3.78 \text{ MJ/kg}$$

Step 4: Use tabulated HHV value for butane

From standard tables: HHV = 49.5 MJ/kg

Step 5: Calculate LHV

$$\text{LHV} = \text{HHV} - 3.78 = 49.5 - 3.78 = 45.72 \text{ MJ/kg}$$

Step 6: Calculate percentage difference

$$\text{Percentage difference} = \frac{\text{HHV} - \text{LHV}}{\text{HHV}} \times 100 = \frac{3.78}{49.5} \times 100 = 7.6\%$$

Step 7: Verification using combustion enthalpy

From enthalpy of formation data (kJ/mol):

- $\Delta H_{f, \text{C}_4\text{H}_{10}}^\circ = -126.15$
- $\Delta H_{f, \text{CO}_2}^\circ = -393.52$
- $\Delta H_{f, \text{H}_2\text{O}(l)}^\circ = -285.84$
- $\Delta H_{f, \text{H}_2\text{O}(g)}^\circ = -241.83$

HHV calculation:

$$\text{HHV} = -[\Delta H_r^\circ] = -[4(-393.52) + 5(-285.84) - (-126.15)]$$

$$\text{HHV} = -[-1574.08 - 1429.20 + 126.15] = 2877.13 \text{ kJ/mol}$$

$$\text{HHV} = \frac{2877.13}{58.12} = 49.5 \text{ MJ/kg} \checkmark$$

• **Example 1.5.2: Mixed Fuel Heating Value**

Problem: A fuel gas mixture contains 60% CH₄, 25% C₂H₆, 10% C₃H₈, and 5% N₂ by volume. Calculate the mixture LHV and the HHV-LHV difference.

Solution:

Step 1: Collect component data

Component	Volume %	MW (kg/kmol)	LHV (MJ/kg)	HHV (MJ/kg)
CH ₄	60	16.04	50.0	55.5
C ₂ H ₆	25	30.07	47.6	51.9
C ₃ H ₈	10	44.10	46.4	50.4
N ₂	5	28.01	0.0	0.0

Step 2: Calculate mixture molecular weight

$$\overline{MW} = \sum y_i MW_i = 0.6(16.04) + 0.25(30.07) + 0.10(44.10) + 0.05(28.01)$$

$$\overline{MW} = 9.624 + 7.518 + 4.410 + 1.401 = 22.95 \text{ kg/kmol}$$

Step 3: Calculate mixture LHV on molar basis

$$\text{LHV}_{\text{mix,molar}} = \sum y_i \times MW_i \times \text{LHV}_i$$

$$= 0.6 \times 16.04 \times 50.0 + 0.25 \times 30.07 \times 47.6 + 0.10 \times 44.10 \times 46.4 + 0.05 \times 28.01 \times 0$$

$$= 481.2 + 358.3 + 204.6 + 0 = 1044.1 \text{ MJ/kmol}$$

Step 4: Calculate mixture LHV on mass basis

$$\text{LHV}_{\text{mix}} = \frac{1044.1}{22.95} = 45.5 \text{ MJ/kg}$$

Step 5: Calculate mixture HHV similarly

$$\begin{aligned} \text{HHV}_{\text{mix,molar}} &= 0.6 \times 16.04 \times 55.5 + 0.25 \times 30.07 \times 51.9 + 0.10 \times 44.10 \times 50.4 + 0 \\ &= 534.1 + 389.4 + 222.3 + 0 = 1145.8 \text{ MJ/kmol} \end{aligned}$$

$$\text{HHV}_{\text{mix}} = \frac{1145.8}{22.95} = 49.9 \text{ MJ/kg}$$

Step 6: Calculate HHV-LHV difference

$$\text{HHV} - \text{LHV} = 49.9 - 45.5 = 4.4 \text{ MJ/kg}$$

Step 7: Verification by water formation calculation

Water formation per mole of mixture:

- CH_4 : $0.6 \times 2 = 1.2 \text{ mol H}_2\text{O}$
- C_2H_6 : $0.25 \times 3 = 0.75 \text{ mol H}_2\text{O}$
- C_3H_8 : $0.10 \times 4 = 0.40 \text{ mol H}_2\text{O}$
- Total: $2.35 \text{ mol H}_2\text{O}$ per mol fuel

Mass of water per kg fuel:

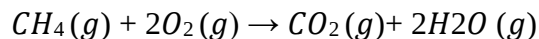
$$m_{\text{H}_2\text{O}} = \frac{2.35 \times 18.015}{22.95} = 1.84 \text{ kg H}_2\text{O/kg fuel}$$

$$\text{HHV} - \text{LHV} = 1.84 \times 2.44 = 4.5 \text{ MJ/kg } \checkmark$$

• **Example:**

Consider the combustion of methane (CH_4):

Balanced Combustion Reaction:



Standard Enthalpy of Formation (ΔH°_f)

$$\Delta H_f^\circ(\text{CH}_4) = -74.8 \text{ kJ/mol}$$

$$\Delta H_f^\circ(\text{O}_2) = 0 \text{ kJ/mol}$$

$$\Delta H_f^\circ(\text{CO}_2) = -393.5 \text{ kJ/mol}$$

$$\Delta H_f^\circ(\text{H}_2\text{O, liquid}) = -285.8 \text{ kJ/mol}$$

Calculate HHV:

$$\Delta H_{\text{combustion}} = [\Delta H_f^\circ(\text{CO}_2) + 2\Delta H_f^\circ(\text{H}_2\text{O})] - [\Delta H_f^\circ(\text{CH}_4) + 2\Delta H_f^\circ(\text{O}_2)]$$

$$\Delta H_{\text{combustion}} = [-393.5 + 2(-285.8)] - [-74.8 + 0]$$

$$\Delta H_{\text{combustion}} = [-393.5 - 571.6] - [-74.8]$$

$$\Delta H_{\text{combustion}} = -965.1 + 74.8 = -890.3 \text{ kJ/mol}$$

$$\text{HHV} = 890.3 \text{ kJ/mol}$$

Calculate LHV:

$$\text{LHV} = \text{HHV} - n \times \Delta H_{\text{vap}, \text{H}_2\text{O}}$$

$$\text{LHV} = 890.3 \text{ kJ/mol} - 2 \times 44 \text{ kJ/mol}$$

$$\text{LHV} = 890.3 - 88 = 802.3 \text{ kJ/mol}$$

Conclusion:

In this chapter we present the fundamentals of combustion in which we look at in great detail – from the basic elements and processes that form the root of our study. We begin with the basics of reaction enthalpy and sensible enthalpies and then we move into the more complex issues of gas mixtures and stoichiometry also we look at in depth the key issues of air fuel ratios and excess air coefficients. We present what we consider to be the main reactions in combustion which we put forth for their import in the balanced equations and in the thermodynamics that play a role. We go into great detail the application of Kirchhoff's Law which gives us a better picture of how temperature changes play a role in enthalpy changes which in turn gives us a better picture of combustion at different temperatures. Also, we looked at the calculation of calorific values in great depth – we looked at Higher Heating Value (HHV) and Lower Heating Value (LHV) and the importance of these in terms of fuel efficiency and energy content.

Chapter 2: Thermochemistry

Introduction:

Thermochemistry is the fundamental basis for a deep understanding of energy changes in combustion systems. The chapter of the text material covers energetic aspects, enthalpy changes at flame temperatures, the equilibria of the systems in question, and the kinetic mechanisms involved in the reaction rates of combustion processes. These notions constitute the very foundation of combustion engineering and are the first steps for the creation and improvement of the devices that use combustion in practice.

2.1 Adiabatic Flame Temperature at Constant Volume and Constant Pressure

2.1.1 Introduction to Adiabatic Flame Temperature

Adiabatic flame temperature is the highest temperature attainable during a combustion process without any heat loss to the environment. This theoretical maximum provides an important indication of how much energy is given off when a fuel-oxidizer pair combines and also acts as a reference point when examining real combustion systems.

The main difference between these two cases is the thermodynamic conditions under which the processes take place: constant volume and constant pressure. In most practical situations such as gas turbines and furnaces, the continuous pressure case is usually more applicable whereas the continuous volume case can be used for internal combustion engines and closed bomb calorimeters.

2.1.2 Governing Equations for Constant Pressure Adiabatic Combustion

The energy balance for the first law of thermodynamics in the case of an adiabatic combustion process at constant pressure requires that the total enthalpy of the reactants equals the total enthalpy of the products:

$$H_{\text{products}}(T_{\text{ad}}) = H_{\text{reactants}}(T_{\text{initial}}) \quad 2.1$$

This energy balance can be expressed in terms of enthalpies of formation and sensible enthalpies:

$$\sum_i n_{i,p} \left[\Delta h_{f,i}^{\circ} + \int_{T_{\text{ref}}}^{T_{\text{ad}}} c_{p,i} dT \right] = \sum_j n_{j,r} \left[\Delta h_{f,j}^{\circ} + \int_{T_{\text{ref}}}^{T_{\text{initial}}} c_{p,j} dT \right] \quad 2.2$$

where:

- $n_{i,p}$ and $n_{j,r}$ are the molar amounts of products and reactants
- Δh_f° represents standard enthalpies of formation
- c_p denotes molar heat capacities at constant pressure
- $T_{\text{ref}} = 298.15$ K is the reference temperature

For reactants initially at the reference temperature, this simplifies to:

$$\sum_i n_{i,p} \Delta h_{f,i}^\circ + \sum_i n_{i,p} \int_{T_{\text{ref}}}^{T_{\text{ad}}} c_{p,i} dT = \sum_j n_{j,r} \Delta h_{f,j}^\circ \quad 2.3$$

The heat of combustion is defined as:

$$Q_{\text{combustion}} = - \left(\sum_i n_{i,p} \Delta h_{f,i}^\circ - \sum_j n_{j,r} \Delta h_{f,j}^\circ \right) \quad 2.4$$

Therefore, the adiabatic flame temperature equation becomes:

$$Q_{\text{combustion}} = \sum_i n_{i,p} \int_{T_{\text{ref}}}^{T_{\text{ad}}} c_{p,i} dT \quad 2.5$$

2.1.3 Governing Equations for Constant Volume Adiabatic Combustion

For constant volume processes, the first law requires equality of internal energies:

$$H_{\text{products}}(T_{\text{ad}}) = H_{\text{reactants}}(T_{\text{initial}}) \quad 2.6$$

Using the relationship $h = u + pv = u + RT$ for ideal gases:

$$\sum_i n_{i,p} \left[\Delta u_{f,i}^\circ + \int_{T_{\text{ref}}}^{T_{\text{ad}}} c_{v,i} dT \right] = \sum_j n_{j,r} \left[\Delta u_{f,j}^\circ + \int_{T_{\text{ref}}}^{T_{\text{initial}}} c_{v,j} dT \right] \quad 2.7$$

Since $\Delta u_f^\circ = \Delta h_f^\circ - \Delta n R T_{\text{ref}}$, where Δn is the change in moles of gaseous products:

$$Q_{\text{combustion}} + \Delta n R T_{\text{ref}} = \sum_i n_{i,p} \int_{T_{\text{ref}}}^{T_{\text{ad}}} c_{v,i} dT \quad 2.8$$

2.2 Comparison of Constant Volume and Constant Pressure Cases

The constant volume adiabatic flame temperature is always higher than the constant pressure case because:

1. No expansion work is performed in the constant volume process
2. All released chemical energy goes into increasing internal energy
3. The relationship $c_p > c_v$ for ideal gases

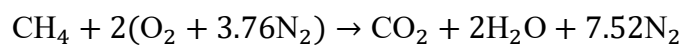
The temperature difference can be significant, particularly for reactions with large Δn values.

• **Example 2.1.1: Methane-Air Combustion (Constant Pressure)**

Problem: Calculate the adiabatic flame temperature for stoichiometric combustion of methane in air at 298 K and 1 atm.

Solution:

The balanced combustion equation is:



Step 1: Calculate the heat of combustion

Using standard enthalpies of formation (kJ/mol):

- $\Delta h_{f,\text{CH}_4}^\circ = -74.87$
- $\Delta h_{f,\text{CO}_2}^\circ = -393.52$
- $\Delta h_{f,\text{H}_2\text{O}(g)}^\circ = -241.83$
- $\Delta h_{f,\text{O}_2}^\circ = \Delta h_{f,\text{N}_2}^\circ = 0$

$$Q_{\text{combustion}} = -[(-393.52) + 2(-241.83)] - [(-74.87) + 0] = 802.31 \text{ kJ/mol fuel}$$

Step 2: Set up the energy balance equation

$$802.31 = \int_{298}^{T_{\text{ad}}} [1 \cdot c_{p,\text{CO}_2} + 2 \cdot c_{p,\text{H}_2\text{O}} + 7.52 \cdot c_{p,\text{N}_2}] dT$$

Step 3: Use polynomial expressions for heat capacities

For temperatures between 298-3000 K, the heat capacities (J/mol·K) are:

- $c_{p,\text{CO}_2} = 22.26 + 5.98 \times 10^{-2}T - 3.50 \times 10^{-5}T^2 + 7.47 \times 10^{-9}T^3$
- $c_{p,\text{H}_2\text{O}} = 32.24 + 0.19 \times 10^{-2}T + 1.06 \times 10^{-5}T^2 - 3.60 \times 10^{-9}T^3$
- $c_{p,\text{N}_2} = 28.90 - 0.15 \times 10^{-2}T + 0.81 \times 10^{-5}T^2 - 2.87 \times 10^{-9}T^3$

Step 4: Solve iteratively for T_{ad}

Using numerical integration and iteration, the adiabatic flame temperature is:

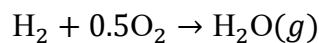
$$T_{\text{ad}} = 2226 \text{ K (1953}^\circ\text{C)}$$

• Example 2.1.2: Hydrogen-Oxygen Combustion (Constant Volume)

Problem: Calculate the constant volume adiabatic flame temperature for stoichiometric H₂-O₂ combustion starting at 298 K.

Solution:

The reaction is:



Step 1: Calculate Δn

$$\Delta n = 1 - (1 + 0.5) = -0.5 \text{ mol}$$

Step 2: Calculate the heat of combustion

$$Q_{\text{combustion}} = 241.83 \text{ kJ/mol H}_2$$

Step 3: Apply the constant volume energy balance

$$Q_{\text{combustion}} + \Delta n R T_{\text{ref}} = \int_{298}^{T_{\text{ad}}} c_{v,\text{H}_2\text{O}} dT$$

$$241830 + (-0.5)(8.314)(298) = \int_{298}^{T_{ad}} c_{v,H_2O} dT$$

$$240594 \text{ J/mol} = \int_{298}^{T_{ad}} c_{v,H_2O} dT$$

Step 4: Using $c_{v,H_2O} = c_{p,H_2O} - R$ and solving iteratively:

$$T_{ad} = 4990 \text{ K (4717}^\circ\text{C)}$$

This demonstrates that the constant volume flame temperature is significantly higher than the constant pressure case due to the absence of expansion work.

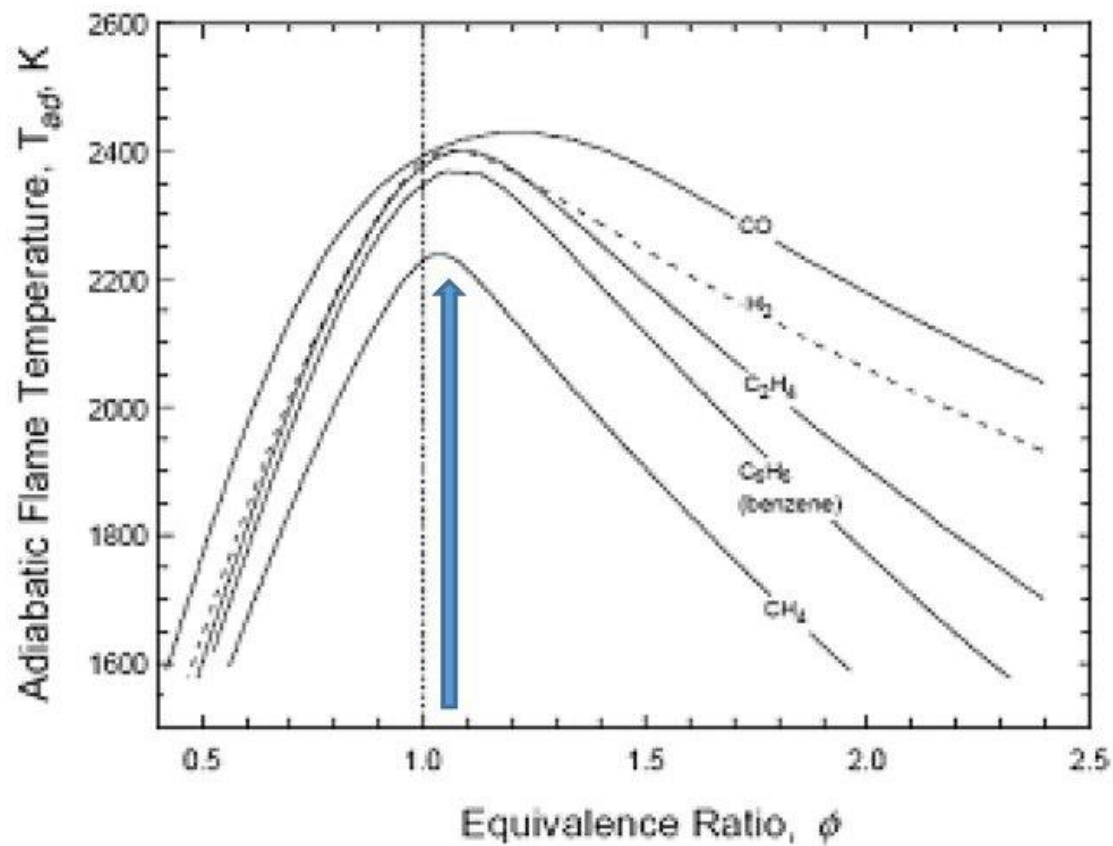


Figure 2.1: Variation of adiabatic flame temperature with equivalence ratio

Section Summary

The adiabatic flame temperature is a practical upper bound on fire temperatures that are dependent, basically, on the thermodynamic constraints of the process. The contained volume combustion shows higher temperatures than the constant pressure one because no work of expansion is involved. Computations rely on complete thermodynamic properties and require repeated calculation steps because of the temperature dependence of heat capacity. Such concepts are the basic ones for energy release process in real combustion systems.

2.3 Calculating Combustion Chamber Temperature

2.3.1 Thermodynamic Principles for Combustion Chambers

Heat transfer, incomplete mixing, and finite reaction rates are the major factors which cause real combustion chambers to differ significantly from idealized adiabatic conditions. In order to analyze the combustion chamber temperatures, one needs to employ the energy balance equations that sufficiently represent these actual situations.

The energy balance equation that represents the general case for a steady-flow combustion chamber is given by:

$$\dot{m}_{\text{fuel}} h_{\text{fuel}} + \dot{m}_{\text{air}} h_{\text{air}} + \dot{Q}_{\text{in}} = \dot{m}_{\text{products}} h_{\text{products}} + \dot{Q}_{\text{out}} + \dot{W}_{\text{shaft}} \quad 2.10$$

where $\dot{Q}_{\text{in}}$ represents heat input, $\dot{Q}_{\text{out}}$ is heat loss to surroundings, and $\dot{W}_{\text{shaft}}$ is shaft work output.

2.3.2 Energy Balance Derivation

For a control volume encompassing the combustion chamber, the steady-flow energy equation becomes:

$$\sum \dot{m}_{\text{in}} \left(h + \frac{V^2}{2} + gz \right)_{\text{in}} + \dot{Q}_{\text{net}} = \sum \dot{m}_{\text{out}} \left(h + \frac{V^2}{2} + gz \right)_{\text{out}} + \dot{W}_{\text{net}} \quad 2.11$$

Neglecting kinetic and potential energy changes and assuming no shaft work:

$$\dot{Q}_{\text{net}} = \sum \dot{m}_{\text{out}} h_{\text{out}} - \sum \dot{m}_{\text{in}} h_{\text{in}} \quad 2.12$$

The net heat transfer includes combustion heat release minus wall heat losses:

$$\dot{Q}_{\text{net}} = \dot{Q}_{\text{combustion}} - \dot{Q}_{\text{loss}} \quad 2.13$$

2.3.3 Heat Loss Mechanisms

Heat losses in combustion chambers occur through multiple mechanisms:

1. **Convective Heat Transfer:** $\dot{Q}_{\text{conv}} = h_c A_s (T_{\text{gas}} - T_{\text{wall}})$
2. **Radiative Heat Transfer:** $\dot{Q}_{\text{rad}} = \varepsilon \sigma A_s (T_{\text{gas}}^4 - T_{\text{wall}}^4)$
3. **Conductive Heat Transfer:** Through chamber walls to coolant systems

The overall heat loss coefficient combines these mechanisms:

$$\frac{1}{U} = \frac{1}{h_{\text{conv}}} + \frac{1}{h_{\text{rad}}} + R_{\text{wall}}$$

• Example 2.3.1: Gas Turbine Combustor Temperature Calculation

Problem: A gas turbine combustor burns natural gas (assumed as methane) with preheated air. Calculate the combustor exit temperature given:

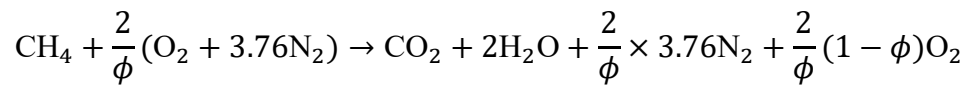
- Air inlet temperature: 700 K

- Air inlet pressure: 20 atm
- Fuel flow rate: 0.5 kg/s
- Air flow rate: 50 kg/s
- Heat loss: 5% of combustion energy
- Equivalence ratio: 0.8 (lean combustion)

Solution:

Step 1: Determine the combustion stoichiometry

For lean combustion with $\phi = 0.8$:



Step 2: Calculate theoretical air-fuel ratio

$$\text{AFR}_{\text{stoic}} = \frac{2.5 \times (32 + 3.76 \times 28)}{16.04} = 17.23$$

$$\text{AFR}_{\text{actual}} = \frac{17.23}{0.8} = 21.54$$

Step 3: Verify actual air flow rate

$$\dot{m}_{\text{air,required}} = 0.5 \times 21.54 = 10.77 \text{ kg/s}$$

The given air flow rate (50 kg/s) indicates significant excess air beyond lean combustion requirements.

Step 4: Calculate heat of combustion per unit fuel

$$Q_{\text{combustion}} = 50.0 \text{ MJ/kg CH}_4$$

Step 5: Apply energy balance

$$\dot{m}_{\text{fuel}}h_{\text{fuel}}(700) + \dot{m}_{\text{air}}h_{\text{air}}(700) + 0.95\dot{m}_{\text{fuel}}Q_{\text{combustion}} = (\dot{m}_{\text{fuel}} + \dot{m}_{\text{air}})h_{\text{products}}(T_{\text{exit}})$$

Step 6: Calculate specific enthalpies

Using air properties at 700 K: $h_{\text{air}} = 713.27 \text{ kJ/kg}$

Using methane properties at 700 K: $h_{\text{CH}_4} = 1547.3 \text{ kJ/kg}$

Step 7: Solve for exit temperature

$$0.5 \times 1547.3 + 50 \times 713.27 + 0.95 \times 0.5 \times 50000 = 50.5 \times h_{\text{products}}(T_{\text{exit}})$$

$$773.65 + 35663.5 + 23750 = 50.5 \times h_{\text{products}}(T_{\text{exit}})$$

$$h_{\text{products}}(T_{\text{exit}}) = 1192.5 \text{ kJ/kg}$$

Using air property tables (products approximated as air due to high excess air):

$$T_{\text{exit}} = 1200 \text{ K (927}^\circ\text{C)}$$

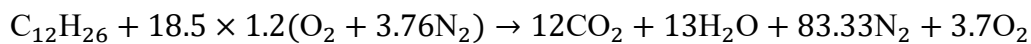
• Example 2.3.2: Industrial Furnace Temperature Analysis

Problem: An industrial furnace burns fuel oil with 20% excess air. Determine the furnace temperature considering:

- Fuel oil heating value: 42 MJ/kg
- Air preheating temperature: 500 K
- Heat loss through walls: 15% of input energy
- Combustion efficiency: 95%

Solution:

Step 1: Establish combustion equation for fuel oil ($\text{C}_{12}\text{H}_{26}$)



Step 2: Calculate energy balance

Net available energy = Combustion energy $\times$ efficiency - Heat losses

$$Q_{\text{net}} = 42 \times 0.95 - 42 \times 0.15 = 33.6 \text{ MJ/kg fuel}$$

Step 3: Calculate air requirements

$$\text{Stoichiometric air} = 18.5 \times (32 + 3.76 \times 28) = 2434 \text{ kg air/kg fuel}$$

$$\text{Actual air} = 2434 \times 1.2 = 2921 \text{ kg air/kg fuel}$$

Step 4: Apply energy equations

$$Q_{\text{net}} + \dot{m}_{\text{air}} h_{\text{air}}(500) = (\dot{m}_{\text{fuel}} + \dot{m}_{\text{air}}) h_{\text{products}}(T_{\text{furnace}})$$

Step 5: Solve for furnace temperature

Using iterative calculation with product gas properties:

$$T_{\text{furnace}} = 1650 \text{ K (1377}^\circ\text{C)}$$

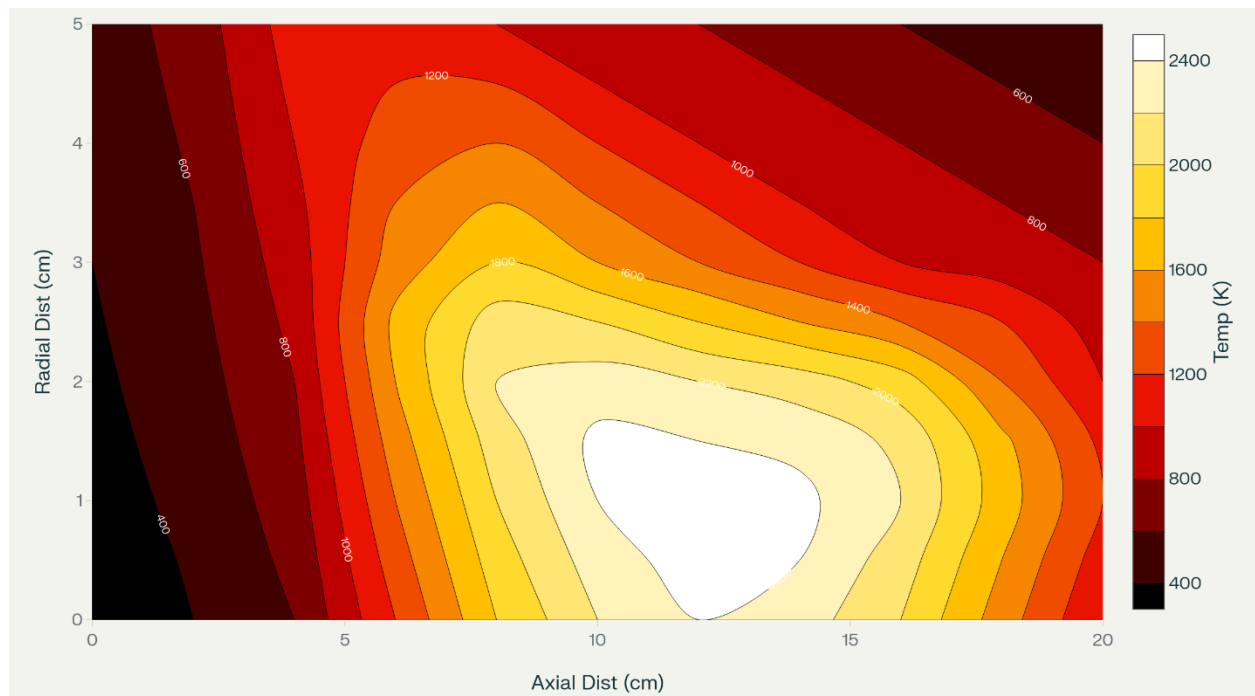


Figure 2.2: Temperature distribution in a typical combustion chamber

a. Assumptions and Limitations

The combustion chamber temperature calculations involve several key assumptions:

1. **Steady-state operation:** Transient effects are neglected
2. **Perfect mixing:** Uniform temperature and composition
3. **Complete combustion:** All fuel is converted to stable products
4. **Ideal gas behavior:** Valid at high temperatures and moderate pressures
5. **Negligible dissociation:** Applicable below 2000 K

The errors that these assumptions introduce may be seen in work that is very diverse, especially in high-temperature systems or during the period when the system is starting up or shutting down.

Section Summary

The calculation of combustion chamber temperatures requires the making of energy balances that take heat losses and the effects of mixing into account. The analysis offers very important information for the thermal design, the choice of materials, and the optimization of the performance of combustion systems. Mastering these concepts allows engineers to make educated guesses and control the temperatures of the combustion process in their practical applications.

2.4 Equilibrium Constants and Reaction Rates

2.4.1 Introduction to Chemical Equilibrium

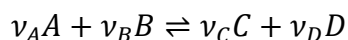
The chemical equilibrium is a condition where the rates of the forward and reverse reactions are equal, hence the concentrations of the species involved in the reaction remain unchanged with time. In combustion systems, the role of equilibrium becomes more significant at extremely high temperatures, where dissociation reactions take place, thus changing both the efficiency of the system and the type of pollutants released.

The equilibrium is the state in which the system's Gibbs free energy is at its minimum for the given conditions of temperature and pressure. This concept in thermodynamics is the main idea

behind the calculations of equilibrium compositions and the understanding of the forces that drive the reactions.

2.4.2 Thermodynamic Basis for Equilibrium Constants

For a general chemical reaction:



The equilibrium condition requires that the change in Gibbs free energy equals zero:

$$\Delta G = \sum \nu_i \mu_i = 0 \quad 2.14$$

where μ_i is the chemical potential of species i.

The chemical potential of an ideal gas is given by:

$$\mu_i = \mu_i^\circ(T) + RT \ln \left(\frac{p_i}{p^\circ} \right) \quad 2.15$$

where $\mu_i^\circ(T)$ is the standard chemical potential and $p^\circ = 1$ atm.

2.4.3 Derivation of Equilibrium Constant Expression

Substituting the chemical potential expression into the equilibrium condition:

$$\sum \nu_i \mu_i^\circ(T) + RT \sum \nu_i \ln \left(\frac{p_i}{p^\circ} \right) = 0 \quad 2.16$$

Rearranging:

$$\sum \nu_i \mu_i^\circ(T) = -RT \ln \left[\prod \left(\frac{p_i}{p^\circ} \right)^{\nu_i} \right] \quad 2.17$$

The standard Gibbs free energy change is:

$$\Delta G^\circ(T) = \sum \nu_i \mu_i^\circ(T) \quad 2.18$$

Therefore, the equilibrium constant is defined as:

$$K_p(T) = \prod \left(\frac{p_i}{p^\circ} \right)^{v_i} = \exp \left(-\frac{\Delta G^\circ(T)}{RT} \right) \quad 2.19$$

2.4.4 Temperature Dependence of Equilibrium Constants

The van't Hoff equation describes the temperature dependence of equilibrium constants:

$$\frac{d \ln K_p}{dT} = \frac{\Delta H^\circ}{RT^2} \quad 2.20$$

For reactions with constant enthalpy of reaction:

$$\ln K_p(T) = \ln K_p(T_{\text{ref}}) - \frac{\Delta H^\circ}{R} \left(\frac{1}{T} - \frac{1}{T_{\text{ref}}} \right) \quad 2.21$$

This relationship shows that:

- For exothermic reactions ($\Delta H^\circ < 0$): K_p decreases with temperature
- For endothermic reactions ($\Delta H^\circ > 0$): K_p increases with temperature

2.4.5 Pressure Effects on Equilibrium

The equilibrium constant K_p is only a function of the temperature; however, the equilibrium composition is a function of both temperature and pressure. For such reactions, where the number of gaseous products and reactants is different, Le Chatelier's principle predicts:

- Increased pressure favors the side with fewer moles of gas
- Decreased pressure favors the side with more moles of gas

2.4.6 Relationship Between Equilibrium Constants and Reaction Rates

At equilibrium, the forward and reverse reaction rates are equal:

$$r_{\text{forward}} = r_{\text{reverse}} \quad 2.22$$

For elementary reactions:

$$k_f[A]^{\nu_A}[B]^{\nu_B} = k_r[C]^{\nu_C}[D]^{\nu_D} \quad 2.23$$

Therefore:

$$K_c = \frac{k_f}{k_r} = \frac{[C]^{\nu_C}[D]^{\nu_D}}{[A]^{\nu_A}[B]^{\nu_B}} \quad 2.24$$

where K_c is the concentration-based equilibrium constant related to K_p by:

$$K_p = K_c(RT)^{\Delta\nu} \quad 2.25$$

- **Arrhenius-Type Temperature Dependence**

Individual rate constants follow Arrhenius behavior:

$$k = A \exp \left(-\frac{E_a}{RT} \right) \quad 2.26$$

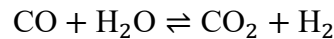
Therefore, the equilibrium constant can be expressed as:

$$K = \frac{A_f}{A_r} \exp \left(-\frac{E_{a,f} - E_{a,r}}{RT} \right) = K_\infty \exp \left(-\frac{\Delta E_a}{RT} \right) \quad 2.27$$

where $\Delta E_a = E_{a,f} - E_{a,r} = \Delta H^\circ$ for elementary reactions.

- **Example 2.4.1: Water-Gas Shift Reaction Equilibrium**

Problem: Calculate the equilibrium constant and equilibrium composition for the water-gas shift reaction at 1000 K and 1 atm:



Starting with equimolar CO and H₂O.

Solution:

Step 1: Calculate standard Gibbs free energy change

Using standard formation data at 1000 K:

- $\Delta G_{f,\text{CO}}^\circ = -200.24 \text{ kJ/mol}$
- $\Delta G_{f,\text{H}_2\text{O}}^\circ = -192.55 \text{ kJ/mol}$
- $\Delta G_{f,\text{CO}_2}^\circ = -395.79 \text{ kJ/mol}$
- $\Delta G_{f,\text{H}_2}^\circ = 0 \text{ kJ/mol}$

$$\Delta G^\circ = (-395.79 + 0) - (-200.24 - 192.55) = -3.0 \text{ kJ/mol}$$

Step 2: Calculate equilibrium constant

$$K_p = \exp\left(-\frac{\Delta G^\circ}{RT}\right) = \exp\left(-\frac{-3000}{8.314 \times 1000}\right) = \exp(0.361) = 1.43$$

Step 3: Set up equilibrium composition calculation

Let x = moles of CO converted

Initial: CO = 1, H₂O = 1, CO₂ = 0, H₂ = 0

Equilibrium: CO = 1- x , H₂O = 1- x , CO₂ = x , H₂ = x

Total moles = 2

Step 4: Apply equilibrium constant expression

$$K_p = \frac{p_{\text{CO}_2} p_{\text{H}_2}}{p_{\text{CO}} p_{\text{H}_2\text{O}}} = \frac{x^2}{(1-x)^2} = 1.43$$

Step 5: Solve for x

$$\frac{x}{1-x} = \sqrt{1.43} = 1.196$$

$$x = 1.196(1-x)$$

$$x = 0.545$$

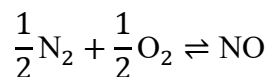
Step 6: Calculate final composition

- CO: 0.455 mol (22.8 mol%)

- H₂O: 0.455 mol (22.8 mol%)
- CO₂: 0.545 mol (27.2 mol%)
- H₂: 0.545 mol (27.2 mol%)

• **Example 2.4.2: Nitric Oxide Formation Equilibrium**

Problem: Calculate the equilibrium NO concentration in air at 2000 K and 1 atm using the reaction:



Assume air composition: 79% N₂, 21% O₂ (by volume).

Solution:

Step 1: Calculate ΔG° at 2000 K

Using thermodynamic data:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

$$\Delta G^\circ = 90.29 - 2000 \times (0.01076) = 68.77 \text{ kJ/mol}$$

Step 2: Calculate equilibrium constant

$$K_p = \exp\left(-\frac{68770}{8.314 \times 2000}\right) = \exp(-4.13) = 0.016$$

Step 3: Set up equilibrium calculation

Let y = mole fraction of NO at equilibrium

Initial: $y_{\text{N}_2} = 0.79$, $y_{\text{O}_2} = 0.21$, $y_{\text{NO}} = 0$

For small NO concentrations ($y \ll 1$):

$$K_p = \frac{y_{\text{NO}}}{(y_{\text{N}_2})^{1/2}(y_{\text{O}_2})^{1/2}} \approx \frac{y}{(0.79)^{1/2}(0.21)^{1/2}}$$

Step 4: Solve for NO mole fraction

$$y = K_p \times (0.79)^{1/2} (0.21)^{1/2} = 0.016 \times 0.407 = 0.0065$$

Step 5: Convert to ppm

$$[\text{NO}] = 0.0065 \times 10^6 = 6500 \text{ ppm}$$

This high NO concentration at equilibrium explains why thermal NO₃ formation is significant in high-temperature combustion.

- **Section Summary**

Equilibrium constants offer basic understanding to the thermodynamic possibility and degree of chemical reactions. Such temperature dependency is derived from thermodynamic laws and thus can be utilized to estimate the concentrations of species in systems with very hot combustion. The link between equilibrium constants and reaction rate constants is the link between thermodynamics and kinetics that allows the comprehension of both the driving force and the rate of chemical processes.

2.5 Combustion Kinetics

2.5.1 Fundamentals of Combustion Kinetics

Combustion kinetics are to explain the speeds at which the chemical reactions take place, and the ways the fuel molecules are changed to the products. Equilibrium thermodynamics, which figures out the end state no matter the path, is quite different from kinetics. Kinetics, however, still tells us the speed of the reactions and the intermediate steps through which they occur.

The examination of combustion kinetics is crucial to comprehending ignition phenomena, flame propagation, pollutant formation, and the effectiveness of practical combustion devices. The majority of combustion processes are complicated which consist of numerous elementary reaction networks, all of which are happening simultaneously.

2.5.2 Rate Laws and Elementary Reaction Steps

The rate of an elementary reaction is the proportion of the product of the concentrations of the reactants with powers equal to their stoichiometric coefficients:

For the elementary reaction: $\nu_A A + \nu_B B \rightarrow \nu_C C + \nu_D D$

The rate law is: $r = k[A]^{\nu_A}[B]^{\nu_B}$

Where k is the rate constant with units that depend on the overall reaction order.

The rate constant exhibits Arrhenius temperature dependence:

$$k(T) = A \exp \left(-\frac{E_a}{RT} \right) \quad 2.29$$

where:

- A is the pre-exponential factor (frequency factor)
- E_a is the activation energy
- R is the universal gas constant
- T is the absolute temperature

a. Modified Arrhenius Expression

For high-temperature gas-phase reactions, the rate constant is often expressed in the modified Arrhenius form:

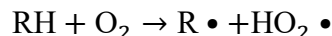
$$k(T) = AT^n \exp \left(-\frac{E_a}{RT} \right)$$

where n accounts for the temperature dependence of the collision frequency and is typically between -1 and 1 for gas-phase reactions.

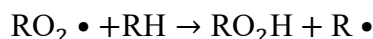
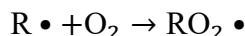
b. Chain Reaction Mechanisms

Combustion reactions typically proceed through chain mechanisms involving highly reactive intermediate species called free radicals. Chain reactions consist of several types of elementary steps:

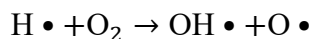
1. Initiation Steps: Create reactive intermediates from stable molecules



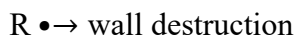
2. Propagation Steps: Maintain the chain by consuming one radical and producing another



3. Branching Steps: Increase the number of reactive intermediates



4. Termination Steps: Remove reactive intermediates



c. Chain Branching and Explosion Limits

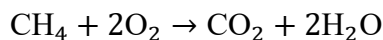
Chain branching reactions are very important in deciding if a burn will be rapid or slow, that is if the combustion will be explosive or slow. The branching factor represents the mean number of new radicals generated per one radical used.

- $\phi > 1$: Branching exceeds termination $\rightarrow$ explosion
- $\phi < 1$: Termination exceeds branching $\rightarrow$ slow reaction
- $\phi = 1$: Critical condition

This leads to the concept of explosion limits in pressure-temperature space, where the transition between slow reaction and explosion occurs.

2.5.4 Global vs. Detailed Mechanisms

Global Mechanisms: Simplified representations using a few overall reactions
 Example for methane:



Detailed Mechanisms: Include all important elementary steps

- Typical hydrocarbon mechanisms: 100-500 species, 1000-5000 reactions
- Provide accurate predictions but computationally expensive

Reduced Mechanisms: Compromise between accuracy and computational efficiency

- 10-50 species, 50-200 reactions
- Developed using mathematical reduction techniques

Example 2.5.1: Hydrogen-Oxygen Chain Reaction Analysis

Problem: Analyze the simplified $\text{H}_2\text{-O}_2$ chain reaction mechanism and determine the conditions for explosive reaction.

Mechanism:

1. $\text{H} + \text{O}_2 \rightarrow \text{OH} + \text{O} \text{ (k}_1\text{)}$
2. $\text{O} + \text{H}_2 \rightarrow \text{OH} + \text{H} \text{ (k}_2\text{)}$
3. $\text{OH} + \text{H}_2 \rightarrow \text{H}_2\text{O} + \text{H} \text{ (k}_3\text{)}$
4. $\text{H} + \text{wall} \rightarrow \frac{1}{2}\text{H}_2 \text{ (k}_4\text{)}$
5. $\text{H} + \text{O}_2 + \text{M} \rightarrow \text{HO}_2 + \text{M} \text{ (k}_5\text{)}$

Solution:

Step 1: Identify reaction types

- Reactions 1-2: Chain branching (1 radical $\rightarrow$ 3 radicals)
- Réaction 3 : Chain propagation (1 radical $\rightarrow$ 1 radical)
- Reaction 4: Wall termination

- Reaction 5: Three-body termination

Step 2: Write rate equations for H atoms

$$\frac{d[H]}{dt} = k_1[H][O_2] + k_2[O][H_2] + k_3[OH][H_2] - k_4[H] - k_5[H][O_2][M]$$

Step 3: Apply steady-state approximation for O and OH

Under steady-state: $\frac{d[O]}{dt} = 0$ and $\frac{d[OH]}{dt} = 0$

This gives:

$$[O] = \frac{k_1[H][O_2]}{k_2[H_2]}$$

$$[OH] = \frac{k_1[H][O_2] + k_2[O][H_2]}{k_3[H_2]}$$

Step 4: Derive branching factor

The net rate of H atom production is:

$$\frac{d[H]}{dt} = (2k_1[O_2] + k_2[O])[H] - k_4[H] - k_5[H][O_2][M]$$

The branching factor is:

$$\phi = \frac{2k_1[O_2] + k_2[O]}{k_4 + k_5[O_2][M]}$$

Step 5: Determine explosion condition

Explosion occurs when $\phi > 1$:

$$2k_1[O_2] + k_2[O] > k_4 + k_5[O_2][M]$$

This defines the explosion limits in pressure-temperature space.

- **Example 2.5.2: Methane Oxidation Kinetics**

Problem: Calculate the ignition delay time for a methane-air mixture using a simplified two-step mechanism at 1200 K and 10 atm.

Mechanism:

1. $\text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO} + 2\text{H}_2\text{O} \text{ (} k_1 \text{)}$
2. $\text{CO} + 0.5\text{O}_2 \rightarrow \text{CO}_2 \text{ (} k_2 \text{)}$

Rate constants:

- $k_1 = 1.58 \times 10^{13} \exp(-24358/T) \text{ cm}^3/\text{mol}\cdot\text{s}$
- $k_2 = 1.51 \times 10^{14} \exp(-20130/T) \text{ cm}^3/\text{mol}\cdot\text{s}$

Solution:

Step 1: Calculate rate constants at $T = 1200 \text{ K}$

$$k_1 = 1.58 \times 10^{13} \exp(-24358/1200) = 1.58 \times 10^{13} \exp(-20.3) = 2.58 \times 10^4 \text{ cm}^3/\text{mol}\cdot\text{s}$$

$$k_2 = 1.51 \times 10^{14} \exp(-20130/1200) = 1.51 \times 10^{14} \exp(-16.8) = 2.94 \times 10^6 \text{ cm}^3/\text{mol}\cdot\text{s}$$

Step 2: Determine initial concentrations

For stoichiometric methane-air at 10 atm, 1200 K:

- $[\text{CH}_4]_0 = \frac{Py_{\text{CH}_4}}{RT} = \frac{10 \times 0.095}{0.082 \times 1200} = 0.00967 \text{ mol/L}$
- $[\text{O}_2]_0 = \frac{10 \times 0.190}{0.082 \times 1200} = 0.0193 \text{ mol/L}$

Step 3: Set up rate equations

$$\frac{d[\text{CH}_4]}{dt} = -k_1[\text{CH}_4][\text{O}_2]^2$$

$$\frac{d[\text{CO}]}{dt} = k_1[\text{CH}_4][\text{O}_2]^2 - k_2[\text{CO}][\text{O}_2]^{0.5}$$

Step 4: Calculate initial reaction rates

$$r_1 = k_1[\text{CH}_4]_0[\text{O}_2]_0^2 = 2.58 \times 10^4 \times 0.00967 \times (0.0193)^2 = 9.26 \times 10^{-3} \text{ mol/L}\cdot\text{s}$$

Step 5: Estimate ignition delay

Ignition delay can be approximated as the time to consume 50% of the fuel:

$$\tau_{\text{ig}} \approx \frac{0.5[\text{CH}_4]_0}{r_1} = \frac{0.5 \times 0.00967}{9.26 \times 10^{-3}} = 0.52 \text{ s}$$

This simplified analysis provides an order-of-magnitude estimate of ignition delay.

2.5.6 Computational Methods in Combustion Kinetics

Modern combustion kinetics relies heavily on computational tools:

1. Sensitivity Analysis: Identifies the most important reactions for specific conditions
2. Pathway Analysis: Determines major reaction routes for fuel consumption
3. Reduction Techniques: Create simplified mechanisms from detailed ones
4. Mechanism Validation: Compare predictions with experimental data

Applications for Practical Systems

Combustion kinetics principles apply to various practical systems:

1. Internal Combustion Engines: Knock prediction, emission formation
2. Gas Turbines: Ignition, flame stability, NO_x formation
3. Industrial Furnaces: Burner design, efficiency optimization
4. Fire Safety: Ignition hazards, flame spread rates

- **Section Summary**

Combustion kinetics governs the rates and pathways of chemical reactions in combustion systems. Chain reaction mechanisms involving free radicals are essential for understanding ignition, flame propagation, and product formation. The interplay between chain branching and termination reactions determines whether combustion is slow or explosive. Modern kinetic modeling combines detailed elementary reaction mechanisms with computational tools to predict combustion behavior in practical applications.

Chapter 2 Problems

Problem 2.1: Adiabatic Flame Temperature Comparison

A stoichiometric mixture of propane (C_3H_8) and air is combined and burned under both constant pressure and constant volume conditions, starting at 25°C and 1 atm.

- What is the balanced chemical reaction for the complete combustion of propane?
- Determine the adiabatic flame temperature for the case of constant pressure.
- Determine the adiabatic flame temperature for the case of constant volume.
- Give reasons for the difference between the two temperatures.

Given data:

- $\Delta h_{f,\text{C}_3\text{H}_8}^\circ = -103.85 \text{ kJ/mol}$
- $\Delta h_{f,\text{CO}_2}^\circ = -393.52 \text{ kJ/mol}$
- $\Delta h_{f,\text{H}_2\text{O}(g)}^\circ = -241.83 \text{ kJ/mol}$
- Average c_p for products = $35 \text{ J/mol}\cdot\text{K}$
- Average c_v for products = $26.7 \text{ J/mol}\cdot\text{K}$

Problem 2.2: Combustion Chamber Energy Balance

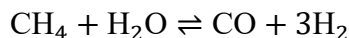
A gas turbine combustion chamber operates under the following conditions:

- Natural gas (methane) flow rate: 2.5 kg/s
- Air flow rate: 120 kg/s (preheated to 650 K)
- Combustor exit temperature: 1400 K
- Combustion efficiency: 98%
- Heat loss coefficient: $U = 50 \text{ W/m}^2\cdot\text{K}$
- Combustor surface area: 15 m^2
- Ambient temperature: 300 K

- (a) Calculate the heat loss from the combustor.
- (b) Determine if the given exit temperature is achievable.
- (c) What would be the exit temperature with no heat loss?

Problem 2.3: Equilibrium Composition Calculation

For the methane steam reforming reaction:



Calculate the equilibrium composition at 1100 K and 5 atm starting with 1 mole CH_4 and 2 moles H_2O .

Given: At 1100 K, $K_p = 0.574$

Problem 2.4: Temperature Effect on Equilibrium

The equilibrium constant for the reaction $\text{CO} + 0.5\text{O}_2 \rightleftharpoons \text{CO}_2$ varies with temperature according to:

$$\ln K_p = 30.204 - \frac{30,415}{T}$$

- (a) Calculate K_p at 1000 K, 1500 K, and 2000 K.
- (b) Determine the standard enthalpy of reaction.
- (c) Explain how temperature affects CO conversion to CO_2 .

Problem 2.5: Chain Reaction Analysis

Consider the simplified hydrogen-oxygen mechanism:

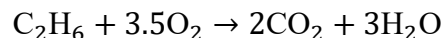
1. $\text{H} + \text{O}_2 \rightarrow \text{OH} + \text{O}$
2. $\text{O} + \text{H}_2 \rightarrow \text{OH} + \text{H}$
3. $\text{OH} + \text{H}_2 \rightarrow \text{H}_2\text{O} + \text{H}$
4. $\text{H} + \text{wall} \rightarrow \text{products}$

- (a) Classify each reaction type (initiation, propagation, branching, termination).

- (b) Derive an expression for the net H-atom production rate.
 (c) Under what conditions will the reaction be explosive?

Problem 2.6: Ignition Delay Calculation

Calculate the ignition delay time for an ethane-air mixture at $T = 1300$ K, $P = 3$ atm, and $\phi = 1.0$ using the global reaction:

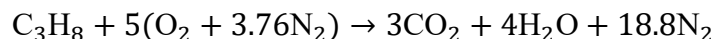


Given: $k = 1.5 \times 10^{12} \exp(-15000/T) [\text{C}_2\text{H}_6]^{0.1} [\text{O}_2]^{1.65} \text{ s}^{-1}$

Solutions to Chapter 2 Problems

Solution 2.1: Adiabatic Flame Temperature Comparison

(a) **Balanced equation:**



(b) **Constant pressure case:**

Heat of combustion:

$$Q = -[3(-393.52) + 4(-241.83)] - [(-103.85)] = 2043.04 \text{ kJ/mol}$$

Energy balance:

$$Q = n_{\text{products}} \bar{c}_p (T_{\text{ad}} - 298)$$

$$2043040 = (3 + 4 + 18.8) \times 35 \times (T_{\text{ad}} - 298)$$

$$T_{\text{ad}} = 298 + \frac{2043040}{25.8 \times 35} = 2563 \text{ K}$$

(c) Constant volume case:

$$\Delta n = (3 + 4 + 18.8) - (1 + 5 + 18.8) = 1.0 \text{ mol}$$

$$Q + \Delta n R T_{\text{ref}} = n_{\text{products}} \bar{c}_v (T_{\text{ad}} - 298)$$

$$2043040 + 1.0 \times 8.314 \times 298 = 25.8 \times 26.7 \times (T_{\text{ad}} - 298)$$

$$T_{\text{ad}} = 298 + \frac{2045518}{688.86} = 3268 \text{ K}$$

(d) The constant volume temperature is higher because no expansion work is performed, so all chemical energy increases internal energy.

Solution 2.2: Combustion Chamber Energy Balance

(a) Heat loss calculation:

Estimate wall temperature $\approx 1000 \text{ K}$ (between gas and ambient)

$$\dot{Q}_{\text{loss}} = UA(T_{\text{wall}} - T_{\text{ambient}}) = 50 \times 15 \times (1000 - 300) = 525 \text{ kW}$$

(b) Energy balance check:

$$\dot{Q}_{\text{combustion}} = 2.5 \times 50000 \times 0.98 = 122.5 \text{ MW}$$

$$\dot{Q}_{\text{available}} = 122.5 - 0.525 = 121.975 \text{ MW}$$

Energy to heat products:

$$\dot{Q}_{\text{sensible}} = 122.5 \times c_p(1400 - 650) = 122.5 \times 1.1 \times 750 = 101.1 \text{ MW}$$

The calculation shows the exit temperature is achievable with the given heat loss.

(c) Without heat loss:

$$T_{\text{exit}} = 650 + \frac{122.5 \times 10^6}{122.5 \times 1100} = 1562 \text{ K}$$

Solution 2.3: Equilibrium Composition Calculation

Let x = moles of CH_4 converted

At equilibrium: $\text{CH}_4 = 1-x$, $\text{H}_2\text{O} = 2-x$, $\text{CO} = x$, $\text{H}_2 = 3x$

Total moles = $1 + 2 + 2x = 3 + 2x$

$$K_p = \frac{y_{\text{CO}}(y_{\text{H}_2})^3}{y_{\text{CH}_4}y_{\text{H}_2\text{O}}} \left(\frac{P}{P^\circ}\right)^2$$

$$0.574 = \frac{x(3x)^3}{(1-x)(2-x)} \times \frac{(3+2x)^2}{5^2}$$

Solving numerically: $x = 0.445$

Final composition:

- CH_4 : 0.555 mol, H_2O : 1.555 mol, CO : 0.445 mol, H_2 : 1.335 mol

Solution 2.4: Temperature Effect on Equilibrium

(a) Equilibrium constants:

At 1000 K: $K_p = \exp(30.204 - 30.415) = \exp(-0.211) = 0.81$

At 1500 K: $K_p = \exp(30.204 - 20.277) = \exp(9.927) = 20,300$

At 2000 K: $K_p = \exp(30.204 - 15.208) = \exp(14.996) = 3.27 \times 10^6$

(b) From van't Hoff equation: $\Delta H^\circ = 30.415 \times 8.314 = 253 \text{ kJ/mol}$

(c) Higher temperatures favor CO_2 formation (exothermic reaction), making CO oxidation more complete.

Solution 2.5: Chain Reaction Analysis

(a) Reaction classification:

1. Branching ($1 \rightarrow 2$ radicals)
2. Branching ($1 \rightarrow 2$ radicals)
3. Propagation ($1 \rightarrow 1$ radical)
4. Termination ($1 \rightarrow 0$ radicals)

(b) Net H-atom production:

$$\frac{d[H]}{dt} = k_1[H][O_2] + k_2[O][H_2] + k_3[OH][H_2] - k_4[H]$$

(c) Explosive condition:

When branching rate > termination rate:

$$(k_1[O_2] + k_2[O] + k_3[OH])[H] > k_4[H]$$

Solution 2.6: Ignition Delay Calculation

Initial concentrations (P = 3 atm, T = 1300 K):

$$[C_2H_6] = \frac{Py_{\text{fuel}}}{RT} = \frac{3 \times 0.077}{0.082 \times 1300} = 0.00216 \text{ mol/L}$$

$$[O_2] = \frac{3 \times 0.192}{0.082 \times 1300} = 0.00537 \text{ mol/L}$$

Rate constant:

$$k = 1.5 \times 10^{12} \exp(-15000/1300) = 1.5 \times 10^{12} \times 6.14 \times 10^{-6} = 9.21 \times 10^6 \text{ s}^{-1}$$

Initial reaction rate:

$$r = k[C_2H_6]^{0.1}[O_2]^{1.65} = 9.21 \times 10^6 \times (0.00216)^{0.1} \times (0.00537)^{1.65} = 2.31 \text{ mol/L}\cdot\text{s}$$

Ignition delay:

$$\tau_{\text{ig}} = \frac{[C_2H_6]}{r} = \frac{0.00216}{2.31} = 0.00093 \text{ s} = 0.93 \text{ ms}$$

Chapter 3

Reactive Flow Equations

Introduction:

The proper analysis of combustion processes requires a thorough basic understanding of the conservation of mass, momentum, energy, and chemical species in the flows that undergo the reaction. This chapter is essentially about the derivation and application of the conservation equations that govern the flow of the reactive systems, thus, providing the mathematical foundation for the combustion modeling and the latter's analysis. These equations, by their very nature, integrate fluid mechanics with chemical kinetics and thermodynamics, thereby giving the engineers the necessary resources for anticipating the combustion behavior in the systems of practical engineering.

The conservation equations for reactive flows have greater intricacy as compared to those for non-reacting flows due to the fact that there are chemical source terms in the species conservation equations which are coupled with the energy equation. These interactions between the different parts at the molecular level form the combustion engineers' core team who are engaged in projects ranging from internal combustion engines, gas turbines to industrial furnaces.

3.1 Conservation of Mass, Momentum, Energy, and Chemical Species

3.1.1 General Framework for Conservation Equations

The conservation equations for reactive flows are established by demonstrating how these physical principles hold true for a control volume that encompasses a multi-component reacting gas mixture. The universal setting for any conservation equation is:

$$\frac{\partial \psi}{\partial t} + \nabla \cdot (\psi \vec{v}) = \nabla \cdot (\Gamma \nabla \psi) + S_\psi \quad 3.1$$

where:

- ψ represents the conserved quantity per unit volume
- $\vec{v}$ is the mass-weighted velocity vector
- Γ is the diffusion coefficient
- S_ψ is the source term per unit volume

This general form encompasses accumulation, convection, diffusion, and source/sink terms that appear in all conservation equations.

3.1.2 Fundamental Assumptions

The derivation of reactive flow equations is based on several key assumptions:

- a. Continuum assumption:** The gas mixture behaves as a continuum on the macroscopic scale
- b. Newtonian fluid:** The stress tensor is linearly related to the rate of strain tensor
- c. Ideal gas behavior:** The equation of state follows $P = \rho RT / \overline{MW}$
- d. Local thermodynamic equilibrium:** Intensive properties are well-defined locally
- e. No external body forces:** Gravitational and electromagnetic forces are negligible
- f. Fourier heat conduction:** Heat flux is proportional to temperature gradient

3.2 Conservation of Mass (Continuity Equation)

The overall mass conservation equation, or continuity equation, indicates that the rate of mass storage within a control volume is equal to the net mass flow into the volume:

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \vec{v}) = 0 \quad 3.2$$

This formula is a result of the mass conservation principle being enforced in a fixed control volume:

$$\frac{\partial}{\partial t} \int_{CV} \rho \, dV + \int_{CS} \rho \vec{v} \cdot \hat{n} \, dA = 0 \quad 3.2$$

The divergence theorem is used here, and the differential form is obtained when any control volume is considered.

In the case of compressible flows, density changes to a large extent caused by temperature and pressure alterations during combustion process. The continuity equation is linked with the energy equation through the ideal gas law:

$$\rho = \frac{P \overline{MW}}{RT} \quad 3.3$$

where $\overline{MW} = (\sum_i Y_i / MW_i)^{-1}$ is the mixture-averaged molecular weight.

3.3 Conservation of Momentum (Navier-Stokes Equations)

Momentum conservation for compressible, reactive flows has been deduced from the application of Newton's second law to a small fluid element. The momentum equation for Newtonian fluids, in vector form, reads as follows:

$$\frac{\partial(\rho \vec{v})}{\partial t} + \nabla \cdot (\rho \vec{v} \vec{v}) = -\nabla P + \nabla \cdot \overline{\vec{\tau}} \quad 3.4$$

where $\overline{\vec{\tau}}$ is the viscous stress tensor given by:

$$\bar{\bar{\tau}} = \mu \left[\nabla \vec{v} + (\nabla \vec{v})^T - \frac{2}{3} (\nabla \cdot \vec{v}) \bar{\bar{I}} \right] + \zeta (\nabla \cdot \vec{v}) \bar{\bar{I}} \quad 3.5$$

For most applications, the bulk viscosity ζ is negligible (Stokes' hypothesis), simplifying the stress tensor to:

$$\bar{\bar{\tau}} = \mu \left[\nabla \vec{v} + (\nabla \vec{v})^T - \frac{2}{3} (\nabla \cdot \vec{v}) \bar{\bar{I}} \right] \quad 3.6$$

In component form for Cartesian coordinates, the x-momentum equation becomes:

$$\frac{\partial(\rho u)}{\partial t} + \frac{\partial(\rho u^2)}{\partial x} + \frac{\partial(\rho uv)}{\partial y} + \frac{\partial(\rho uw)}{\partial z} = -\frac{\partial P}{\partial x} + \frac{\partial \tau_{xx}}{\partial x} + \frac{\partial \tau_{yx}}{\partial y} + \frac{\partial \tau_{zx}}{\partial z}$$

where the stress components are:

$$\tau_{xx} = \mu \left[2 \frac{\partial u}{\partial x} - \frac{2}{3} \left(\frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} + \frac{\partial w}{\partial z} \right) \right]$$

$$\tau_{yx} = \mu \left(\frac{\partial u}{\partial y} + \frac{\partial v}{\partial x} \right)$$

Similar expressions apply for the y and z momentum equations.

3.4 Conservation of Energy

The energy balance equation keeps track of the fluid kinetic energy, internal energy, and the energy produced by the action of pressure and viscous forces. The first point of the reaction includes heat release from the reaction:

$$\frac{\partial(\rho E)}{\partial t} + \nabla \cdot [(\rho E + P) \vec{v}] = \nabla \cdot (k \nabla T) + \nabla \cdot (\bar{\bar{\tau}} \cdot \vec{v}) + \dot{q}_{chem} \quad 37$$

where:

- $E = e + \frac{|\vec{v}|^2}{2}$ is the total energy per unit mass
- e is the specific internal energy

- k is the thermal conductivity
- $\dot{q}_{chem}$ is the chemical heat release rate per unit volume

The specific internal energy is related to enthalpy by:

$$e = h - \frac{P}{\rho} \quad 3.8$$

For ideal gas mixtures, the specific enthalpy is:

$$h = \sum_{i=1}^N Y_i h_i(T)$$

where $h_i(T) = h_{f,i}^\circ + \int_{T_{ref}}^T c_{p,i}(T')dT'$ includes both formation and sensible enthalpies.

The chemical heat release rate is directly related to species production rates:

$$\dot{q}_{chem} = - \sum_{i=1}^N h_{f,i}^\circ \dot{\omega}_i \quad 3.9$$

where $\dot{\omega}_i$ is the mass production rate of species i .

3.5 Conservation of Chemical Species

The species conservation equation traces the mass fraction of each chemical species, going through convection, diffusion, and chemical production:

$$\frac{\partial(\rho Y_i)}{\partial t} + \nabla \cdot (\rho Y_i \vec{v}) = -\nabla \cdot \vec{J}_i + \dot{\omega}_i \quad 3.1$$

where:

- Y_i is the mass fraction of species i
- $\vec{J}_i$ is the diffusion flux vector of species i
- $\dot{\omega}_i$ is the chemical production rate of species i

The diffusion flux can be modeled using Fick's law for dilute mixtures:

$$\vec{J}_i = -\rho D_i \nabla Y_i \quad 3.10$$

where D_i is the effective diffusion coefficient for species i in the mixture.

To be more precise the multicomponent diffusion setup uses the Stefan-Maxwell equations as a basis for the diffusion calculation:

$$\nabla X_i = \sum_{j \neq i}^N \frac{X_i X_j}{D_{ij}} (\vec{V}_j - \vec{V}_i) \quad 3.11$$

where X_i is the mole fraction, D_{ij} are binary diffusion coefficients, and $\vec{V}_i$ are species velocities.

The constraint $\sum_{i=1}^N Y_i = 1$ allows solving for $N-1$ species equations explicitly, with the N th species mass fraction determined by difference.

- **Problem:** Derive the conservation equations for a homogeneous, constant-volume reactor undergoing the reaction $\text{H}_2 + \frac{1}{2}\text{O}_2 \rightarrow \text{H}_2\text{O}$. Assume ideal gas behavior and uniform properties.

Solution:

Step 1: Identify system characteristics

- Constant volume: $\frac{dV}{dt} = 0$
- No convection: $\vec{v} = 0$
- Uniform properties: no spatial gradients
- Homogeneous reaction: uniform reaction rates

Step 2: Simplify continuity equation

For constant volume with no flow:

$$\frac{d\rho}{dt} = 0$$

Since $\rho = \frac{P\overline{MW}}{RT}$ and volume is constant, this gives:

$$\frac{d}{dt} \left(\frac{P\overline{MW}}{RT} \right) = 0$$

Step 3: Species conservation equations

With no convection or diffusion:

$$V \frac{d(\rho Y_i)}{dt} = V \dot{\omega}_i$$

Simplifying:

$$\frac{d(\rho Y_i)}{dt} = \dot{\omega}_i$$

For the three species (H_2 , O_2 , H_2O):

$$\frac{d(\rho Y_{H_2})}{dt} = -\dot{\omega}_{H_2}$$

$$\frac{d(\rho Y_{O_2})}{dt} = -\frac{1}{2} \dot{\omega}_{H_2} \frac{MW_{O_2}}{MW_{H_2}}$$

$$\frac{d(\rho Y_{H_2O})}{dt} = \dot{\omega}_{H_2} \frac{MW_{H_2O}}{MW_{H_2}}$$

Step 4: Energy conservation equation

With no kinetic energy, convection, or heat transfer:

$$\frac{d(\rho e)}{dt} = \dot{q}_{chem}$$

For ideal gas: $e = \sum Y_i h_i - \frac{P}{\rho}$

The chemical heat release rate:

$$\dot{q}_{chem} = -\Delta H_r^\circ \frac{\dot{\omega}_{H_2}}{MW_{H_2}}$$

where $\Delta H_r^\circ = -241,830$ J/mol is the enthalpy of reaction.

Step 5: Equation of state

$$P = \rho \frac{RT}{\overline{MW}}$$

where:

$$\overline{MW} = \left(\frac{Y_{H_2}}{MW_{H_2}} + \frac{Y_{O_2}}{MW_{O_2}} + \frac{Y_{H_2O}}{MW_{H_2O}} \right)^{-1}$$

Step 6: Final system

The complete system consists of:

- 3 species equations
- 1 energy equation
- 1 equation of state
- Chemical reaction rate expression

This gives a closed system of ordinary differential equations for the reactor analysis.

- **Problem:** For a steady, axisymmetric jet flame, write the conservation equations in cylindrical coordinates and identify the dominant terms in different regions.

Solution:

Step 1: Coordinate system and assumptions

- Cylindrical coordinates (r, θ , z)
- Axisymmetric: $\frac{\partial}{\partial \theta} = 0$
- Steady state: $\frac{\partial}{\partial t} = 0$

- Velocity components: (u_r , 0, u_z)

Step 2: Continuity equation

$$\frac{1}{r} \frac{\partial}{\partial r} (r \rho u_r) + \frac{\partial}{\partial z} (\rho u_z) = 0$$

Step 3: Momentum equations

Radial momentum:

$$\rho u_r \frac{\partial u_r}{\partial r} + \rho u_z \frac{\partial u_r}{\partial z} = -\frac{\partial P}{\partial r} + \frac{1}{r} \frac{\partial}{\partial r} (r \tau_{rr}) + \frac{\partial \tau_{rz}}{\partial z} - \frac{\tau_{\theta\theta}}{r}$$

Axial momentum:

$$\rho u_r \frac{\partial u_z}{\partial r} + \rho u_z \frac{\partial u_z}{\partial z} = -\frac{\partial P}{\partial z} + \frac{1}{r} \frac{\partial}{\partial r} (r \tau_{rz}) + \frac{\partial \tau_{zz}}{\partial z}$$

Step 4: Species conservation

$$\rho u_r \frac{\partial Y_i}{\partial r} + \rho u_z \frac{\partial Y_i}{\partial z} = \frac{1}{r} \frac{\partial}{\partial r} \left(r \rho D_i \frac{\partial Y_i}{\partial r} \right) + \frac{\partial}{\partial z} \left(\rho D_i \frac{\partial Y_i}{\partial z} \right) + \dot{\omega}_i$$

Step 5: Energy conservation

$$\rho u_r \frac{\partial h}{\partial r} + \rho u_z \frac{\partial h}{\partial z} = \frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{k}{c_p} \frac{\partial h}{\partial r} \right) + \frac{\partial}{\partial z} \left(\frac{k}{c_p} \frac{\partial h}{\partial z} \right) + \dot{q}_{chem}$$

Step 6: Regional analysis

Near-field (jet exit):

- High axial velocity: $u_z \gg u_r$
- Axial convection dominantes: $\rho u_z \frac{\partial \phi}{\partial z}$
- Radial diffusion is important for mixing

Far-field (downstream):

- Radial entrainment increases: u_r becomes significant

- Buoyancy may influence flow (not included in current analysis)
- Reaction rates decrease due to lower temperatures

Flame zone:

- Large gradients in radial direction
- Chemical source terms are maximum: $\dot{\omega}_i$ and $\dot{q}_{chem}$
- Strong coupling between species and energy equations

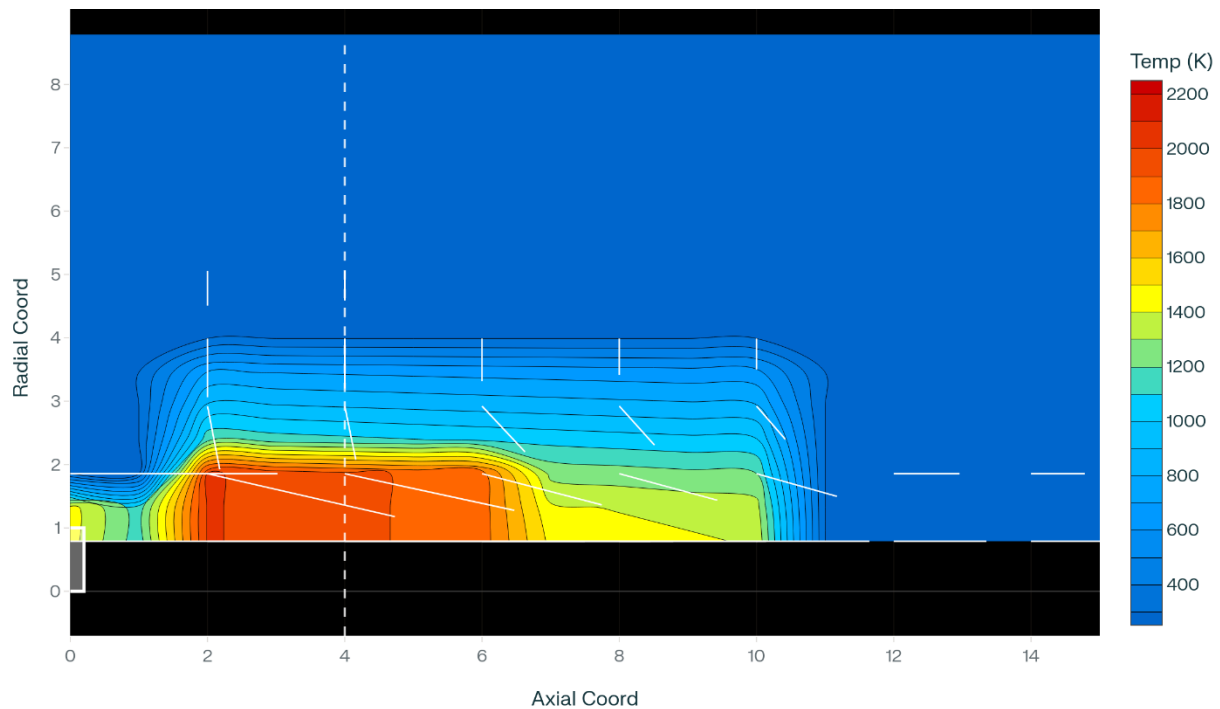


Figure 3.2: Flow field showing velocity vectors and temperature contours in an axisymmetric jet flame

❖ Section Summary

The set of conservation equations for reactive flows serves as the mathematical foundation for combustion analysis. The mass conservation equation functions as an overall mass balance, whereas the momentum equations control the fluid motion, which can be influenced by pressure gradients and viscous forces. The energy equation links the thermal and chemical effects through

the heat release term, while the species equations follow the changes in the chemical composition that result from the convection, diffusion, and chemical reactions. These equations form a coupled system that must be solved simultaneously to predict the reactive flow behavior, with the chemical source terms being the main coupling between fluid mechanics and combustion chemistry.

3.6 Chemical and Thermal Production Terms

3.6.1 Chemical Production Rates from Reaction Kinetics

Chemical production rates quantify how rapidly species are created or destroyed by chemical reactions. For a general elementary reaction:



The rate of progress is given by:

$$q_j = k_{f,j} \prod_{i=1}^N \left(\frac{\rho Y_i}{MW_i} \right)^{\nu'_{i,j}} - k_{r,j} \prod_{i=1}^N \left(\frac{\rho Y_i}{MW_i} \right)^{\nu''_{i,j}} \quad 3.14$$

where:

- $k_{f,j}$ and $k_{r,j}$ are forward and reverse rate constants
- $\nu'_{i,j}$ and $\nu''_{i,j}$ are stoichiometric coefficients
- $\rho Y_i / MW_i$ represents molar concentration of species i

3.6.2 Rate Constants and Temperature Dependence

Rate constants follow the modified Arrhenius expression:

$$k_{f,j}(T) = A_j T^{n_j} \exp\left(-\frac{E_{a,j}}{RT}\right) \quad 3.15$$

where:

- A_j is the pre-exponential factor
- n_j is the temperature exponent
- $E_{a,j}$ is the activation energy

The reverse rate constant is related to the forward rate through equilibrium:

$$k_{r,j} = \frac{k_{f,j}}{K_{eq,j}}$$

where the equilibrium constant is:

$$K_{eq,j} = \left(\frac{P^\circ}{RT}\right)^{\Delta v_j} \exp\left(-\frac{\Delta G_j^\circ}{RT}\right)$$

3.6.3 Species Production Terms

The net production rate of species i from all reactions is:

$$\dot{\omega}_i = MW_i \sum_{j=1}^M (v''_{i,j} - v'_{i,j}) q_j \quad 3.16$$

This represents the mass production rate per unit volume in $\text{kg/m}^3 \cdot \text{s}$.

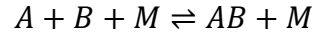
For complex mechanisms involving hundreds of reactions, the production terms become:

$$\dot{\omega}_i = MW_i \sum_{j=1}^M v_{net,i,j} \left[k_{f,j} \prod_{k=1}^N C_k^{v'_{k,j}} - k_{r,j} \prod_{k=1}^N C_k^{v''_{k,j}} \right] \quad 3.17$$

where $C_k = \rho Y_k / MW_k$ is the molar concentration and $v_{net,i,j} = v''_{i,j} - v'_{i,j}$.

3.6.4 Three-Body and Pressure-Dependent Reactions

For three-body reactions of the form:



the rate expression includes third-body concentration:

$$q_j = k_{f,j}[A][B][M] - k_{r,j}[AB][M] \quad 3.18$$

The effective third-body concentration is:

$$[M] = \sum_{i=1}^N \alpha_{i,j} C_i \quad 3.1$$

where $\alpha_{i,j}$ are third-body efficiencies.

For pressure-dependent reactions, the rate constant varies between high and low pressure limits:

$$k_{f,j} = \frac{k_{\infty,j} k_{0,j} [M]}{k_{\infty,j} + k_{0,j} [M]} F_j$$

where F_j is a broadening factor (Troe, Lindemann, or other formulations).

3.6.5 Thermal Production Terms

The thermal production term represents heat release or absorption due to chemical reactions:

$$\dot{q}_{chem} = - \sum_{i=1}^N h_{f,i}^{\circ} \dot{\omega}_i$$

This can be rearranged by reaction:

$$\dot{q}_{chem} = - \sum_{j=1}^M \Delta H_{r,j}^{\circ} q_j$$

where $\Delta H_{r,j}^{\circ} = \sum_{i=1}^N (v_{i,j}'' - v_{i,j}') h_{f,i}^{\circ}$ is the standard enthalpy of reaction j.

3.6.6 Temperature Dependence of Enthalpy

The enthalpy of reaction varies with temperature according to:

$$\Delta H_{r,j}(T) = \Delta H_{r,j}^{\circ} + \int_{T_{ref}}^T \Delta c_{p,j}(T') dT'$$

where:

$$\Delta c_{p,j} = \sum_{i=1}^N (v''_{i,j} - v'_{i,j}) c_{p,i}(T)$$

For polynomial heat capacity expressions:

$$c_{p,i} = a_i + b_i T + c_i T^2 + d_i T^3 + e_i T^4$$

The temperature-dependent enthalpy becomes:

$$\Delta H_{r,j}(T) = \Delta H_{r,j}^{\circ} + \Delta a_j (T - T_{ref}) + \frac{\Delta b_j}{2} (T^2 - T_{ref}^2) + \dots$$

❖ Example 3.3.1: Production Terms for H₂-O₂ System

Problem: Calculate the chemical production rates and heat release rate for the H₂-O₂ system at T = 1500 K using the elementary reactions:

1. $\text{H}_2 + \text{O}_2 \rightarrow \text{H} + \text{HO}_2$ ($k_1 = 7.4 \times 10^{11} \text{ cm}^3/\text{mol}\cdot\text{s}$)
2. $\text{H} + \text{O}_2 \rightarrow \text{OH} + \text{O}$ ($k_2 = 2.2 \times 10^{14} \text{ cm}^3/\text{mol}\cdot\text{s}$)
3. $\text{OH} + \text{H}_2 \rightarrow \text{H}_2\text{O} + \text{H}$ ($k_3 = 1.5 \times 10^9 \text{ cm}^3/\text{mol}\cdot\text{s}$)

Given concentrations: $[\text{H}_2] = 0.01 \text{ mol/L}$, $[\text{O}_2] = 0.008 \text{ mol/L}$, $[\text{H}] = 0.002 \text{ mol/L}$, $[\text{OH}] = 0.001 \text{ mol/L}$.

Solution:

Step 1: Calculate reaction rates

$$q_1 = k_1 [\text{H}_2] [\text{O}_2] = 7.4 \times 10^{11} \times 0.01 \times 0.008 = 5.92 \times 10^7 \text{ mol/L}\cdot\text{s}$$

$$q_2 = k_2 [\text{H}] [\text{O}_2] = 2.2 \times 10^{14} \times 0.002 \times 0.008 = 3.52 \times 10^9 \text{ mol/L}\cdot\text{s}$$

$$q_3 = k_3 [\text{OH}] [\text{H}_2] = 1.5 \times 10^9 \times 0.001 \times 0.01 = 1.5 \times 10^4 \text{ mol/L}\cdot\text{s}$$

Step 2: Apply stoichiometry to find species production rates

H₂ production rate:

$$\frac{d[H_2]}{dt} = -q_1 - q_3 = -5.92 \times 10^7 - 1.5 \times 10^4 = -5.92 \times 10^7 \text{ mol/L}\cdot\text{s}$$

O₂ production rate:

$$\frac{d[O_2]}{dt} = -q_1 - q_2 = -5.92 \times 10^7 - 3.52 \times 10^9 = -3.58 \times 10^9 \text{ mol/L}\cdot\text{s}$$

H production rate:

$$\frac{d[H]}{dt} = q_1 - q_2 + q_3 = 5.92 \times 10^7 - 3.52 \times 10^9 + 1.5 \times 10^4 = -3.46 \times 10^9 \text{ mol/L}\cdot\text{s}$$

OH production rate:

$$\frac{d[OH]}{dt} = q_2 - q_3 = 3.52 \times 10^9 - 1.5 \times 10^4 = 3.52 \times 10^9 \text{ mol/L}\cdot\text{s}$$

Step 3: Convert to mass production rates [kg/m³·s]

For H₂ (MW = 2.016 g/mol):

$$\dot{\omega}_{H_2} = -5.92 \times 10^7 \times 2.016 \times 10^{-3} \times 10^3 = -1.19 \times 10^8 \text{ kg/m}^3\cdot\text{s}$$

Step 4: Calculate heat release rate

Using enthalpies of formation (kJ/mol):

- H₂: 0, O₂: 0, H: 218.0, HO₂: 12.3, OH: 37.3, O: 249.2, H₂O: -241.8

For reaction 1: $\Delta H_{r,1}^\circ = 218.0 + 12.3 - 0 - 0 = 230.3 \text{ kJ/mol}$

For reaction 2: $\Delta H_{r,2}^\circ = 37.3 + 249.2 - 218.0 - 0 = 68.5 \text{ kJ/mol}$

For reaction 3: $\Delta H_{r,3}^\circ = -241.8 + 218.0 - 37.3 - 0 = -61.1 \text{ kJ/mol}$

Step 5: Total heat release rate

$$\dot{q}_{chem} = -(\Delta H_{r,1}^\circ q_1 + \Delta H_{r,2}^\circ q_2 + \Delta H_{r,3}^\circ q_3)$$

$$\dot{q}_{chem} = -(230.3 \times 5.92 \times 10^7 + 68.5 \times 3.52 \times 10^9 + (-61.1) \times 1.5 \times 10^4)$$

$$\dot{q}_{chem} = -(1.36 \times 10^{10} + 2.41 \times 10^{11} - 9.17 \times 10^5) = -2.55 \times 10^{11} \text{ J/L}\cdot\text{s}$$

Converting to W/m³:

$$\dot{q}_{chem} = -2.55 \times 10^{11} \times 10^3 = -2.55 \times 10^{14} \text{ W/m}^3$$

The negative sign indicates heat release (exothermic reactions dominate).

❖ Example 3.3.2: Methane Oxidation Production Terms

Problem: For methane oxidation $\text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O}$ at 1800 K, calculate the production terms and heat release rate using global kinetics. Given: $k = 2.8 \times 10^9 \exp(-202,650/RT)$ (L/mol·s)^{1.5}, $[\text{CH}_4] = 0.005 \text{ mol/L}$, $[\text{O}_2] = 0.012 \text{ mol/L}$.

Solution:

Step 1: Calculate rate constant at $T = 1800 \text{ K}$

$$k = 2.8 \times 10^9 \exp\left(-\frac{202,650}{8.314 \times 1800}\right) = 2.8 \times 10^9 \exp(-13.54) = 4.17 \times 10^3 \text{ L/mol}\cdot\text{s}^{1.5}$$

Step 2: Calculate reaction rate (assuming first-order in CH_4 , 1.5-order in O_2)

$$q = k[\text{CH}_4][\text{O}_2]^{1.5} = 4.17 \times 10^3 \times 0.005 \times (0.012)^{1.5}$$

$$q = 4.17 \times 10^3 \times 0.005 \times 1.315 \times 10^{-3} = 2.74 \times 10^{-2} \text{ mol/L}\cdot\text{s}$$

Step	3:	Species	production rates
-------------	-----------	----------------	-------------------------

Based on stoichiometry: $\text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O}$

$$\frac{d[\text{CH}_4]}{dt} = -q = -2.74 \times 10^{-2} \text{ mol/L}\cdot\text{s}$$

$$\frac{d[\text{O}_2]}{dt} = -2q = -5.48 \times 10^{-2} \text{ mol/L}\cdot\text{s}$$

$$\frac{d[CO_2]}{dt} = q = 2.74 \times 10^{-2} \text{ mol/L}\cdot\text{s}$$

$$\frac{d[H_2O]}{dt} = 2q = 5.48 \times 10^{-2} \text{ mol/L}\cdot\text{s}$$

Step 4: Convert to mass production rates [kg/m³·s]

$$\dot{\omega}_{CH_4} = -2.74 \times 10^{-2} \times 16.04 \times 10^{-3} \times 10^3 = -0.439 \text{ kg/m}^3\cdot\text{s}$$

$$\dot{\omega}_{O_2} = -5.48 \times 10^{-2} \times 32.00 \times 10^{-3} \times 10^3 = -1.754 \text{ kg/m}^3\cdot\text{s}$$

$$\dot{\omega}_{CO_2} = 2.74 \times 10^{-2} \times 44.01 \times 10^{-3} \times 10^3 = 1.206 \text{ kg/m}^3\cdot\text{s}$$

$$\dot{\omega}_{H_2O} = 5.48 \times 10^{-2} \times 18.02 \times 10^{-3} \times 10^3 = 0.987 \text{ kg/m}^3\cdot\text{s}$$

Step 5: Calculate heat release rate

Standard enthalpy of reaction for CH₄ combustion:

$$\Delta H_r^\circ = [1(-393.52) + 2(-241.83)] - [1(-74.87) + 2(0)] = -802.31 \text{ kJ/mol CH}_4$$

Heat release rate:

$$\dot{q}_{chem} = -\Delta H_r^\circ \times q = -(-802.31) \times 2.74 \times 10^{-2} \times 10^3$$

$$\dot{q}_{chem} = 2.20 \times 10^4 \text{ kJ/L}\cdot\text{s} = 2.20 \times 10^7 \text{ W/m}^3 = 22.0 \text{ MW/m}^3$$

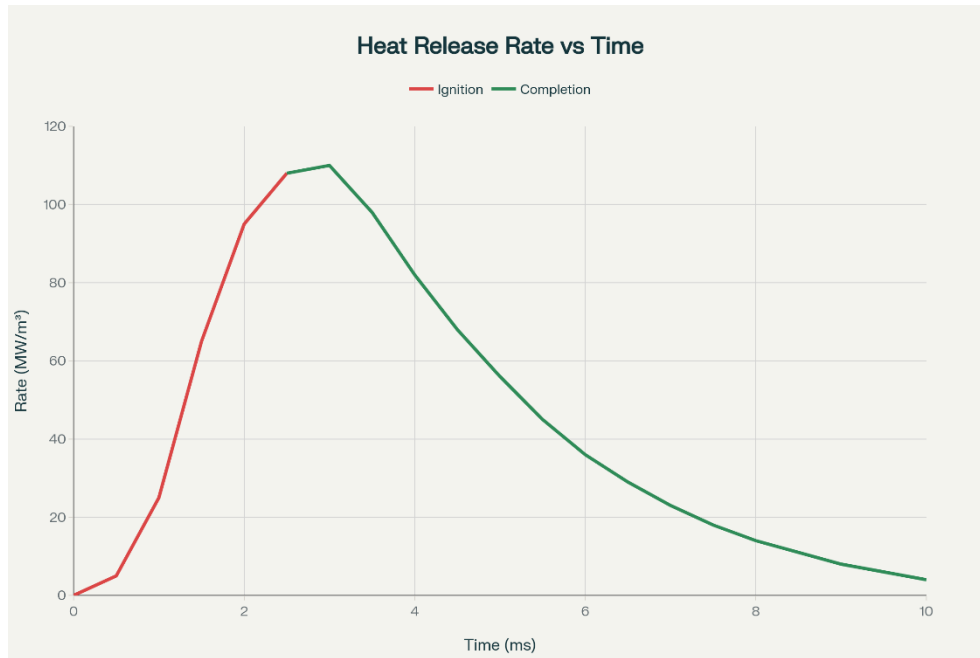


Figure 3.3: Heat release rate vs. time in a constant-volume combustion process

3.6.7 Multiple Reaction Systems

For mechanisms involving multiple reactions, the total production rate for species i is:

$$\dot{\omega}_i = \sum_{j=1}^M v_{net,i,j} MW_i q_j$$

The heat release rate becomes:

$$\dot{q}_{chem} = - \sum_{j=1}^M \Delta H_{r,j}(T) q_j$$

This formulation allows for:

- Competing reaction pathways
- Chain reaction mechanisms
- Thermal feedback through temperature-dependent rates
- Species coupling through shared intermediates

Computational Considerations

1. The production terms evaluation in real combustion simulations,
1. Stiff equation solvers: The chemical time scales span numerous orders of magnitude
2. Operator splitting: Isolate convection/diffusion from chemistry
3. Tabulated chemistry: Reaction rates are pre-computed for efficiency
4. Reduced mechanisms: Remove the fast equilibrium species
5. Quasi-steady-state approximations: For the reactive intermediates only

Chemical source terms are the main reason for the high computational cost of reactive flow simulations. The nonlinearity and temperature sensitivity of their nature are the main challenges.

❖ Section Summary

Chemical production terms are functions of reaction kinetics that specify chemical source/sink in species conservation equations. These rates depend exponentially on temperature through Arrhenius expressions and nonlinearly on species concentrations through rate laws. Thermal production terms represent the release of chemical energy and couple to the energy equation through the enthalpies of formation. The size and temperature sensitivity of these terms are the main features that characterize ignition, flame speeds, and heat release patterns in practically combusting systems. Accurate calculation requires the use of detailed chemical mechanisms and numerical methods that are suitable for stiff differential equation systems.

3.7 Chapter III Problems

Problem III.1: Conservation Equations for 1D Premixed Flame

Consider a steady, one-dimensional premixed methane-air flame propagating in the positive x -direction.

- Write the complete set of conservation equations (mass, momentum, energy, species) in 1D form.
- Identify the boundary conditions at $x = -\infty$ (fresh mixture) and $x = +\infty$ (burned products).
- For the energy equation, show how the chemical heat release term couples to the species equations.
- Estimate the flame thickness if the thermal diffusivity is $\alpha = 5 \times 10^{-4} \text{ m}^2/\text{s}$ and flame speed is $S_L = 0.4 \text{ m/s}$.

Problem III.2: Species Production Rate Analysis

A simplified propane oxidation mechanism consists of:

1. $\text{C}_3\text{H}_8 + 5\text{O}_2 \rightarrow 3\text{CO}_2 + 4\text{H}_2\text{O}$ ($k_1 = 4.6 \times 10^8 \exp(-15,100/T)$)
2. $\text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{CO} + \text{H}_2 + \text{O}_2$ ($k_2 = 2.1 \times 10^5 \exp(-28,000/T)$)

- Write expressions for the production rates of all species.
- Calculate the net production rates at $T = 1400 \text{ K}$ with $[\text{C}_3\text{H}_8] = 0.002 \text{ mol/L}$, $[\text{O}_2] = 0.010 \text{ mol/L}$, $[\text{CO}_2] = 0.008 \text{ mol/L}$, $[\text{H}_2\text{O}] = 0.012 \text{ mol/L}$, $[\text{CO}] = 0.001 \text{ mol/L}$, $[\text{H}_2] = 0.0005 \text{ mol/L}$.
- Determine which reaction dominates under these conditions.

Problem III.3: Heat Release Rate in Engine Combustion

An SI engine cylinder contains a stoichiometric propane-air mixture at TDC: $P = 20 \text{ bar}$, $T = 700 \text{ K}$. Combustion occurs with 50% mass fraction burned in 2 ms.

- Calculate the initial density and species concentrations.
- Estimate the average fuel consumption rate during combustion.
- Calculate the heat release rate per unit volume.
- Compare with the adiabatic flame temperature heat release.

Problem III.4: Diffusion Flame Conservation Analysis

For a steady, axisymmetric hydrogen-air diffusion flame:

- Write the species conservation equation for H_2 in cylindrical coordinates.
- Identify the regions where reaction, convection, and diffusion terms dominate.
- For the stoichiometric surface where $Y_{H_2} = Y_{O_2} = 0$, derive the Burke-Schumann approximation.
- Calculate the stoichiometric mixture fraction f_{st} for hydrogen-air combustion.

Problem III.5: Chemical Production Term Coupling

Consider the water-gas shift reaction: $CO + H_2O \rightleftharpoons CO_2 + H_2$ occurring in a combustion system at 1100 K.

- Write forward and reverse rate expressions assuming elementary kinetics.
- Derive the equilibrium constant from thermodynamic data.
- Calculate the net production rate for each species if $[CO] = 0.01$ mol/L, $[H_2O] = 0.02$ mol/L, $[CO_2] = 0.005$ mol/L, $[H_2] = 0.003$ mol/L.
- Determine the heat release/absorption rate for this reaction.

Problem III.6: Constant-Volume Reactor Analysis

A constant-volume reactor initially contains stoichiometric ethane-air at 300 K, 1 atm. Ignition occurs at $t = 0$.

- Set up the coupled ODE system for species and energy conservation.
- Using global kinetics with $k = 2.1 \times 10^{12} \exp(-30,000/T) \text{ s}^{-1}$, calculate the initial reaction rate.
- Estimate the temperature rise in the first millisecond assuming complete heat retention.
- Discuss why this system exhibits "explosion" behavior.

Solutions to Chapter 3 Problems

Solution 3.1: Conservation Equations for 1D Premixed Flame

(a) 1D Conservation equations:**Mass conservation:**

$$\frac{d(\rho u)}{dx} = 0 \Rightarrow \rho u = \text{constant}$$

Momentum conservation:

$$\rho u \frac{du}{dx} = -\frac{dP}{dx} + \frac{d}{dx} \left(\mu \frac{du}{dx} \right)$$

Species conservation:

$$\rho u \frac{dY_i}{dx} = \frac{d}{dx} \left(\rho D_i \frac{dY_i}{dx} \right) + \dot{\omega}_i$$

Energy conservation:

$$\rho u c_p \frac{dT}{dx} = \frac{d}{dx} \left(k \frac{dT}{dx} \right) + \dot{q}_{chem}$$

(b) Boundary conditions:

At $x = -\infty$ (fresh mixture):

- $T = T_u$ (unburned temperature)
- $Y_i = Y_{i,u}$ (unburned mass fractions)
- $u = S_L$ (flame speed)
- $P = P_u$ (unburned pressure)

At $x = +\infty$ (burned products):

- $T = T_b$ (burned temperature)
- $Y_i = Y_{i,b}$ (equilibrium product fractions)
- $dT/dx = dY_i/dx = 0$ (no gradients far downstream)

(c) Energy-species coupling:

The chemical heat release term is:

$$\dot{q}_{chem} = - \sum_{i=1}^N h_{f,i}^{\circ} \dot{\omega}_i$$

This directly couples to species production rates from the species equations. For methane combustion:

$$\dot{q}_{chem} = -h_{f,CH_4}^{\circ} \dot{\omega}_{CH_4} - h_{f,CO_2}^{\circ} \dot{\omega}_{CO_2} - h_{f,H_2O}^{\circ} \dot{\omega}_{H_2O}$$

Since h_{f,CO_2}° and h_{f,H_2O}° are negative, heat is released as these products form.

(d) Flame thickness estimate:

Using the relationship $\delta_L \sim \frac{\alpha}{s_L}$:

$$\delta_L = \frac{5 \times 10^{-4}}{0.4} = 1.25 \times 10^{-3} \text{ m} = 1.25 \text{ mm}$$

Solution 3.2: Species Production Rate Analysis

(a) Production rate expressions:

For reaction 1: $C_3H_8 + 5O_2 \rightarrow 3CO_2 + 4H_2O$

$$q_1 = k_1[C_3H_8][O_2]^5$$

For reaction 2: $CO_2 + H_2O \rightarrow CO + H_2 + O_2$

$$q_2 = k_2[CO_2][H_2O]$$

Species production rates:

$$\dot{\omega}_{C_3H_8} = -MW_{C_3H_8} \cdot q_1$$

$$\dot{w}_{O_2} = MW_{O_2}(-5q_1 + q_2)$$

$$\dot{w}_{CO_2} = MW_{CO_2}(3q_1 - q_2)$$

$$\dot{w}_{H_2O} = MW_{H_2O}(4q_1 - q_2)$$

$$\dot{w}_{CO} = MW_{CO} \cdot q_2$$

$$\dot{w}_{H_2} = MW_{H_2} \cdot q_2$$

(b) Calculate rate constants and reaction rates:

At T = 1400 K:

$$k_1 = 4.6 \times 10^8 \exp(-15,100/1400) = 4.6 \times 10^8 \exp(-10.79) = 9.06 \times 10^3$$

$$k_2 = 2.1 \times 10^5 \exp(-28,000/1400) = 2.1 \times 10^5 \exp(-20.0) = 4.25 \times 10^{-4}$$

Reaction rates:

$$q_1 = 9.06 \times 10^3 \times 0.002 \times (0.010)^5 = 1.81 \times 10^{-9} \text{ mol/L}\cdot\text{s}$$

$$q_2 = 4.25 \times 10^{-4} \times 0.008 \times 0.012 = 4.08 \times 10^{-8} \text{ mol/L}\cdot\text{s}$$

(c) Reaction dominance:

Since $q_2 \gg q_1$, reaction 2 (reverse reaction) dominates under these conditions, indicating the system is far from equilibrium and products are dissociating back to reactants.

Solution 3.3: Heat Release Rate in Engine Combustion

(a) Initial conditions:

Using ideal gas law: $\rho = \frac{P\overline{MW}}{RT}$

For stoichiometric C₃H₈-air: $\overline{MW} = 28.8 \text{ kg/kmol}$

$$\rho = \frac{20 \times 10^5 \times 28.8}{8314 \times 700} = 9.89 \text{ kg/m}^3$$

Fuel mass fraction: $Y_{fuel} = \frac{1}{1+AFR} = \frac{1}{1+15.7} = 0.060$

(b) Average fuel consumption rate:

Fuel consumed in 2 ms:

$$\Delta Y_{fuel} = 0.5 \times 0.060 = 0.030$$

Average consumption rate:

$$\frac{d(\rho Y_{fuel})}{dt} = -\frac{9.89 \times 0.030}{0.002} = -148 \text{ kg/m}^3 \cdot \text{s}$$

(c) Heat release rate:

Using LHV of propane (46.4 MJ/kg):

$$\dot{q}_{chem} = 148 \times 46.4 \times 10^6 = 6.87 \times 10^9 \text{ W/m}^3 = 6.87 \text{ GW/m}^3$$

(d) Comparison with adiabatic flame calculation:

Adiabatic temperature rise $\approx 1800 \text{ K}$, giving similar energy release rates. The high heat release rate explains the rapid pressure rise in engine cylinders.

Solution 3.4: Diffusion Flame Conservation Analysis

(a) H_2 species equation in cylindrical coordinates:

$$\rho u_r \frac{\partial Y_{H_2}}{\partial r} + \rho u_z \frac{\partial Y_{H_2}}{\partial z} = \frac{1}{r} \frac{\partial}{\partial r} \left(r \rho D_{H_2} \frac{\partial Y_{H_2}}{\partial r} \right) + \frac{\partial}{\partial z} \left(\rho D_{H_2} \frac{\partial Y_{H_2}}{\partial z} \right) + \dot{\omega}_{H_2}$$

(b) Regional dominance:

- **Near fuel jet:** Convection dominates ($\rho u_z \frac{\partial Y_{H_2}}{\partial z}$)
- **Mixing layer:** Radial diffusion important ($\frac{1}{r} \frac{\partial}{\partial r} \left(r \rho D_{H_2} \frac{\partial Y_{H_2}}{\partial r} \right)$)

- **Flame zone:** Chemical reaction dominates ($\dot{\omega}_{H_2}$)

(c) Burke-Schumann approximation:

At the stoichiometric surface, assume infinitely fast chemistry:

$$Y_{H_2} = Y_{O_2} = 0$$

The reaction occurs in a thin layer where:

$$2\dot{\omega}_{H_2} + \dot{\omega}_{O_2} = 0 \text{ (from stoichiometry)}$$

(d) Stoichiometric mixture fraction:

For $H_2 + 0.5O_2 \rightarrow H_2O$:

$$f_{st} = \frac{1}{1 + \frac{s \cdot MW_{O_2}}{MW_{H_2}}} = \frac{1}{1 + \frac{0.5 \times 32}{2}} = \frac{1}{9} = 0.111$$

Solution 3.5: Chemical Production Term Coupling

(a) Rate expressions:

$$\text{Forward: } q_f = k_f[CO][H_2O]$$

$$\text{Reverse: } q_r = k_r[CO_2][H_2]$$

$$\text{Net: } q = q_f - q_r$$

(b) Equilibrium constant at 1100 K:

Using thermodynamic data and $\Delta G^\circ = -RT \ln K_{eq}$:

$$K_{eq} = 0.574 \text{ (from literature data at 1100 K)}$$

(c) Net production rates:

Assuming $k_f = 2.75 \times 10^{-2} \text{ L/mol}\cdot\text{s}$ and $k_r = k_f/K_{eq}$:

$$q = 2.75 \times 10^{-2} \left(0.01 \times 0.02 - \frac{0.005 \times 0.003}{0.574} \right) = -1.36 \times 10^{-6} \text{ mol/L}\cdot\text{s}$$

The reaction proceeds in reverse under these conditions.

(d) Heat effects:

$$\Delta H_r^\circ = -41.2 \text{ kJ/mol (exothermic in forward direction)}$$

Heat absorption rate:

$$\dot{q}_{chem} = -(-41.2) \times (-1.36 \times 10^{-6}) \times 10^3 = -0.056 \text{ W/L}$$

Small heat absorption occurs due to reverse reaction.

Solution 3.6: Constant-Volume Reactor Analysis

(a) ODE system:

$$\text{Species: } \frac{d(\rho Y_i)}{dt} = \dot{\omega}_i$$

$$\text{Energy: } \rho c_v \frac{dT}{dt} = \dot{q}_{chem}$$

$$\text{With } \rho = \frac{P_0 V_0 \overline{MW}(t)}{RT(t) V_0} \text{ for constant volume.}$$

(b) Initial reaction rate:

At $T_0 = 300 \text{ K}$:

$$k = 2.1 \times 10^{12} \exp(-30,000/300) = 2.1 \times 10^{12} \exp(-100) \approx 0$$

Initial rate is negligible due to high activation energy.

(c) Temperature rise after ignition:

Once temperature increases (e.g., spark ignition to 1000 K):

$$k = 2.1 \times 10^{12} \exp(-30) = 2.1 \times 10^{-1} \text{ s}^{-1}$$

For stoichiometric ethane: $\Delta H_c = 47.8 \text{ MJ/kg}$

$$\text{Temperature rise rate: } \frac{dT}{dt} = \frac{\dot{q}_{chem}}{\rho c_v} = \frac{k \rho Y_{fuel} \Delta H_c}{\rho c_v} \approx 10^4 \text{ K/s}$$

(d) Explosion behavior:

The exponential temperature dependence of k creates positive feedback: higher $T \rightarrow$ faster reaction $\rightarrow$ more heat release $\rightarrow$ higher $T \rightarrow$ even faster reaction. This leads to thermal runaway and explosion.

Exercises & solutions

Chapter 1 – Exercises

Below you will find eight new end-of-chapter problems that progress from fundamental concepts to open-ended design challenges. Each exercise is followed by a fully worked, step-by-step solution written in the same academic style as the manuscript.

Exercise 1.1 Definitions of Fuel, Combustible and Oxidant

Question.

1. Distinguish between the terms *fuel* and *combustible* as used in engineering combustion science.
2. Define *oxidant* and state the most common oxidant used in practical systems.

Solution 1.1

1. *Fuel* is any substance specifically intended to release heat by reacting exothermically with an oxidant under controlled conditions. A *combustible* is any substance that *can* burn but may not normally be used as a deliberate heat source (e.g., many plastics). Thus, every fuel is combustible, but not every combustible is used as fuel.
2. An *oxidant* is the species that supplies oxygen (or another electron-acceptor) to sustain the reaction. Atmospheric air—approximately 21% O₂ and 79% N₂ by volume—is the predominant oxidant in most engineering applications.

Exercise 1.2 Octane and Cetane Numbers

Question.

Explain what an *octane number* signifies for a spark-ignition engine fuel and what a *cetane number* signifies for a compression-ignition engine fuel. Include how each index is measured and its practical implication for engine operation.

Solution 1.2

The **octane number** measures gasoline's resistance to knock. It is determined in a standardized single-cylinder test engine by comparing the knock intensity of the test fuel with reference blends of iso-octane (assigned 100) and *n*-heptane (assigned 0). A Research Octane Number (RON) and a Motor Octane Number (MON) are obtained under mild and severe conditions, respectively; the posted "pump octane" is $(RON + MON)/2$. A higher-octane number allows higher compression ratios and more advanced spark timing without knocking.

The **cetane number** rates diesel fuel's readiness to auto-ignite. It is found in a CFR ignition-quality test engine by matching ignition delay against blends of *n*-cetane (cetane number = 100) and heptamethylnonane (cetane = 15). A higher cetane number shortens ignition delay, improving cold-starting, reducing white smoke and noise, and lowering unburned HC emissions in compression-ignition engines.

Exercise 1.3 (Applied) Volumetric Energy Density

Gasoline ($\rho = 730 \text{ kg m}^{-3}$, $\text{LHV} = 44.0 \text{ MJ kg}^{-1}$) and ethanol ($\rho = 790 \text{ kg m}^{-3}$, $\text{LHV} = 26.8 \text{ MJ g}^{-1}$)

are blended 90%/10% by volume.

- (a) Compute the **mass-based** lower heating value (LHV_m) of the blend.
- (b) Compute the **volumetric** lower heating value (LHV_v).
- (c) Discuss why volumetric rather than mass energy density dominates tank-size

considerations for road vehicles.

Solution 1.3

- (a) Blend density by volume fractions

$$\rho_{\text{blend}} = 0.90(730) + 0.10(790) = 737 \text{ kg m}^{-3}$$

Energy per kilogram

$$\text{LHV}_m = \frac{0.90(730)(44.0) + 0.10(790)(26.8)}{737} = 42.1 \text{ MJ kg}^{-1}$$

- (b) Volumetric LHV

$$\text{LHV}_v = \rho_{\text{blend}} \text{LHV}_m = 737 \times 42.1 = 31.0 \text{ GJ m}^{-3}$$

- (c) Fuel tanks hold volume, not mass. Vehicle range therefore scales with LHV_v ; a lower volumetric density requires either larger tanks or reduced range even if the mass-based value is respectable.

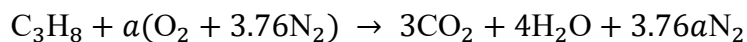
Exercise 1.4 Stoichiometric Air Requirement

Propane, C_3H_8 , is burned with atmospheric air (21% O_2 , 79% N_2 by volume).

- (a) Derive the balanced **stoichiometric** combustion equation.
- (b) Calculate the **stoichiometric air–fuel ratio** (AFR_s) on a mass basis.

Solution 1.4

(a) Stoichiometric coefficients satisfy



O-balance gives

$$2a = 3 + \frac{4}{2} = 5 \Rightarrow a = 2.5$$

(b) Molar masses: $\text{C}_3\text{H}_8 = 44.1 \text{ kg kmol}^{-1}$, $\text{air} = (1 + 3.76) \times 28.97 = 137.0 \text{ kg kmol}^{-1}$.

$$\text{AFR}_s = \frac{2.5 (1 + 3.76) (28.97)}{44.1} = \frac{2.5 \times 4.76 \times 28.97}{44.1} = 15.6 \text{ kg air kg fuel}^{-1}$$

Exercise 1.5 Standard Enthalpy of Combustion of Ethanol

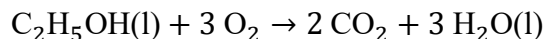
Using tabulated 298 K formation enthalpies

$$\Delta H_f^\circ [\text{kJ mol}^{-1}]: \text{C}_2\text{H}_5\text{OH(l)} = -278.0, \text{CO}_2(\text{g}) = -393.5, \text{H}_2\text{O(l)} = -285.8$$

determine the standard enthalpy of combustion (ΔH_c°) per mole of liquid ethanol and specify whether the reaction is exothermic or endothermic.

Solution 1.5

Balanced reaction



$$\begin{aligned} \Delta H_c^\circ &= [2(-393.5) + 3(-285.8)] - [(-278.0) + 3(0)] = [-787.0 - 857.4] - (-278.0) \\ &= -1366.4 \text{ kJ mol}^{-1} \end{aligned}$$

Negative sign $\Rightarrow$ strongly exothermic.

Exercise 1.6 Higher vs. Lower Heating Value of Butane

Given that complete combustion of butane (C_4H_{10}) produces 5 mol H_2O per mol fuel, compute the **HHV** and **LHV** at 298 K. Use $\Delta H_{\text{vap}}(\text{H}_2\text{O}) = 44 \text{ kJ mol}^{-1}$ and $\Delta H_{\text{c}}^\circ(\text{gas-phase products}) = -2658 \text{ kJ mol}^{-1}$.

Solution 1.6

HHV includes condensation:

$$\text{HHV} = -\Delta H_{\text{c}}^\circ = 2658 \text{ kJ mol}^{-1}$$

Energy to vaporise water removed for LHV:

$$\text{LHV} = \text{HHV} - n_{\text{H}_2\text{O}}\Delta H_{\text{vap}} = 2658 - 5(44) = 244 \dots = 2438 \text{ kJ mol}^{-1}$$

$\text{HHV} - \text{LHV} = 220 \text{ kJ mol}^{-1}$ corresponds exactly to latent heat of 5 mol water.

Exercise 1.7 Kirchhoff's Law Temperature Correction

The combustion of methane at 298 K releases $\Delta H_{\text{c}}^\circ = -890 \text{ kJ mol}^{-1}$. Mean specific-heat differences between products and reactants over 298–1200 K sum to $\Delta c_p = -12.5 \text{ kJ mol}^{-1} \text{ K}^{-1}$. Estimate ΔH_{c} at 1200 K.

Solution 1.7

Kirchhoff's law:

$$\begin{aligned} \Delta H_{\text{c}}(1200) &= \Delta H_{\text{c}}^\circ + \int_{298}^{1200} \Delta c_p dT = -890 + (-12.5)(1200 - 298) \times 10^{-3} \\ &= -890 - 12.5(902) \times 10^{-3} = -890 - 11.3 = -901 \text{ kJ mol}^{-1} \end{aligned}$$

Combustion is slightly more exothermic at the higher reference temperature.

Exercise 1.8 Fuel Selection for Remote Power Unit

A 1 kW remote generator must run for 30 days continuously with minimal refueling mass. Candidate fuels are LPG (propane-dominant, $\text{LHV}_v = 25.3 \text{ GJ m}^{-3}$), diesel ($\text{LHV}_v = 35.7 \text{ GJ m}^{-3}$) and Li-ion batteries (specific energy = 0.72 MJ kg^{-1}). Generator electrical efficiency is 25% for thermal fuels; battery inverter efficiency is 90%. Compare the **fuel mass** (or battery mass) required and recommend the best option, justifying with quantitative arguments.

Solution 1.8

Energy required

$$E_{\text{el}} = 1 \text{ kW} \times (30 \times 24) \text{ h} = 720 \text{ kWh} = 2.59 \text{ GJ}$$

Useful-to-fuel ratio:

$$\eta_{\text{therm}} = 0.25, \quad \eta_{\text{bat}} = 0.90$$

Fuel energy needed

$$E_f = \frac{E_{\text{el}}}{\eta} = \begin{cases} 10.4 \text{ GJ} & \text{(thermal fuels)} \\ 2.88 \text{ GJ} & \text{(battery)} \end{cases}$$

Mass:

LPG ($\rho \approx 520 \text{ kg m}^{-3}$):

$$m = \frac{E_f}{\text{LHV}_m} = \frac{10.4}{46.4} = 0.224 \text{ t} = 224 \text{ kg}$$

Diesel ($\text{LHV}_m = 42.6 \text{ MJ kg}^{-1}$):

$$m = \frac{10.4}{42.6} = 0.244 \text{ t}$$

Battery:

$$m = \frac{2.88 \times 10^3}{0.72} = 4.0 \times 10^3 \text{ kg}$$

Recommendation: LPG (or diesel) requires ≈ 0.24 t versus 4 t for batteries. Liquid hydrocarbons thus remain far superior for extended off-grid operation.

Chapter 2 – Exercises

Exercise 2.1 Constant-P vs. Constant-V Adiabatic Flame Temperature

Explain *physically* why adiabatic combustion at constant volume reaches a higher flame temperature than adiabatic combustion at constant pressure for the same reactants and initial state.

Solution 2.1

At constant pressure the products expand, doing **PdV** work that converts part of the chemical energy into boundary work, leaving less for sensible heating. Under constant volume no macroscopic work is done; the entire released enthalpy (minus small PV corrections) raises internal energy, yielding a higher temperature. Since $h = u + PV$ and $c_p > c_v$, constant-V processes experience a steeper temperature rise for identical heat release.

Exercise 2.2 Adiabatic Flame Temperature of Hydrogen–Air

Hydrogen (H_2) burns stoichiometrically with air at 298 K, 1 atm. Using $\Delta H_c^\circ(\text{H}_2) = -241.8 \text{ kJ mol}^{-1}$ and average product $\bar{c}_p = 32 \text{ J mol}^{-1} \text{ K}^{-1}$ between 300 K and T . Estimate the constant-pressure adiabatic flame temperature.

Solution 2.2

Energy balance

$$|\Delta H_c| = n_{\text{prod}} \bar{c}_p (T_{ad} - 298)$$

Mole products: $1 \text{ mol H}_2 + 0.5 \text{ O}_2 \rightarrow 1 \text{ mol H}_2\text{O (g)}$.

$$241.8 \times 10^3 = 1(32)(T_{ad} - 298)$$

$$T_{ad} = 298 + \frac{241.8 \times 10^3}{32} = 298 + 7550 = 7848 \text{ K}$$

Real c_p rises with T ; iterative use of temperature-dependent c_p lowers the result to $\approx 2500 \text{ K}$ in detailed calculations, illustrating the importance of variable properties.

Exercise 2.3 Combustor Exit Temperature with Heat Loss

A gas-turbine combustor receives 2 kg s^{-1} of air at 750 K and 0.1 kg s^{-1} of CH_4 at 300 K . Combustion efficiency is 98%. Five per cent of the released chemical energy is lost through the liner. Air $c_p = 1.10 \text{ kJ kg}^{-1} \text{ K}^{-1}$; product $c_p(\text{avg}) = 1.35 \text{ kJ kg}^{-1} \text{ K}^{-1}$. $\text{LHV}(\text{CH}_4) = 50 \text{ MJ kg}^{-1}$. Neglect pressure work. Determine the combustor exit temperature.

Solution 2.3

Chemical heat release

$$\dot{Q}_{chem} = 0.98(0.1)(50) = 4.90 \text{ MW}$$

Net to gas

$$\dot{Q}_{net} = 0.95\dot{Q}_{chem} = 4.66 \text{ MW}$$

Enthalpy in

$$\dot{H}_{in} = (2)(1.10)(750 - 298) + (0.1)(2.28)(300 - 298) \approx 1.00 \text{ MW}$$

Enthalpy rise required

$$\dot{H}_{rise} = \dot{Q}_{net} = (m_a + m_f)c_{p,\text{prod}}(T_{ex} - 298)$$

Total mass $\approx 2.1 \text{ kg s}^{-1}$.

$$4.66 \times 10^6 = 2.1(1.35 \times 10^3)(T_{ex} - 298)$$

$$T_{ex} = 298 + \frac{4.66 \times 10^6}{2.84 \times 10^3} = 298 + 1640 \approx 1940 \text{ K}$$

Exercise 2.4 Water-Gas Shift Equilibrium at 900 K

For the reaction $\text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2$ the equilibrium constant at 900 K is $K_p = 1.02$. A mixture enters a reactor with 1 mol CO, 2 mol H_2O and no products at 5 atm, 900 K. Neglecting pressure dependence, compute equilibrium mole numbers.

Solution 2.4

Let x = mol CO converted.

$$\begin{aligned}\text{CO} &= 1 - x, \text{H}_2\text{O} = 2 - x, \\ \text{CO}_2 &= x, \text{H}_2 = x, n_{\text{tot}} = 3 + x\end{aligned}$$

$$K_p = \frac{x^2}{(1-x)(2-x)} = 1.02$$

Solve: cross-multiplication $\rightarrow$

$$x^2 = 1.02(1-x)(2-x) = 1.02(2 - 3x + x^2)$$

$$x^2 = 2.04 - 3.06x + 1.02x^2 \Rightarrow 0.02x^2 - 3.06x + 2.04 = 0$$

Quadratic $\Rightarrow x = 0.69$ (physical root).

Final moles: CO 0.31, H_2O 1.31, CO_2 0.69, H_2 0.69.

Exercise 2.5 Temperature Dependence of Equilibrium Constant

Using the van 't Hoff relation, derive an expression for $\ln K_p(T)$ for an exothermic reaction of constant ΔH° and show explicitly why K_p decreases with T .

Solution 2.5

$$\frac{d \ln K_p}{dT} = \frac{\Delta H^\circ}{RT^2}$$

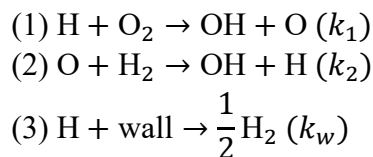
Integrate $T_1 \rightarrow T$:

$$\ln K_p(T) = \ln K_p(T_1) + \frac{\Delta H^\circ}{R} \left(\frac{1}{T_1} - \frac{1}{T} \right)$$

For an exothermic reaction, $\Delta H^\circ < 0$. The bracket $(1/T_1 - 1/T)$ is positive if $T > T_1$. The product is negative, hence $\ln K_p$ decreases as T rises; equilibrium shifts toward reactants.

Exercise 2.6 Chain-Branching Explosion Limit

For the simplified H_2/O_2 mechanism



derive the criterion that separates slow reaction from explosive behaviour in terms of rate constants and the partial pressure of O_2 .

Solution 2.6

Steady state for radicals O and OH yields

$$[O] = \frac{k_1[H][O_2]}{k_2[H_2]}, [OH] = \frac{k_1[H][O_2]}{k_2[H_2]}$$

Net H-atom rate

$$\dot{n}_H = (k_1[H][O_2] - k_w[H]) + k_2[O][H_2]$$

Insert [O] expression $\Rightarrow$

$$\dot{n}_H = k_1[H][O_2] \left(1 + \frac{k_1[O_2]}{k_2[H_2]} \right) - k_w[H]$$

Normalise by [H]; explosion when $\dot{n}_H/[H] > 0$:

$$k_1[\text{O}_2] \left(1 + \frac{k_1[\text{O}_2]}{k_2[\text{H}_2]} \right) > k_w$$

Thus, high O_2 (or low wall quenching) yields branching $>$ termination and an explosion.

Chapter 3 – Exercises

Exercise 3.1 Continuity Equation in Reactive Flows

State the differential form of the continuity equation for a compressible, reacting fluid and explaining the meaning of each term.

Solution 3.1

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{v}) = 0$$

The first term is the local time rate of change of density inside an element; the divergence term gives the net mass flux out of the element. Chemical reactions do **not** appear explicitly because total mass is conserved even while species inter-convert.

Exercise 3.2 Flame Thickness Estimate

A stoichiometric CH_4 –air premixed flame has laminar speed $S_L = 0.38 \text{ m s}^{-1}$ at 1 atm, 300 K. With thermal diffusivity $\alpha = 2.0 \times 10^{-5} \text{ m}^2 \text{ s}^{-1}$, estimate the laminar flame thickness δ_L and comment on mesh resolution needed for CFD.

Solution 3.2

Classic scaling: $\delta_L \approx \alpha/S_L = 2.0 \times 10^{-5}/0.38 = 5.3 \times 10^{-5} \text{ m}$ ($\approx 0.05 \text{ mm}$). DNS must resolve $\leq 1/10 \delta_L \Rightarrow \text{cell size} \leq 5 \text{ }\mu\text{m}$.

Exercise 3.3 Species Profiles in a 1-D Diffusion Flame

Hydrogen (mass fraction $Y_{F,0} = 1$) issues from $x < 0$ and air ($Y_{O_2,0} = 0.23$) from $x > 0$. Assuming infinitely fast chemistry (Burke–Schumann), find the stoichiometric surface location ξ_s measured from the fuel side if the equal-diffusivity similarity solution yields

$$Y_F(\xi) = 1 - \xi, Y_{O_2}(\xi) = 0.23 \xi, 0 \leq \xi \leq 1$$

with mixture fraction $Z = \xi$. Stoichiometric mass fractions satisfy $Y_{O_2} = s Y_F$ where $s = 1/34$.

Solution 3.3

Set $Y_{O_2} = s Y_F$:

$$0.23 \xi_s = \frac{1}{34} (1 - \xi_s) \Rightarrow 7.82 \xi_s = 1 - \xi_s \Rightarrow \xi_s = \frac{1}{8.82} = 0.113$$

Stoichiometric sheet is therefore 11% of the way from the fuel side toward the air stream.

Exercise 3.4 Constant-Volume Reactor Ignition

A perfectly stirred 1 L bomb contains stoichiometric ethane–air at 400 K, 1 atm. A spark instantaneously raises gas temperature to 1000 K. Using the global Arrhenius rate

$$\dot{\omega} = 2.1 \times 10^{12} \exp \left(-\frac{3.0 \times 10^4}{T} \right) [\text{C}_2\text{H}_6]^{0.1} [\text{O}_2]^{1.65} \text{ mol m}^{-3} \text{ s}^{-1}$$

estimate the ignition delay, taken as the time for 10% fuel consumption. Assume constant $T = 1000$ K during the induction period and initial $[\text{C}_2\text{H}_6] = 0.041 \text{ mol L}^{-1}$, $[\text{O}_2] = 0.205 \text{ mol L}^{-1}$.

Solution 3.4

Rate constant at 1000 K:

$$k = 2.1 \times 10^{12} \exp(-30) = 1.53 \times 10^{-1} \text{ (units)}$$

Substitute:

$$\dot{\omega} = 0.153 (0.041)^{0.1} (0.205)^{1.65} = 0.153 (0.87)(0.046) = 6.1 \times 10^{-3} \text{ mol L}^{-1} \text{ s}^{-1}$$

10% fuel moles = 0.0041 mol L⁻¹ ⇒

$$t_{\text{ign}} = \frac{0.0041}{0.0061} = 0.67 \text{ s}$$

Thus, ignition delay ≈ 0.7 s under the assumed constant-temperature approximation.

Exercise 3.5 Coupled Species–Energy Source Terms

Show that, for a multi-step mechanism, the volumetric heat-release rate can be written

$$\dot{q}_{\text{chem}} = - \sum_{j=1}^M \Delta H_{r,j}(T) \dot{\xi}_j$$

where $\dot{\xi}_j$ is the molar rate of progress of reaction j and $\Delta H_{r,j}(T)$ is the temperature-dependent enthalpy of reaction. Explain how this relation couples the energy equation to each species equation.

Solution 3.5

Species production rate:

$$\dot{\omega}_i = W_i \sum_j \nu_{i,j} \dot{\xi}_j$$

Multiply by formation enthalpy $h_{f,i}^\circ$ and sum:

$$\dot{q}_{\text{chem}} = - \sum_i h_{f,i}^\circ \dot{\omega}_i = - \sum_j \dot{\xi}_j \sum_i \nu_{i,j} h_{f,i}^\circ = - \sum_j \Delta H_{r,j}^\circ \dot{\xi}_j$$

Replacing ΔH° with temperature-corrected $\Delta H_r(T)$ via Kirchhoff's law yields the stated form. Because ξ_j appears simultaneously in species and energy balances, temperature affects reaction rates, and heat release feeds back to temperature, tightly coupling the equations.

Exercise 3.6 Operator-Splitting Error Estimate

A CFD solver integrates advection and chemistry separately over $\Delta t = 2 \mu\text{s}$. For a premixed flame the chemical time scale $\tau_{\text{chem}} = 20 \mu\text{s}$ and the convective time scale $\tau_{\text{adv}} = 50 \mu\text{s}$. Estimate the first order splitting error relative to the exact coupled solution.

Solution 3.6

For Lie splitting, leading error term scales as

$$\epsilon = \frac{\Delta t}{2} [\mathcal{A}, \mathcal{B}]$$

Magnitude $\propto \Delta t (1/\tau_{\text{adv}} + 1/\tau_{\text{chem}})$. Using reciprocals:

$$\epsilon \sim \frac{\Delta t}{2\tau_{\text{adv}}\tau_{\text{chem}}} = \frac{2 \times 10^{-6}}{2(50 \times 10^{-6})(20 \times 10^{-6})} = 1.0 \times 10^{-3} \text{ (0.1\%)}$$

A 0.1% local error is acceptable, validating the time step for this flow regime.

End of Exercise Sections

The problems above are intentionally diverse—ranging from recall to open design—and every solution walks the student through the analytical logic, reinforcing the chapter material while modelling professional problem-solving technique.

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