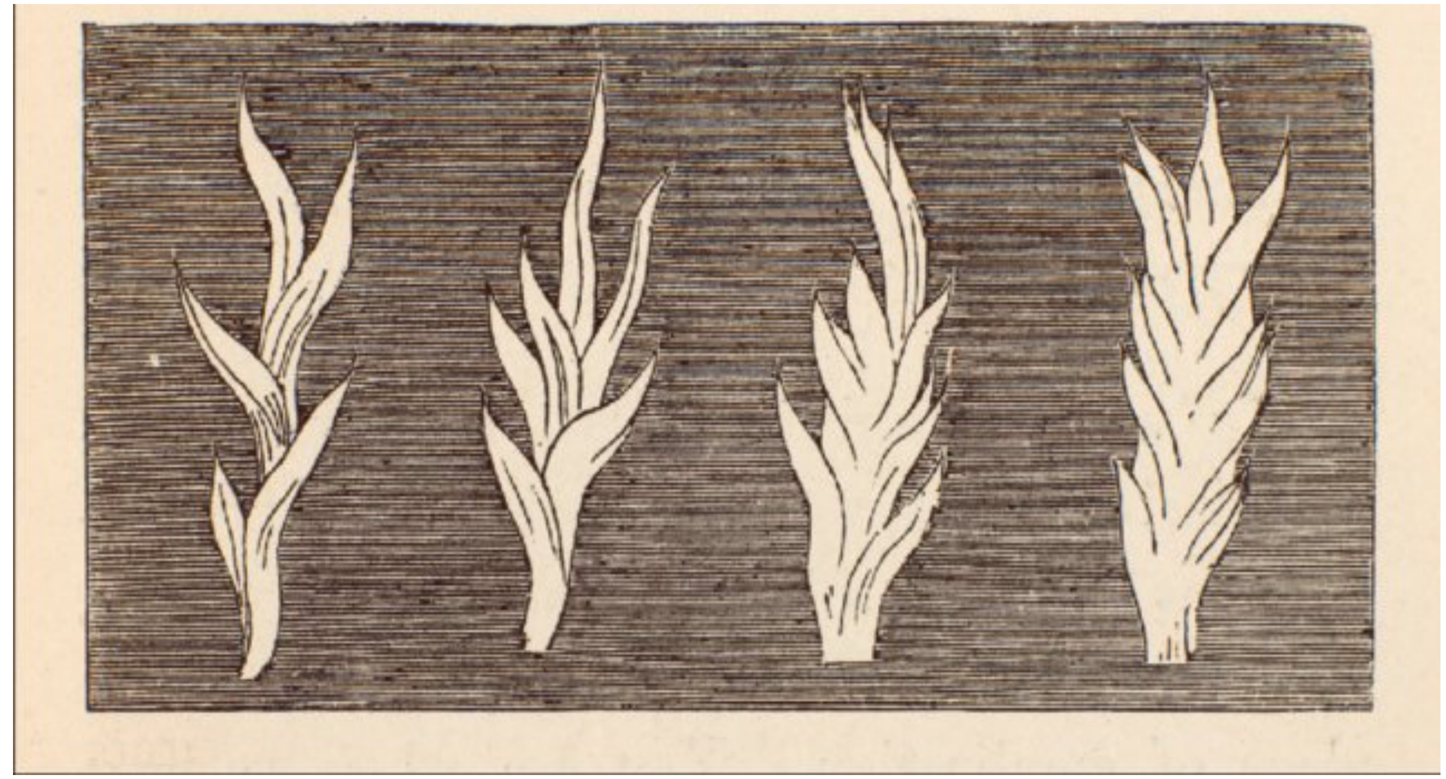
COMBUSTION FUNDAMENTALS



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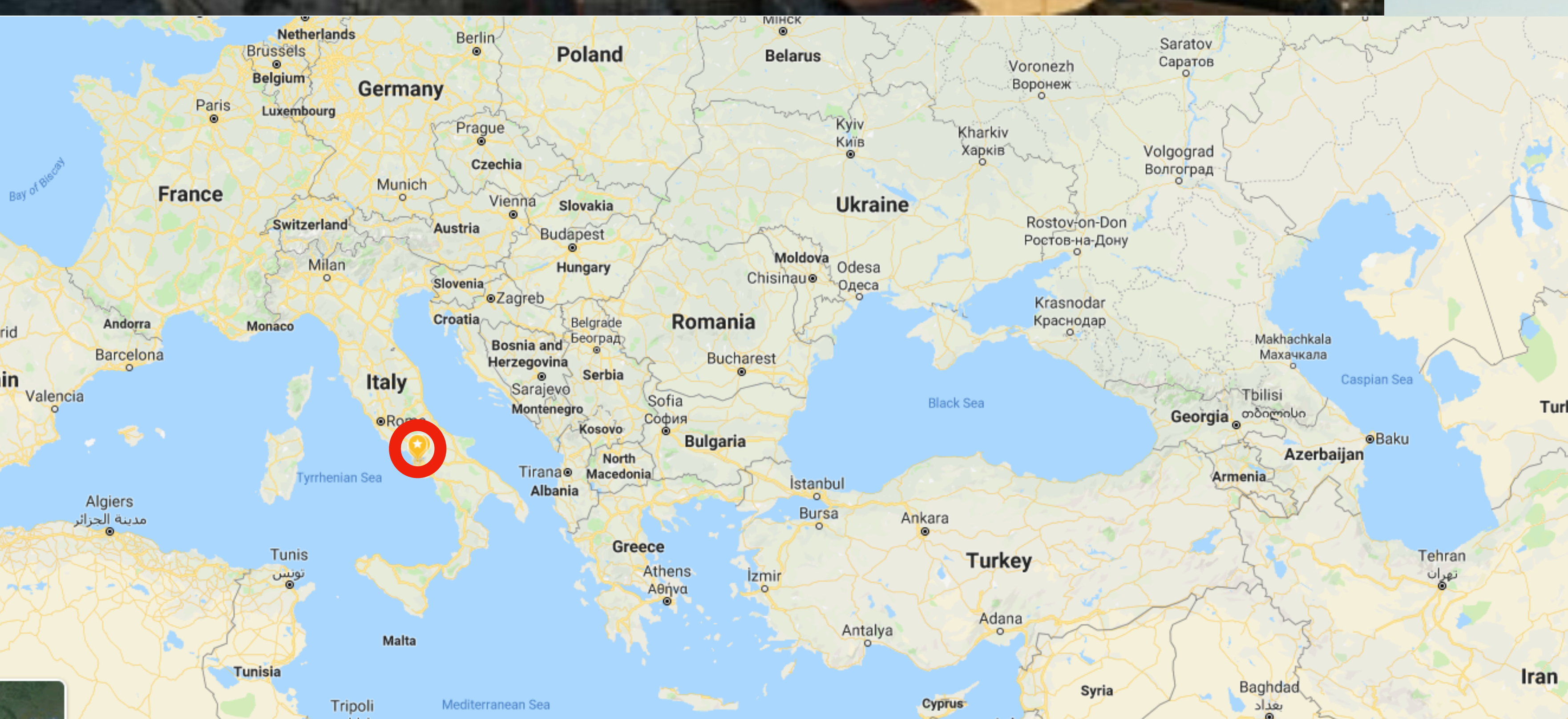
Naples (Italy)

The University of Naples Federico II was the first public university founded by Frederick II in 1224.
It is considered to be the oldest public and state university in the world.



ACKNOWLEDGEMENT

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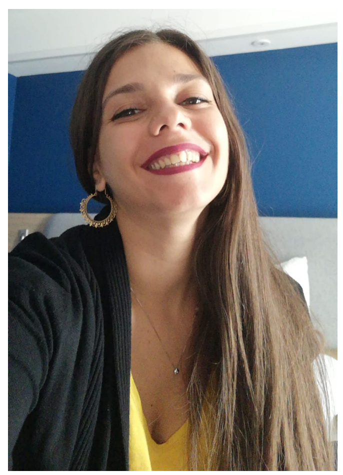

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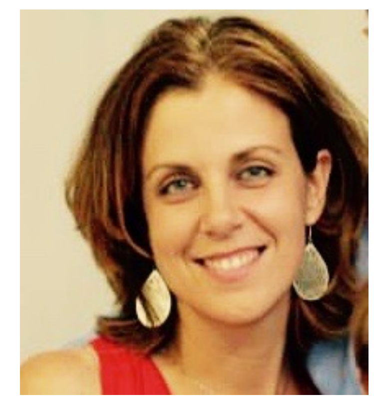

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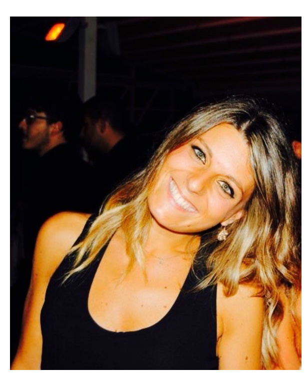

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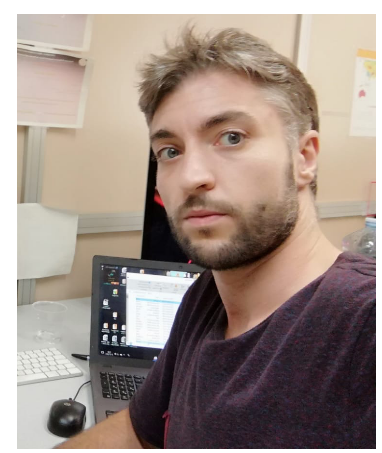

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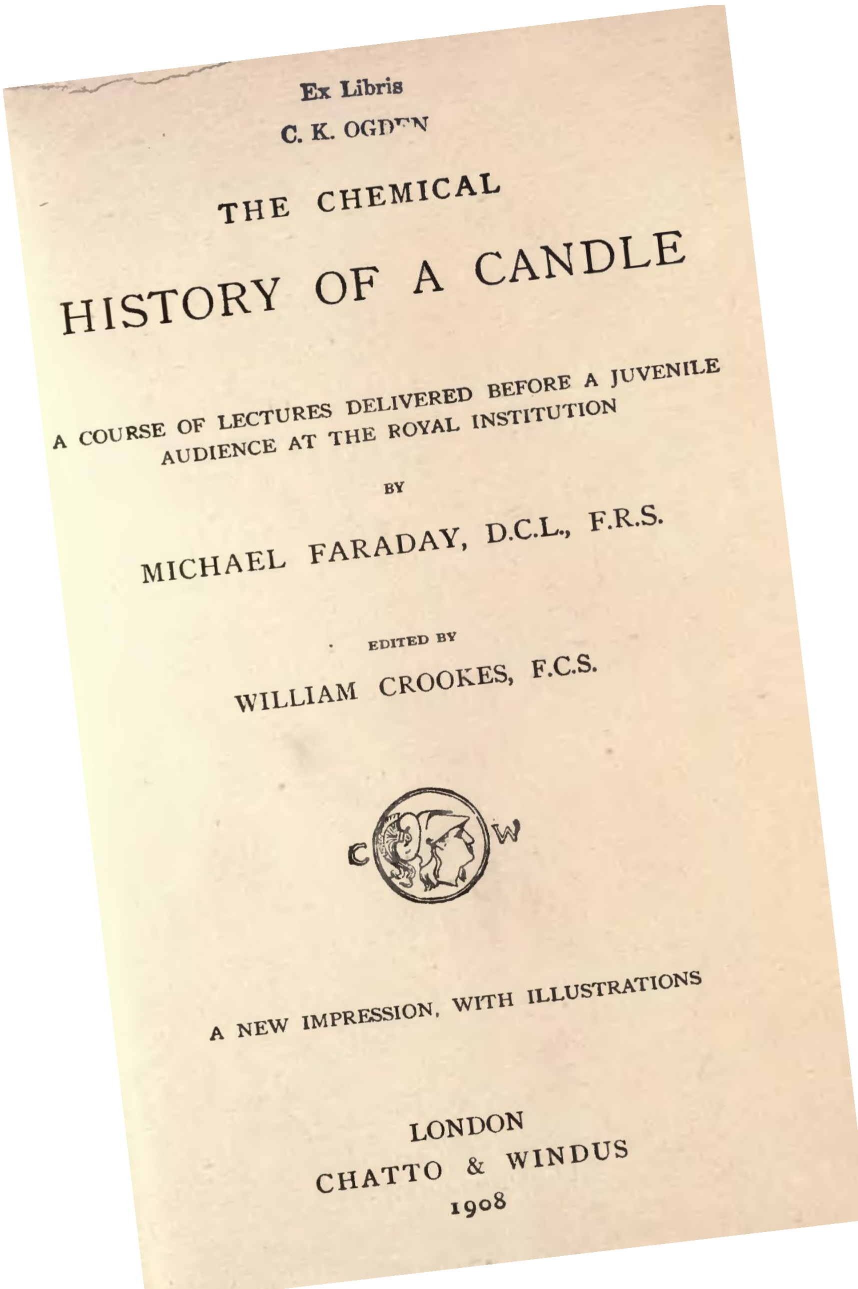
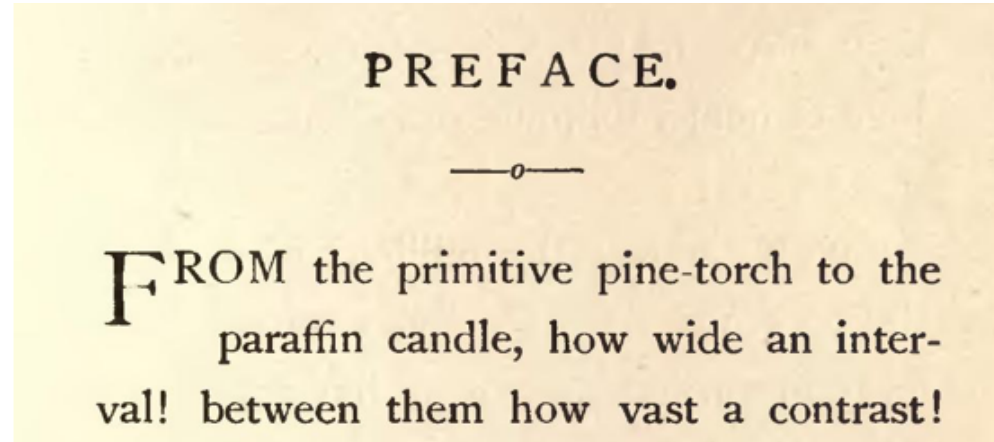
COMBUSTION SCIENCE

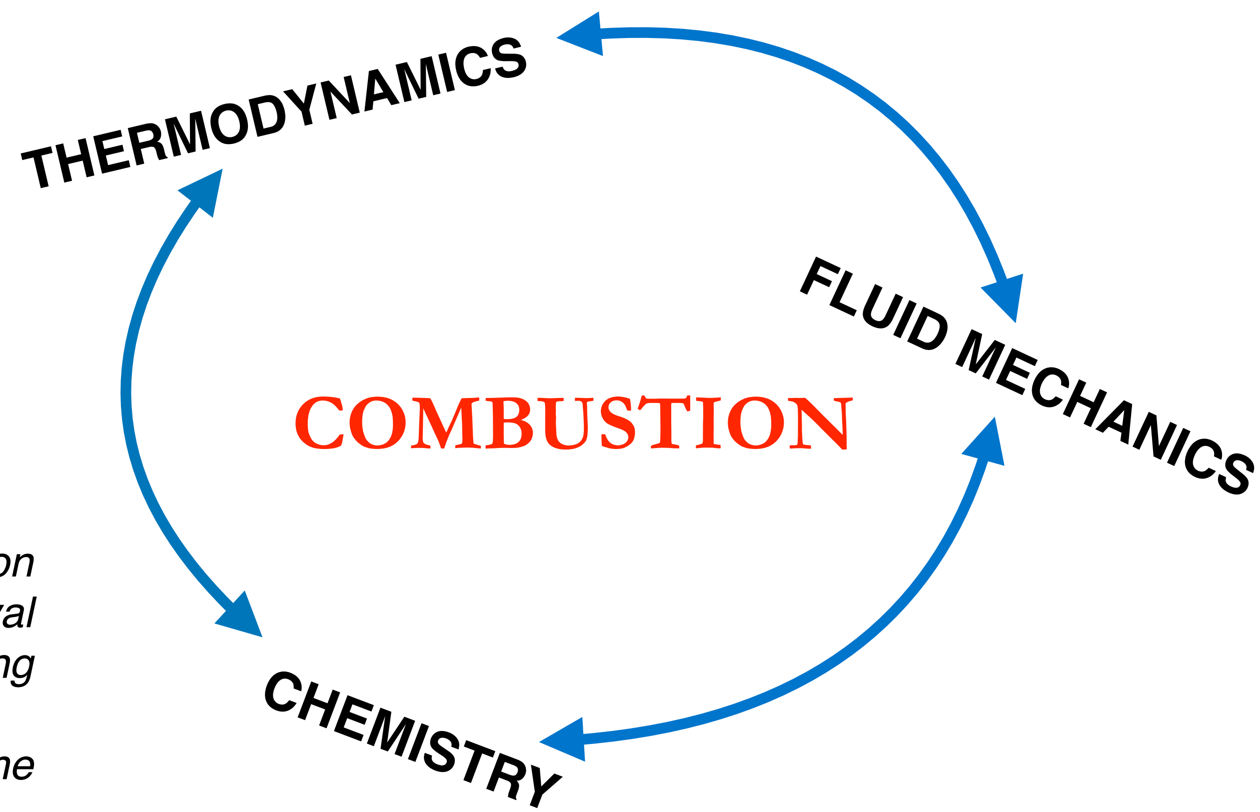

Ex Libris
C. K. OGDEN
THE CHEMICAL
HISTORY OF A CANDLE
A COURSE OF LECTURES DELIVERED BEFORE A JUVENILE AUDIENCE AT THE ROYAL INSTITUTION
BY
MICHAEL FARADAY, D.C.L., F.R.S.
EDITED BY
WILLIAM CROOKES, F.C.S.
A NEW IMPRESSION, WITH ILLUSTRATIONS
LONDON
CHATTO & WINDUS
1908

Combustion research started many years ago


PREFACE.

FROM the primitive pine-torch to the paraffin candle, how wide an interval! between them how vast a contrast!

Study of chemically reacting flows with highly exothermic, temperature-sensitive reactions



The Chemical History of a Candle was the title of a series of six lectures on the chemistry and physics of flames given by Michael Faraday at the Royal Institution in 1848, as part of the series of Christmas lectures for young people founded by Faraday in 1825 and still given there every year.
The lectures described the different zones of combustion in the candle flame and the presence of carbon particles in the luminescent zone.

COMBUSTION SCIENCE

Everyone knows what combustion is,
but a generally accepted definition does not exist.

A possible definition:
Combustion is chemical transformation with significant heat release.

Several typical combustion reactions:

combustion of methane	$CH_4 + 2\,O_2 = CO_2 + 2\,H_2O$
hydrogen-chlorine flame	$H_2 + Cl_2 = 2\,HCl$
termite reaction	$2\,Al + Fe_2O_3 = 2\,Fe + Al_2O_3$

Wrong definitions of combustion:
- reaction of oxygen with a fuel
-reaction of gases accompanied with light emission

flame: high temperature reaction front

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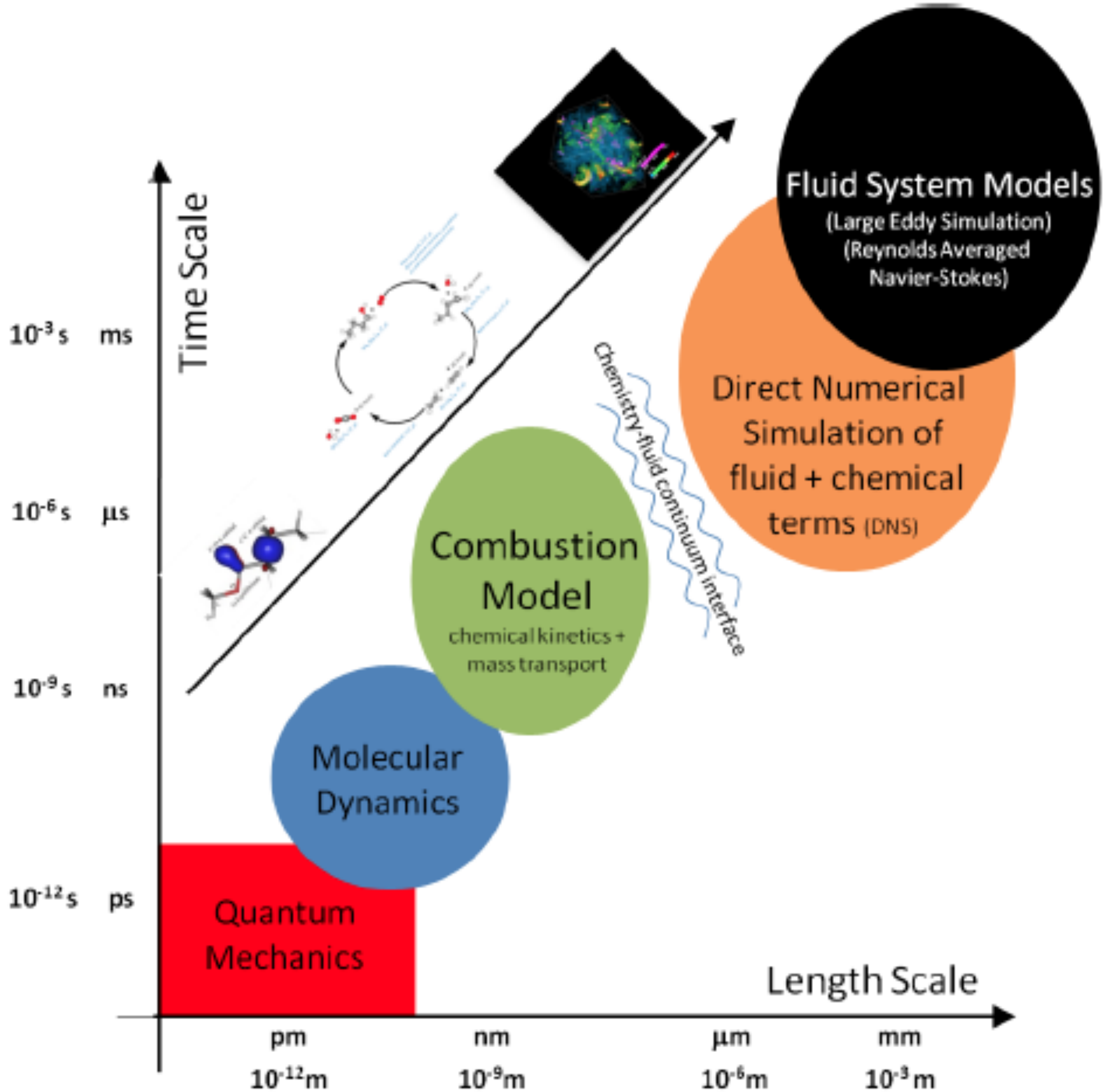
COMBUSTION SCIENCE

COMBUSTION IS A MULTI-PHYSICS & MULTI-SCALE SCIENCE

IT IS BOTH A COMPLICATED AND COMPLEX PROCESS.



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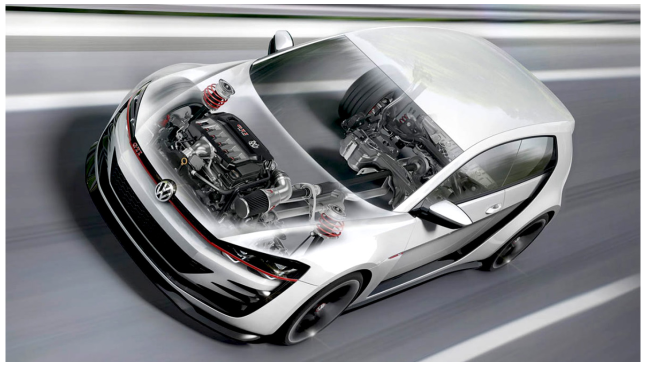
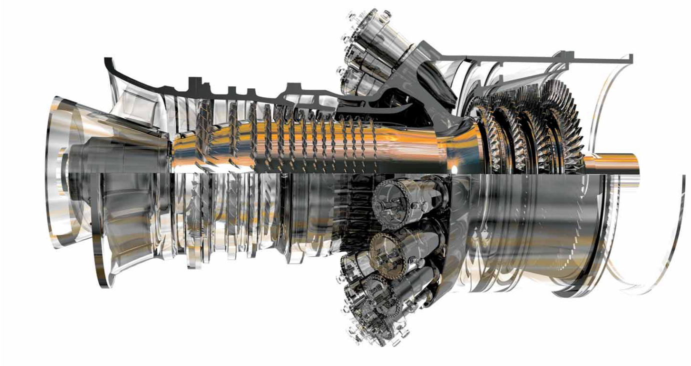
COMBUSTION AND TECHNOLOGY ADVANCEMENT





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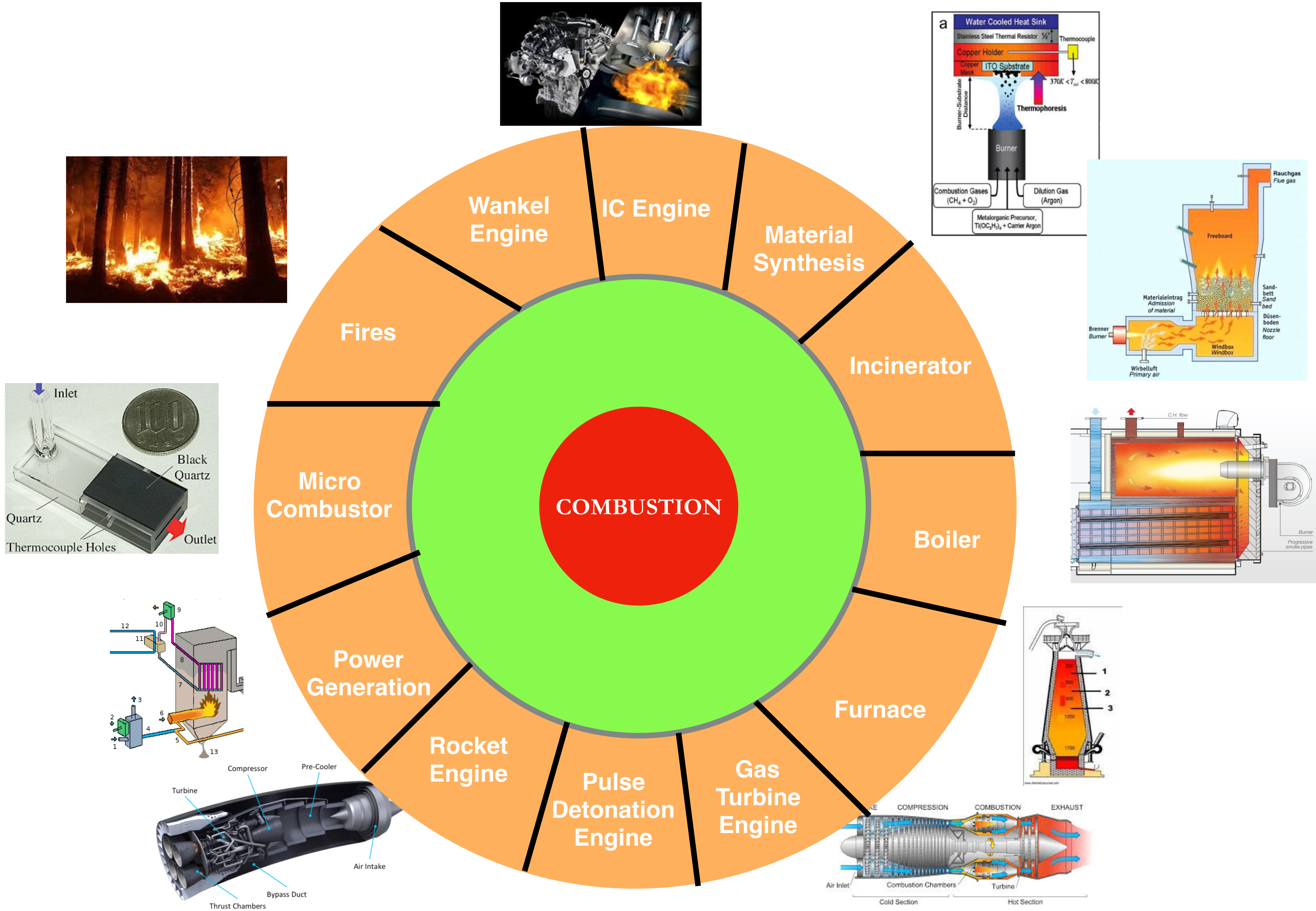
COMBUSTION APPLICATIONS…



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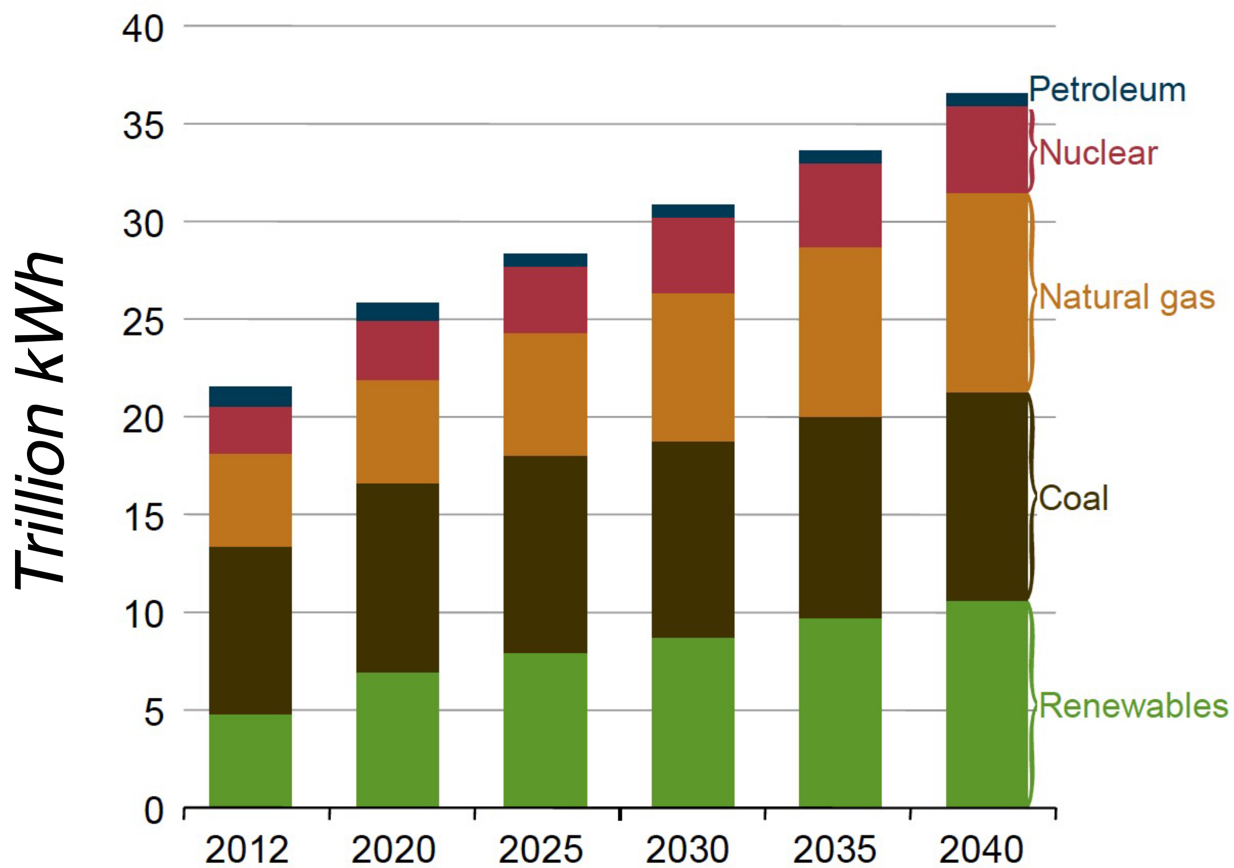
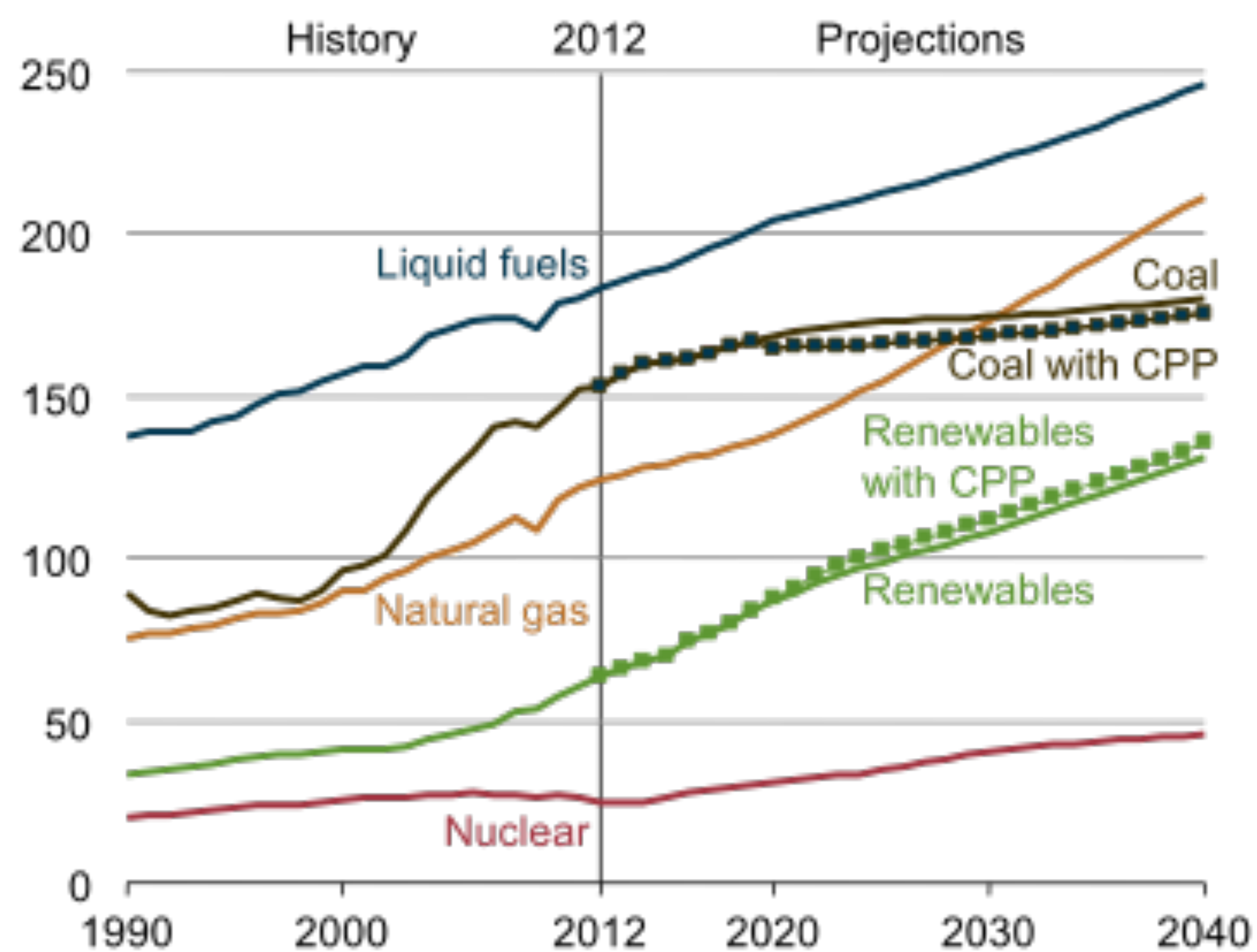
WORLD ENERGY CONSUMPTION





Source: EIA's International Energy Outlook, 2016

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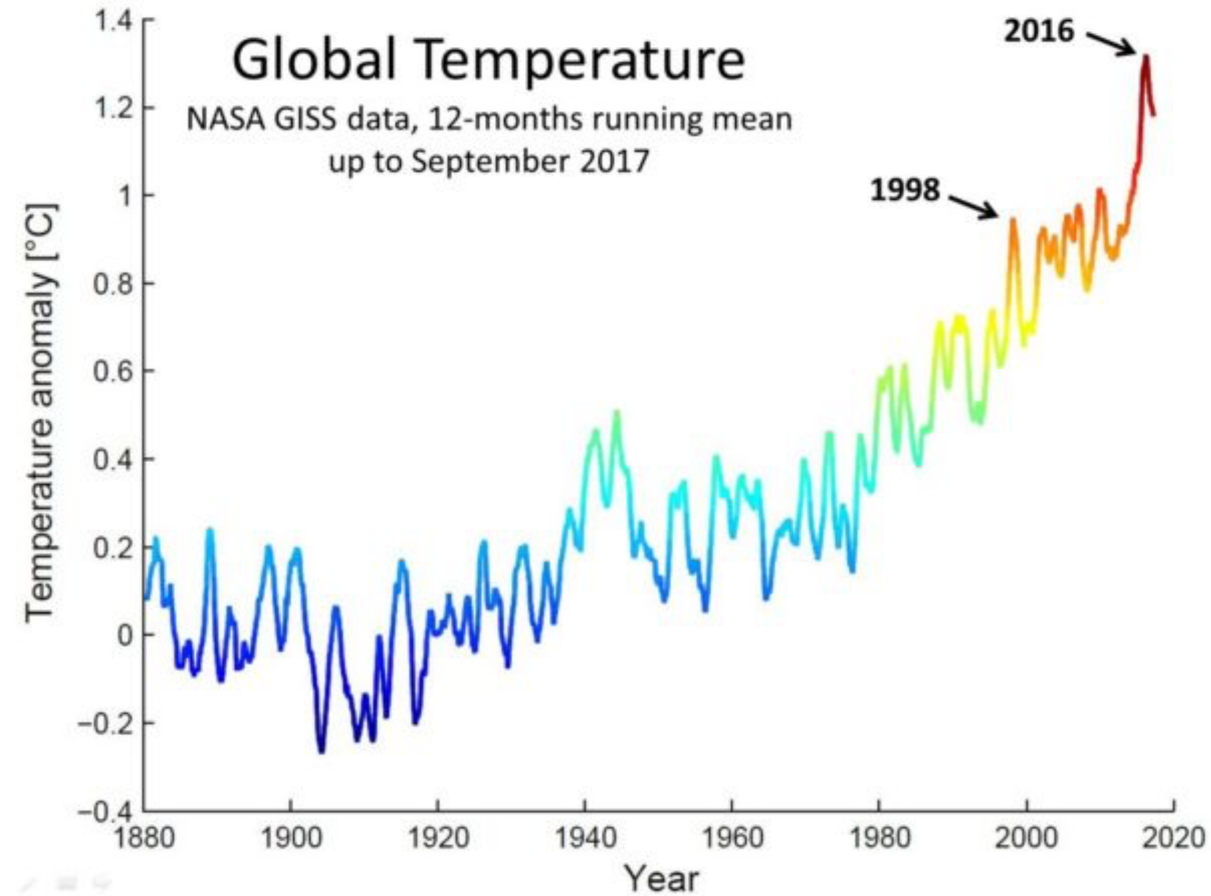
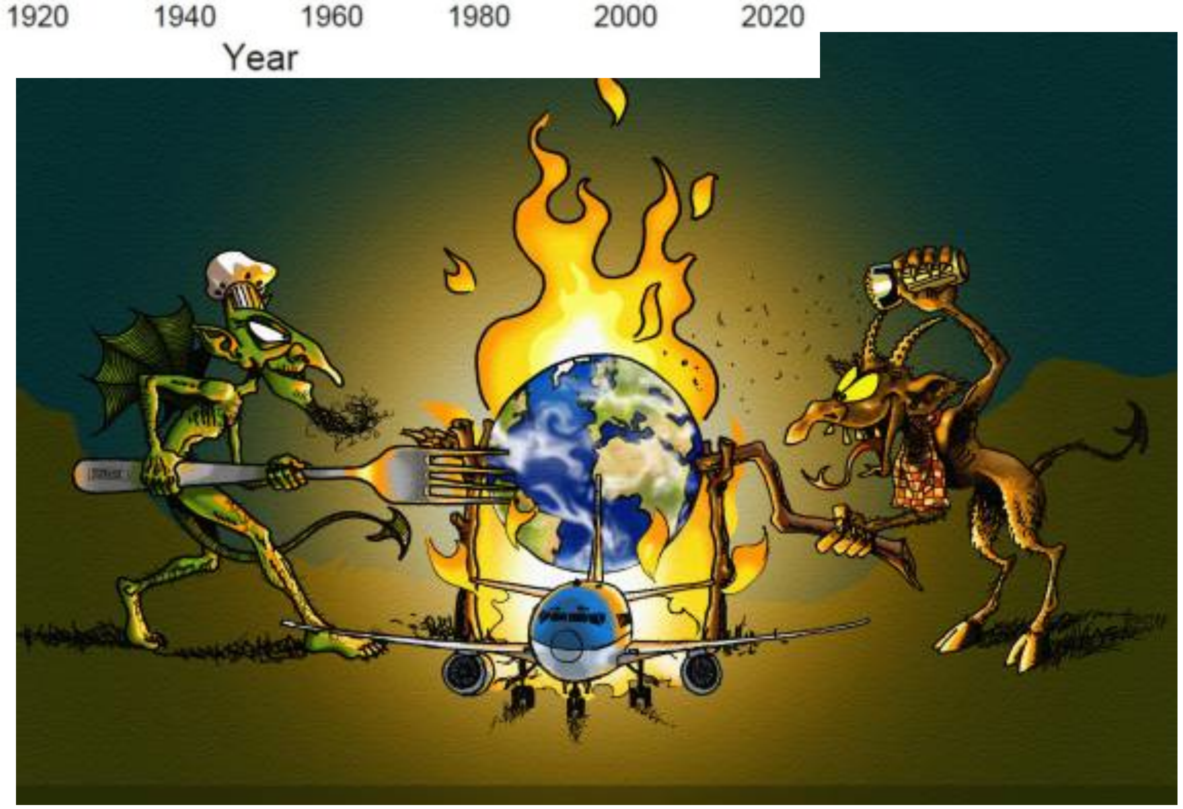
EMISSIONS, CLIMATE IMPACT AND GLOBAL WARMING…





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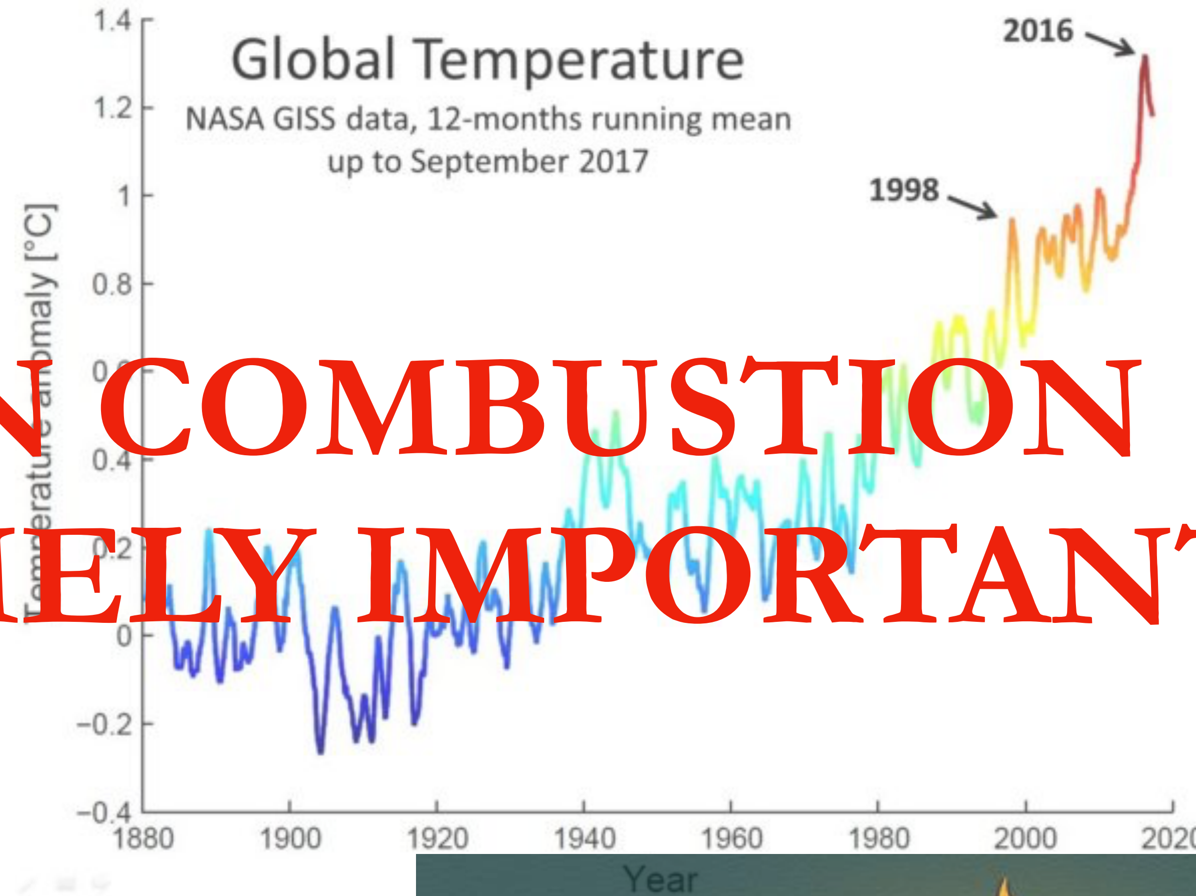
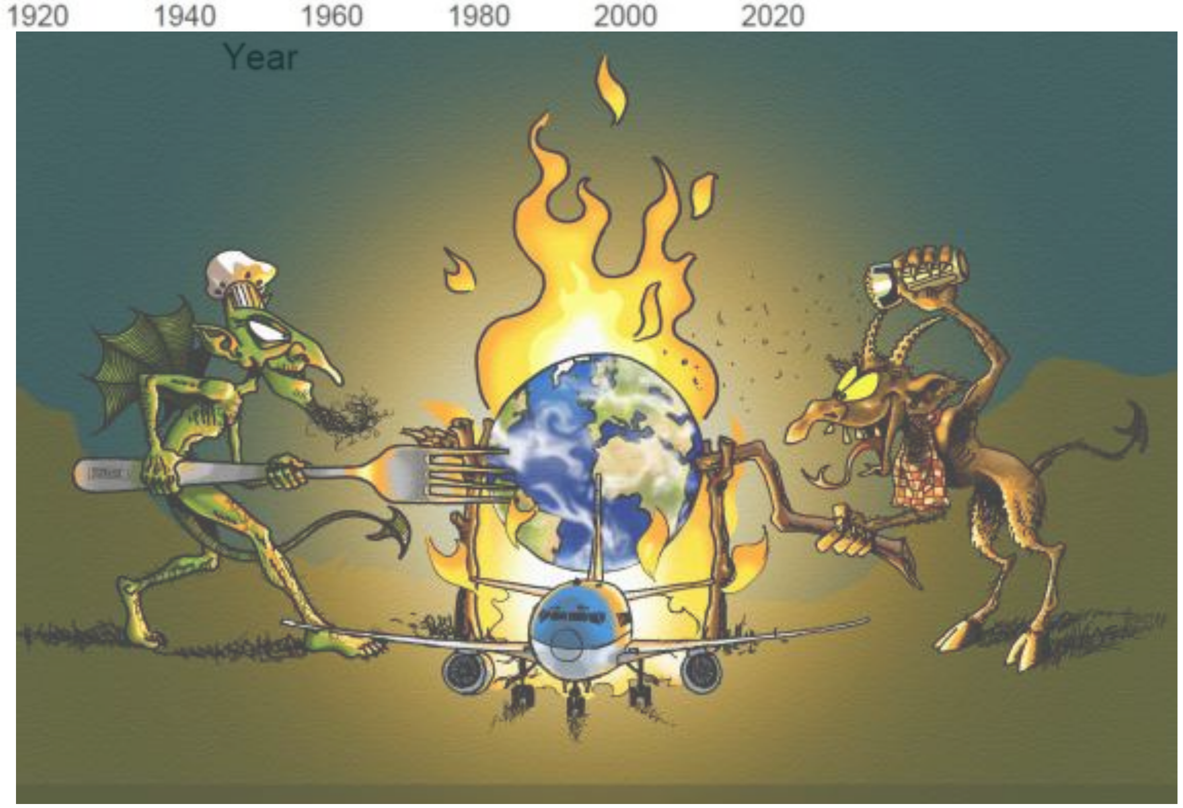


CLEAN COMBUSTION EXTREMELY IMPORTANT!



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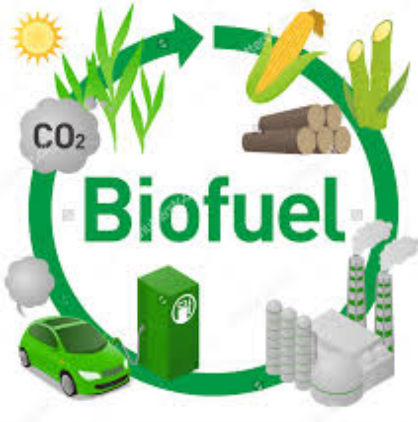
OPPORTUNITIES AND NEW FRONTIERS…

Primary energy and conversion processes

- Cleaner fuels and technologies (MILD, LTC, …)
- Biofuels

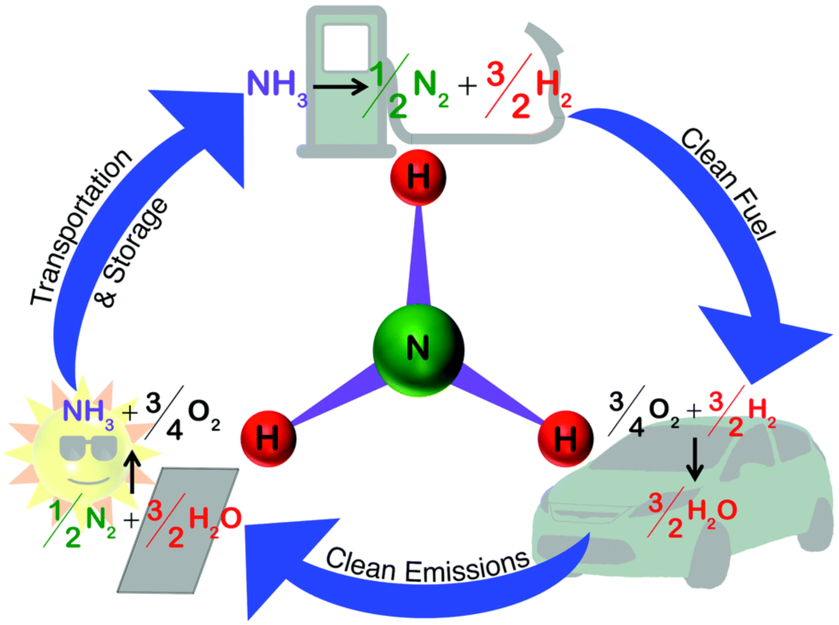
Tailor-made fuels from biomass



- Carbon-free fossil fuel
- Renewable Electricity

Storage

- E-fuels
- Ammonia
- Hydrogen



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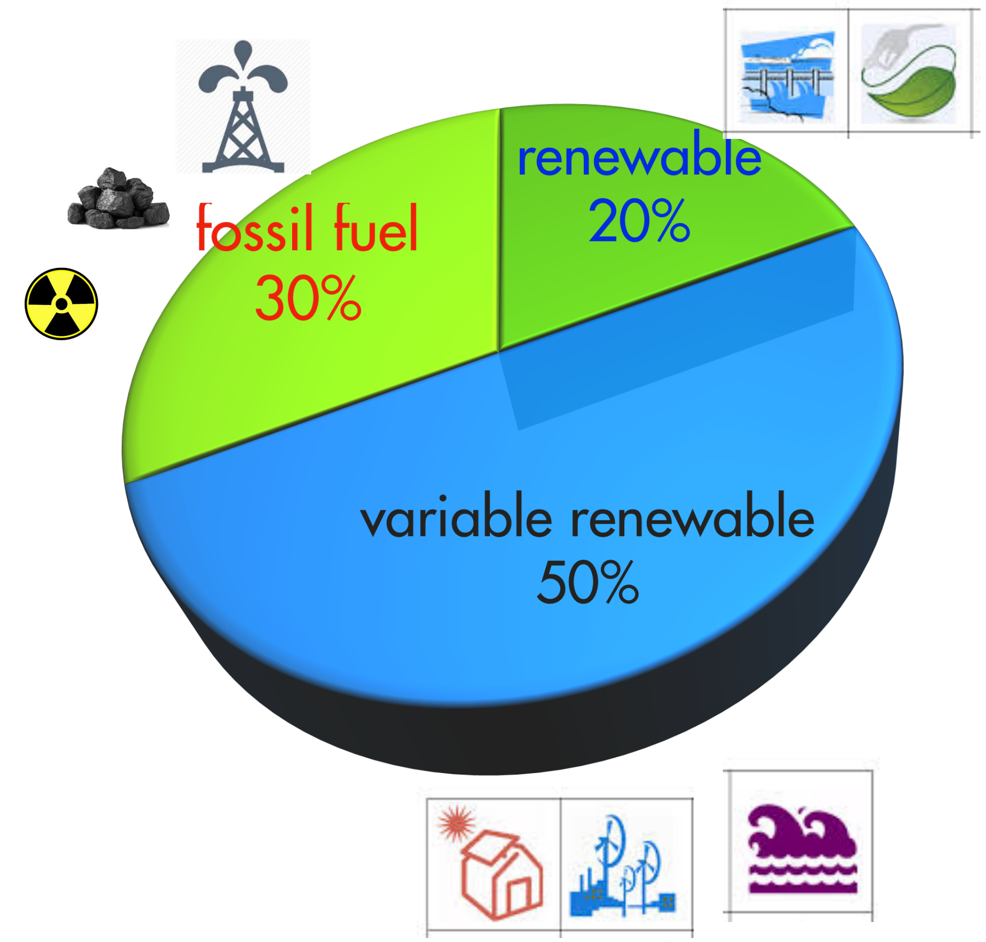
INTEGRATION IN THE ENERGY MIX…

Equity

The accessibility and affordability of energy supply across the population

energy supply system



Sustainability

Efficient and from renewable, (low-carbon) sources

Security

Effectiveness of primary energy supply

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AIM OF THIS COURSE…

Develop understanding of combustion processes from physical and chemical perspectives

• Fundamentals:
– Thermodynamics
– Kinetics
– Fluid mechanics

• Elementary Structures:
– 0D
– 1D
– 2D ???

FOR A CLEAR UNDERSTANDING OF MODELLING and APPLICATIONS (see parallel courses)

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COURSE OVERVIEW

DAY 1

Introduction

a. Definition and relevance of Combustion Science. Applications.
b. Governing equations of multi-component chemically-reacting gas mixtures
c. Thermodynamics, transport, flame temperature and equilibrium

Homogeneous Combustion – AutoIgnition

a. Chain-branching and Thermal Explosions, H_2/O_2 System
b. Auto-ignition. CH_4/O_2 system.
c. Stratified AutoIgnition. Dilution effects.
d. Back-Mixed Ignition. Steady and Unsteady conditions.
e. Heat loss effects. High molecular weight paraffin systems nC_7H_{16}, iC_8H_{18}

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COURSE OVERVIEW

DAY 2

Combustion with Flame Propagation

a. One Dimensional Steady Flow formulation.
b. Rayleigh and Rankine-Hugoniot equations.
c. Detonation.
d. Deflagration. Thermal theory. Flame Speed Dependencies.

Laminar Diffusion Flames

a. Flame Structure and Mixture Fraction.
b. Infinitely fast chemistry. Flamelet concept.
c. 1D Steady Diffusion flames. Strained/Unstrained.
d. 1D Unsteady Diffusion flames. Strained/Unstrained.
e. Diluted conditions. Diffusion Ignition processes.

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COURSE OVERVIEW

DAY 3

Complex Flame Structures

a. The Structure of Triple Flames
b. Lifted flames and lift-off height
c. Triple flame propagation

Turbulence, Mixing and Aerodynamics

a. Characteristics and Description of Turbulent Flows
b. Turbulent Premixed Combustion. Scales and Dimensionless Quantities.
c. Borghi Diagram
d. Flame stabilization, Ignition and Extinction
e. Flashback and Blowoff
f. Swirl and reverse flows

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COURSE OVERVIEW

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GOVERNING EQUATIONS OF MULTI-COMPONENT CHEMICALLY-REACTING GAS MIXTURES

We assume that the fluid is **continuous** and **homogeneous** in structure (the properties of the smallest subdivisions are the same as large samples).

Two common ways to describe a fluid motion

Lagrangian - we follow individual particles

Eulerian - we fix our attention on a point in space x,y,z and consider the primitive variable distributions (velocity, temperature, density, etc…)

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GOVERNING EQUATIONS …

Governing equations for multicomponent chemically reacting gas mixtures can be described through *primitive variables (intensive properties)*:

Eulerian Velocity	$\underline{v}$
Mass Fraction of species i	Y_i
Density	ρ
Temperature	T

for each of them we can obtain the corresponding conservative quantities (extensive):

Momentum	$M\underline{v}$
Mass of species i	M_i
Total Mass	M
Sensible enthalpy	H^s

$$h^s = \sum_i Y_i \int_{T_o}^{T} c_{p_i}(T)\,dT$$

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GOVERNING EQUATIONS …

for each of them we can obtain the corresponding densities :

$$\{\varphi\} = \{\rho \underline{\mathrm{v}},\ \rho Y_i,\ \rho,\ \rho h^s\}$$

where the vector $\{\varphi\}$ is related to *n* species, 3 velocity components and 2 scalar quantities ρ and ρh^s

Therefore it has *n*+5 components.

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GOVERNING EQUATIONS …

- Basics: equations of continuum mechanics

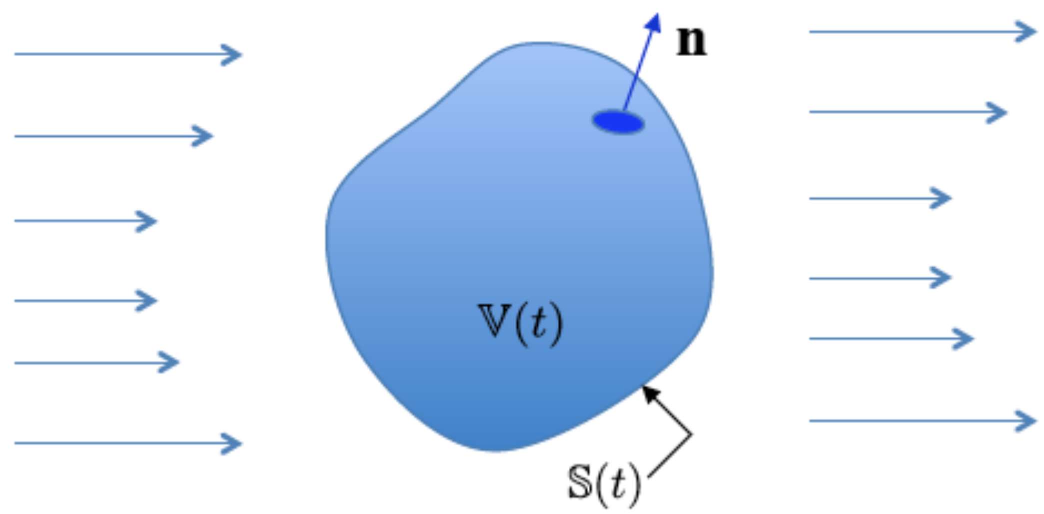
balance equations for mass and momentum
balance equations for the energy and the chemical species

- Associated with the release of thermal energy and the increase in temperature there is a local decrease in density which in turn affects the momentum balance.

- Therefore, all the equations are closely coupled to each other.

NON-LINEARITY

GOVERNING EQUATIONS …



Fixed control volume
(fixed position and shape)

For each component of the vector $\{\varphi\}$ it is possible to obtain a balance equation on a generic fixed control volume.

We obtain the general form of the Governing equation:

$$\frac{\partial \varphi}{\partial t} + \underline{\nabla} \cdot \left(\underline{v} \varphi \right) + \underline{\nabla} \cdot \underline{J}_{\varphi} = \dot{\varphi}$$

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GOVERNING EQUATIONS …

1	CONTINUITY	$$\frac{\partial \rho}{\partial t} + \underline{\nabla}\cdot(\rho\underline{v}) = 0$$
3	MOMENTUM	$$\frac{\partial \rho\underline{v}}{\partial t} + \underline{\nabla}\cdot(\rho\underline{v}\,\underline{v}) + \underline{\nabla}\cdot \underline{J}_{v} = -\underline{\nabla}p$$
N	SPECIES	$$\frac{\partial \rho Y_i}{\partial t} + \underline{\nabla}\cdot(\rho\underline{v}Y_i) + \underline{\nabla}\cdot \underline{J}_{Y_i} = \dot{\rho}_i$$
1	ENERGY	$$\frac{\partial \rho h^s}{\partial t} + \underline{\nabla}\cdot(\rho\underline{v}h^s) + \underline{\nabla}\cdot \underline{J}_{h^s} = -\sum \dot{\rho}_i h_i^o$$

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GOVERNING EQUATIONS …

neglected terms…

MOMENTUM	$\rho \underline{g}$	GRAVITY
SENSIBLE ENTHALPY	$\partial p / \partial t + \underline{v} \cdot \underline{\nabla} p$	COMPRESSIBILITY
SENSIBLE ENTHALPY	$\underline{J}_v : \underline{\nabla}\, \underline{v}$	VISCOSITY
SENSIBLE ENTHALPY	$\underline{\nabla} \cdot \underline{J}_r$	RADIATIVE FLUXES
SENSIBLE ENTHALPY	$\sum \underline{J}_{Y_i} h_i^s$	MASS DIFFUSION

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GOVERNING EQUATIONS …

Derived ones…

ENTHALPY OF FORMATION

$$\frac{\partial \rho h^o}{\partial t} + \underline{\nabla} \cdot \left(\rho \underline{v} h^o\right) + \underline{\nabla} \cdot \underline{J}_{h^o} = \sum \dot{\rho}_i h_i^o$$

$$h = h^o + h^s$$

ENTHALPY

$$\frac{\partial \rho h}{\partial t} + \underline{\nabla} \cdot \left(\rho \underline{v} h\right) + \underline{\nabla} \cdot \underline{J}_h = 0$$

$$h^{tot} = h + e_c = h^s + h^o + e_c = \sum_i Y_i \int_{T_0}^{T} c_{p_i}(T) dT + \sum_i Y_i h_i^o + e_c$$

TOTAL ENTHALPY

$$\frac{\partial \left(\rho h^{tot}\right)}{\partial t} + \underline{\nabla} \cdot \left(\rho \underline{v} h^{tot}\right) + \underline{\nabla} \cdot \underline{J}_{h^{tot}} = 0$$

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GOVERNING EQUATIONS …

The conservation equations are supplemented (i.e. completed) by the specifications of diffusion fluxes:

MOMENTUM $$J_{\underline{v}} = -\rho\nu \left(\underline{\nabla}\ \underline{v} + \underline{\nabla}^T \underline{v} \right)$$

SPECIES $$J_{Y_i} = -\rho D_{im} \left(\underline{\nabla}\ Y_i \right)$$

ENERGY $$J_{h^s} = -\rho\alpha \left(\underline{\nabla}\ h^s \right)$$

$$\nu = \left(\sum m_i^{1/2} X_i \nu_i\right) / \left(\sum m_i^{1/2} X_i\right)$$

$$\alpha = \left(\sum m_i^{1/3} X_i \alpha_i\right) / \left(\sum m_i^{1/3} X_i\right)$$

$$\frac{1}{D_{i,m}} = \sum \left(X_i / D_{i,j} \right)$$

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GOVERNING EQUATIONS …

Production term:

$$\dot{\rho}_i = m_i \dot{C}_i = m_i \sum_j^r \nu_{i,j} \dot{\omega}_j$$

Difference between products stoichiometric coefficients ($\nu_{i,j}''$) and reactants ones ($\nu_{i,j}'$), related to reaction j for the species i.

$$\dot{\omega}_j = k_j \prod_k^s C_k^{\nu'_{jk}}$$

REACTION RATE

Arrhenius Law

$$k_j = A_j e^{\left(-E_j / RT\right)}$$

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GOVERNING EQUATIONS …

$$\nu'_F F + \nu'_O O \rightarrow Products$$

$$\left(\frac{Y_O}{Y_F}\right)_{st} = \frac{\nu'_O W_O}{\nu'_F W_F} = s$$

Stoichiometric Ratio

$$\phi = s\frac{Y_F}{Y_O} = \left(\frac{Y_F}{Y_O}\right) / \left(\frac{Y_F}{Y_O}\right)_{st}$$

Equivalence ratio

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AUXILIARY RELATIONS

- Ideal Gas Equation of State

$$p = \rho R^o T \Big/ \sum_{i=1}^{N} X_i W_i = \rho R^o T \sum_{i=1}^{N} \frac{Y_i}{W_i} = \frac{\rho R^o T}{\overline{W}},$$

- Energy–Enthalpy Relation

$$h = \sum_{i=1}^{N} Y_i h_i = e + p / \rho .$$

- Calorific Equation of State

$$h_i = h_i^0(T^o) + h_i^s(T;T^o) \qquad h_i^s(T;T^o) = \int_{T^o}^{T} c_{p,i}\, dT .$$

- Mole and Mass Fractions

$$X_i = \frac{Y_i / W_i}{\sum_{j=1}^{N} Y_j / W_j}, \qquad Y_i = \frac{X_i W_i}{\sum_{j=1}^{N} X_j W_j}.$$

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AUXILIARY RELATIONS

The dependence of the binary diffusion coefficients $\mathcal{D}_i$ (which actually stands for $\mathcal{D}_{i,N}$) on pressure and temperature is

$$\mathcal{D}_i \sim T^\alpha/p \qquad 3/2 \leq \alpha \leq 2$$

Typical values at $p = 1\,\mathrm{atm}$ are in the range $0.01 - 10\,\mathrm{cm}^2/\mathrm{s}$.

The kinematic viscosity μ/ρ has the same units and the same pressure and temperature dependence as the binary diffusion coefficients

$$\mu/\rho \sim T^\alpha/p \qquad 3/2 \leq \alpha \leq 2$$

Typical values at $p = 1\,\mathrm{atm}$ are in the range $0.1 - 1\,\mathrm{cm}^2/\mathrm{s}$.

The thermal conductivity depends mostly on temperature, and behaves as

$$\lambda \sim T^\alpha/p \qquad 1/2 \leq \alpha \leq 1$$

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AUXILIARY RELATIONS

More relevant, however, is the thermal diffusivity $\lambda/\rho c_p$ which has the same units and the same temperature and pressure dependence as the diffusion coefficients and the kinematic viscosity. In particular

$$\lambda/\rho c_p \sim T^\alpha/p \qquad 3/2 \leq \alpha \leq 2$$

Typical values at $p = 1\,\mathrm{atm}$ are in the range $0.1 - 1\,\mathrm{cm}^2/\mathrm{s}$.

Since $\lambda/\rho c_p, \mu/\rho, \mathcal{D}_i$ have the same dependence on temperature, their ratios are nearly constant.

$$\frac{\lambda/\rho c_p}{\mathcal{D}_i} = Le_i \qquad \text{Lewis number}$$

$$\frac{\mu/\rho}{\lambda/\rho c_p} = \mathrm{Pr} \qquad \text{Prandtl number}$$

$$\frac{\mu/\rho}{\mathcal{D}_i} = \mathrm{Sc}_i \qquad \text{Schmidt number}$$

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MULTICOMPONENT MIXTURE

A gas mixture consists of N species (i=1,2, …, N)

The quantitative description of chemical reaction between species requires a precise definition of *Concentration*

The Concentration C_i is defined as the number of moles of species i per unite volume:

$$C_i = \frac{n_i}{\mathbb{V}} \qquad i = 1, 2, \ldots, N$$

where n_i is the number of moles of species i in the mixture.
From the definition of the Avogadro number, there are $6.023\ 10^{23}$ molecules in 1 mole.

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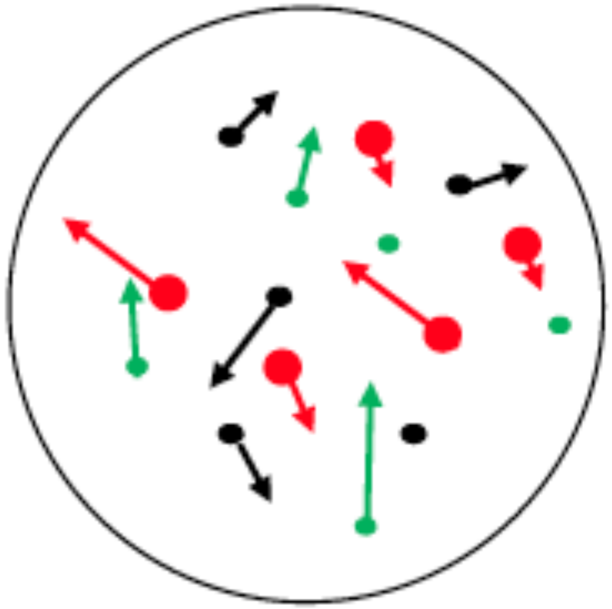
MULTICOMPONENT MIXTURE

Total pressure: $$p = \sum_{k=1}^{N} p_k$$

$$\rho_k = \rho Y_k$$



Partial pressure: p_k

$$\begin{cases} p_1 V = n_1 RT \\ \dots \\ p_k V = n_k RT \\ \dots \\ p_N V = n_N RT \end{cases} \Leftrightarrow p_k = \frac{\rho_k}{W_k} RT$$

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MULTICOMPONENT MIXTURE

The mass m_i of all molecules of species i is related to the number of moles by

$$m_i = W_i n_i \qquad i = 1, 2, \ldots, N$$

where W_i is the molecular weight of species i.

The density ρ_i is defined as the mass of species i per unit volume

$$\rho_i = m_i/\mathbb{V} \quad i = 1, 2, \ldots, N$$

$$\sum_{i=1}^{N} \rho_i = \frac{1}{\mathbb{V}} \sum_{i=1}^{N} m_i = \frac{m}{\mathbb{V}} = \rho$$ density of the mixture

$$\sum_{i=1}^{N} C_i = \frac{1}{\mathbb{V}} \sum_{i=1}^{N} n_i = \frac{n}{\mathbb{V}} = C$$ concentration of the mixture

MULTICOMPONENT MIXTURE

Mole fraction

$$X_i = \frac{C_i}{C} = \frac{n_i}{n} \qquad 0 \le X_i \le 1 \qquad \sum_{i=1}^{N} X_i = 1$$

Mass fraction

$$Y_i = \frac{m_i}{m} = \frac{m_i/\mathbb{V}}{m/\mathbb{V}} = \frac{\rho_i}{\rho} \qquad 0 \le Y_i \le 1 \qquad \sum_{i=1}^{N} Y_i = 1$$

$$m_i = mY_i$$
$$n_i W_i = nWY_i$$

$$Y_i = \frac{X_i W_i}{W} \qquad X_i = \frac{Y_i W}{W_i}$$

relation between mass and mole fraction

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MULTICOMPONENT MIXTURE

Mixture molecular weight

$$m = \sum_{i=1}^{N} m_i = \sum_{i=1}^{N} n_i W_i = n \cdot \underbrace{\sum_{i=1}^{N} X_i W_i}_{W} \quad \Rightarrow \quad W = \sum_{i=1}^{N} X_i W_i$$

$$Y_i = \frac{X_i W_i}{W} \quad \Rightarrow \quad \sum_{i=1}^{N} \frac{Y_i}{W_i} = \sum_{i=1}^{N} \frac{X_i}{W} = \frac{1}{W} \sum_{i=1}^{N} X_i = \frac{1}{W}$$

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

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COURSE OVERVIEW

DAY 1

Introduction

a. Definition and relevance of Combustion Science. Applications.
b. Governing equations of multi-component chemically-reacting gas mixtures
c. Thermodynamics, transport, flame temperature and equilibrium

Homogeneous Combustion – AutoIgnition

a. Chain-branching and Thermal Explosions, H_2/O_2 System
b. Auto-ignition. CH_4/O_2 system.
c. Stratified AutoIgnition. Dilution effects.
d. Back-Mixed Ignition. Steady and Unsteady conditions.
e. Heat loss effects. High molecular weight paraffin systems nC_7H_{16}, iC_8H_{18}

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THERMODYNAMIC QUANTITIES

First law of thermodynamics - balance between different forms of energy

-Internal Energy du
Specific Work due to volumetric changes : $\delta w = -pdv$
Specific heat transfer from the surroundings: δq

- Related quantities
specific enthalpy (general definition): $h=u+pv$
specific enthalpy for an ideal gas: $h=u+RT/M$

-Energy balance for a closed system (no mass exchange): $du = \delta q + \delta w$

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MULTICOMPONENT SYSTEM

Specific internal energy and specific enthalpy of mixtures

$$u = \sum_{i=1}^{k} Y_i \, u_i, \quad h = \sum_{i=1}^{k} Y_i \, h_i.$$

Relation between internal energy and enthalpy of single species

$$h_i = u_i + \frac{\mathcal{R}T}{M_i} \qquad i = 1, 2, \ldots, k$$

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MULTICOMPONENT SYSTEM

Partial molar enthalpy $h_{i,m}$ is

$$h_{i,m} = M_i h_i$$

and its temperature dependence is

$$h_{i,m} = h_{i,m,\mathrm{ref}} + \int_{T_{ref}}^{T} c_{\mathrm{p}i,m} dT$$

where the molar specific heat at constant pressure is

$$c_{\mathrm{p}i,m} = M_i c_{\mathrm{p}i}$$

- In a multicomponent system, the specific specific heat at constant pressure of the mixture is

$$c_{\mathrm{p}} = \sum_{i=1}^{n} Y_i \, c_{\mathrm{p}i} \qquad \Big| \qquad c_{\mathrm{p},m} = \sum_{i=1}^{n} X_i \, c_{\mathrm{p}i,m}$$

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DETERMINATION OF PROPERTIES

Reference enthalpies of chemical species at reference temperature are listed in tables

Reference enthalpies of chemical elements (O_2, N_2) and solid carbon Cs were chosen as zero, because they represent the chemical elements

Reference enthalpies of combustion products such that CO_2 and H_2O are typically negative

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DETERMINATION OF PROPERTIES

$$\frac{c_{\mathrm{p},m}}{\mathcal{R}} = a_1 + a_2\, T/\mathrm{K} + a_3\,(T/\mathrm{K})^2 + a_4\,(T/\mathrm{K})^3 + a_5\,(T/\mathrm{K})^4$$

$$\frac{h_m}{\mathcal{R}T} = a_1 + a_2\frac{T/\mathrm{K}}{2} + a_3\frac{(T/\mathrm{K})^2}{3} + a_4\frac{(T/\mathrm{K})^3}{4} + a_5\frac{(T/\mathrm{K})^4}{5} + \frac{a_6}{T/\mathrm{K}}$$

$$\frac{s_m}{\mathcal{R}} = a_1 \ln(T/\mathrm{K}) + a_2\, T/\mathrm{K} + a_3\frac{(T/\mathrm{K})^2}{2} + a_4\frac{(T/\mathrm{K})^3}{3} + a_5\frac{(T/\mathrm{K})^4}{4} + a_7 + ln(\frac{p}{p_0})$$

a_j for each species i are listed in tables

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POLYNOMIALS…

TABLE A–2

Ideal-gas specific heats of various common gases (*Concluded*)

(*c*) As a function of temperature

$$\bar{c}_p = a + bT + cT^2 + dT^3$$

(T in K, c_p in kJ/kmol·K)

Substance	Formula	*a*	*b*	*c*	*d*	Temperature range, K	% error Max.	% error Avg.
Nitrogen	N_2	28.90	-0.1571×10^{-2}	0.8081×10^{-5}	-2.873×10^{-9}	273–1800	0.59	0.34
Oxygen	O_2	25.48	1.520×10^{-2}	-0.7155×10^{-5}	1.312×10^{-9}	273–1800	1.19	0.28
Air	—	28.11	0.1967×10^{-2}	0.4802×10^{-5}	-1.966×10^{-9}	273–1800	0.72	0.33
Hydrogen	H_2	29.11	-0.1916×10^{-2}	0.4003×10^{-5}	-0.8704×10^{-9}	273–1800	1.01	0.26
Carbon monoxide	CO	28.16	0.1675×10^{-2}	0.5372×10^{-5}	-2.222×10^{-9}	273–1800	0.89	0.37
Carbon dioxide	CO_2	22.26	5.981×10^{-2}	-3.501×10^{-5}	7.469×10^{-9}	273–1800	0.67	0.22
Water vapor	H_2O	32.24	0.1923×10^{-2}	1.055×10^{-5}	-3.595×10^{-9}	273–1800	0.53	0.24
Nitric oxide	NO	29.34	-0.09395×10^{-2}	0.9747×10^{-5}	-4.187×10^{-9}	273–1500	0.97	0.36
Nitrous oxide	N_2O	24.11	5.8632×10^{-2}	-3.562×10^{-5}	10.58×10^{-9}	273–1500	0.59	0.26
Nitrogen dioxide	NO_2	22.9	5.715×10^{-2}	-3.52×10^{-5}	7.87×10^{-9}	273–1500	0.46	0.18
Ammonia	NH_3	27.568	2.5630×10^{-2}	0.99072×10^{-5}	-6.6909×10^{-9}	273–1500	0.91	0.36
Sulfur	S	27.21	2.218×10^{-2}	-1.628×10^{-5}	3.986×10^{-9}	273–1800	0.99	0.38
Sulfur dioxide	SO_2	25.78	5.795×10^{-2}	-3.812×10^{-5}	8.612×10^{-9}	273–1800	0.45	0.24
Sulfur trioxide	SO_3	16.40	14.58×10^{-2}	-11.20×10^{-5}	32.42×10^{-9}	273–1300	0.29	0.13
Acetylene	C_2H_2	21.8	9.2143×10^{-2}	-6.527×10^{-5}	18.21×10^{-9}	273–1500	1.46	0.59
Benzene	C_6H_6	−36.22	48.475×10^{-2}	-31.57×10^{-5}	77.62×10^{-9}	273–1500	0.34	0.20
Methanol	CH_4O	19.0	9.152×10^{-2}	-1.22×10^{-5}	-8.039×10^{-9}	273–1000	0.18	0.08
Ethanol	C_2H_6O	19.9	20.96×10^{-2}	-10.38×10^{-5}	20.05×10^{-9}	273–1500	0.40	0.22
Hydrogen chloride	HCl	30.33	-0.7620×10^{-2}	1.327×10^{-5}	-4.338×10^{-9}	273–1500	0.22	0.08
Methane	CH_4	19.89	5.024×10^{-2}	1.269×10^{-5}	-11.01×10^{-9}	273–1500	1.33	0.57
Ethane	C_2H_6	6.900	17.27×10^{-2}	-6.406×10^{-5}	7.285×10^{-9}	273–1500	0.83	0.28
Propane	C_3H_8	−4.04	30.48×10^{-2}	-15.72×10^{-5}	31.74×10^{-9}	273–1500	0.40	0.12
n-Butane	C_4H_{10}	3.96	37.15×10^{-2}	-18.34×10^{-5}	35.00×10^{-9}	273–1500	0.54	0.24
i-Butane	C_4H_{10}	−7.913	41.60×10^{-2}	-23.01×10^{-5}	49.91×10^{-9}	273–1500	0.25	0.13
n-Pentane	C_5H_{12}	6.774	45.43×10^{-2}	-22.46×10^{-5}	42.29×10^{-9}	273–1500	0.56	0.21
n-Hexane	C_6H_{14}	6.938	55.22×10^{-2}	-28.65×10^{-5}	57.69×10^{-9}	273–1500	0.72	0.20
Ethylene	C_2H_4	3.95	15.64×10^{-2}	-8.344×10^{-5}	17.67×10^{-9}	273–1500	0.54	0.13
Propylene	C_3H_6	3.15	23.83×10^{-2}	-12.18×10^{-5}	24.62×10^{-9}	273–1500	0.73	0.17

Source of Data: B. G. Kyle, *Chemical and Process Thermodynamics* (Englewood Cliffs, NJ: Prentice–Hall, 1984).

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ENTHALPY FOR COMBUSTION

First law of thermodynamics for a system at constant pressure

$du = \delta q + \delta w$
$h=u+pv$
$dh=du+pdv+vdp=\delta q + \delta w+pdv+vdp=\delta q-pdv+pdv+vdp=\delta q+vdp$
if $dp=0$ (constant pressure)
$\mathbf{dh=\delta q}$

Heat release for combustion :

$$\Delta h_m = \sum \nu_i h_{i,m}$$

Example: $CH_4+2O_2=CO_2+2H_2O$

Reaction Enthalpy: $\Delta h_m = h_{CO_2} + 2h_{H_2O} - h_{CH_4} + 2h_{O_2}$

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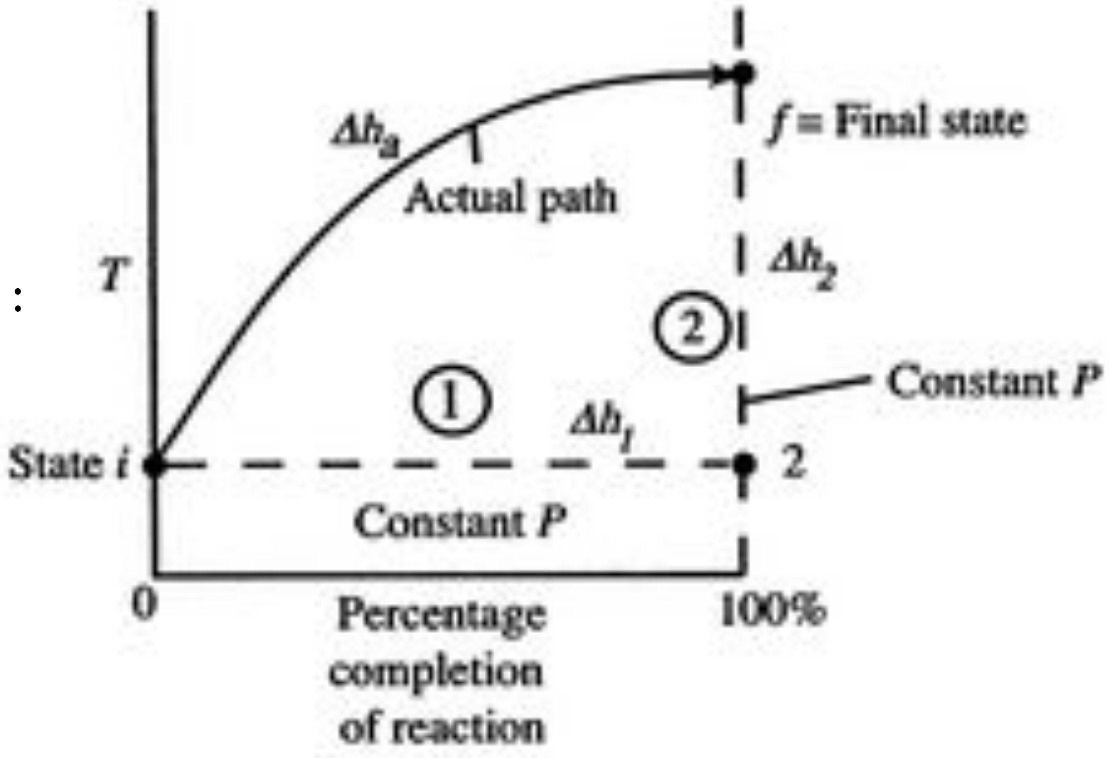
REACTION ENTHALPY

Enthalpy is a state function and therefore we can assume that reaction occurs at $T = T_{ref}$:

$$h_{i,m} = h_{i,m,ref} + \int_{T_{ref}}^{T} C_{pi,m} dT$$



Example : formation reaction of H_2O $\quad H_2+1/2O_2=H_2O$

$$\Delta h_{H_2O} = h_{H_2O} - h_{H_2} - \frac{1}{2} h_{O_2} = h_{H_2O,ref}$$

$h_{i,ref}$ (enthalpy of formation) is the chemical energy of a species with respect to its chemical state

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ENTHALPY OF FORMATION

Standard Enthalpies of Formation, ΔH_f°, at 298 K

Substance	Formula	ΔH_f° (kJ/mol)	Substance	Formula	ΔH_f° (kJ/mol)
Acetylene	$C_2H_2(g)$	226.7	Hydrogen chloride	$HCl(g)$	−92.30
Ammonia	$NH_3(g)$	−46.19	Hydrogen fluoride	$HF(g)$	−268.60
Benzene	$C_6H_6(l)$	49.0	Hydrogen iodide	$HI(g)$	25.9
Calcium carbonate	$CaCO_3(s)$	−1207.1	Methane	$CH_4(g)$	−74.80
Calcium oxide	$CaO(s)$	−635.5	Methanol	$CH_3OH(l)$	−238.6
Carbon dioxide	$CO_2(g)$	−393.5	Propane	$C_3H_8(g)$	−103.85
Carbon monoxide	$CO(g)$	−110.5	Silver chloride	$AgCl(s)$	−127.0
Diamond	$C(s)$	1.88	Sodium bicarbonate	$NaHCO_3(s)$	−947.7
Ethane	$C_2H_6(g)$	−84.68	Sodium carbonate	$Na_2CO_3(s)$	−1130.9
Ethanol	$C_2H_5OH(l)$	−277.7	Sodium chloride	$NaCl(s)$	−410.9
Ethylene	$C_2H_4(g)$	52.30	Sucrose	$C_{12}H_{22}O_{11}(s)$	−2221
Glucose	$C_6H_{12}O_6(s)$	−1273	Water	$H_2O(l)$	−285.8
Hydrogen bromide	$HBr(g)$	−36.23	Water vapor	$H_2O(g)$	−241.8

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REACTION ENTHALPY

Type of reactions:

Exothermic reaction: $\Delta h_m < 0$

Endothermic reaction: $\Delta h_m > 0$

Lower heating value (LHV)

$$\text{LHV} = \frac{(-\Delta h_m)}{M_{\text{Fuel}}}$$

Higher heating value (HHV)

$$\text{HHV} = \text{LHV} + H_v \left(\frac{n_{H_2O,\text{out}}}{n_{\text{fuel,in}}} \right)$$

H_V is the heat of vaporization of water

For Hydrocarbons : HHV is ~10% larger than LHV

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ADIABATIC FLAME TEMPERATURE

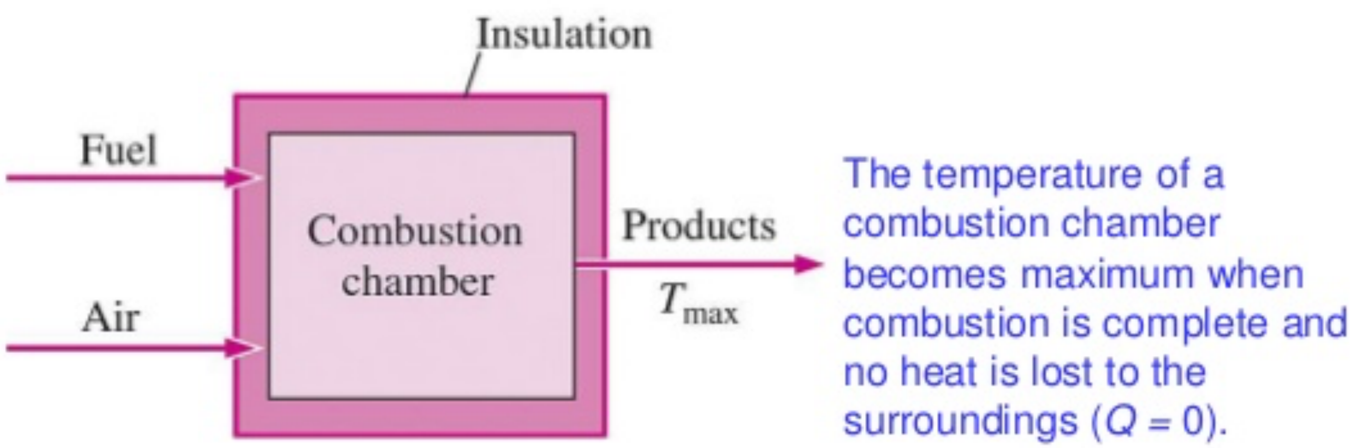
First law of thermodynamics for an adiabatic system at constant pressure ($\delta q = 0$, $dp = 0$) with only reversible work ($\delta w = -pdv$)

$$du = \delta q + \delta w = - pdv$$
$$dh = du+pdv+vdp= -pdv+pdv+vdp$$

if $dp=0$ then $dh=0$

Integrated from the unburnt (u), to burnt (b) gives :

$$h_u=h_b$$



and therefore

$$\sum_i Y_{i,u} h_{i,u} = \sum_i Y_{i,b} h_{i,b}$$

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ADIABATIC FLAME TEMPERATURE

$$\sum_i Y_{i,u} h_{i,u} = \sum_i Y_{i,b} h_{i,b}$$

If

$$h_{i,m} = h_{i,m,ref} + \int_{T_{ref}}^{T} C_{pi,m} \, dT$$

then:

$$\sum_i (Y_{i,u} - Y_{i,b}) h_{i,ref} = \int_{T_{ref}}^{T_b} C_{p,b} \, dT - \int_{T_{ref}}^{T_u} C_{p,u} \, dT$$

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ADIABATIC FLAME TEMPERATURE

COMPLETE CONVERSION

$$\sum_i (Y_{i,u} - Y_{i,b}) h_{i,ref} = \int_{T_{ref}}^{T_b} C_{p,b}\, dT - \int_{T_{ref}}^{T_u} C_{p,u}\, dT$$

For a one-step global reaction (A+B=C+D)

$$Y_{i,u} - Y_{i,b} = (Y_{F,u} - Y_{F,b}) \frac{\nu_i M_i}{\nu_F M_F}$$

and therefore:

$$\sum_{i=1}^{k} (Y_{i,u} - Y_{i,b}) h_{i,\mathrm{ref}} = \frac{(Y_{F,u} - Y_{F,b})}{\nu_F M_F} \sum_{i=1}^{k} \nu_i M_i h_{i,\mathrm{ref}}$$

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ADIABATIC FLAME TEMPERATURE

COMPLETE CONVERSION

We define the Heat of Combustion:

$$Q = -\sum_i \nu_i M_i h_i = -\sum_i \nu_i M_i h_{i,m}$$

Assumption that it is not dependent on the temperature and therefore:

$$Q = -\sum_i \nu_i M_i h_{i,ref}$$

Simplification:

- $T_u = T_{ref}$ and $c_{p,b}$ approximately constant
- For combustion in air, nitrogen is dominant in calculating $c_{p,b}$
- We can set the specific heat for burnt gas of about 1.40 kJ/kg/K

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ADIABATIC FLAME TEMPERATURE

COMPLETE CONVERSION

$$\frac{(Y_{F,u}-Y_{F,b})}{\nu_F M_F}\sum_i \nu_i M_i h_{i,ref} = \int_{T_{ref}}^{T_b} C_{p,b}\, dT - \int_{T_{ref}}^{T_u} C_{p,u}\, dT$$

Under the assumption of c_p constant and Q = Qref,
the Adiabatic flame temperature at complete conversion for a **lean mixture** ($Y_{F,b}$ = 0) is calculated from:

$$\frac{(Y_{F,u}-Y_{F,b})}{\upsilon_F M_F}\sum_i \upsilon_i M_i h_{i,ref} = C_p (T_b - T_u)$$

and therefore:

$$\Delta T_{ad} = T_b - T_u = \frac{Q_{ref} Y_{F,u}}{C_p \upsilon_F M_F}$$

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ADIABATIC FLAME TEMPERATURE

COMPLETE CONVERSION

For a **rich mixture**

the Adiabatic flame temperature at complete conversion ($Y_{O2,b} = 0$) is calculated from:

$$Y_{i,u} - Y_{i,b} = (Y_{F,u} - Y_{F,b})\frac{\nu_i M_i}{\nu_F M_F}$$

and therefore:

$$Y_{i,u} - Y_{i,b} = (Y_{O_2,u} - Y_{O_2,b})\frac{\nu_i M_i}{\nu_F M_F}$$

$$\Delta T_{ad} = T_b - T_u = \frac{Q_{ref} Y_{O_2,u}}{C_p \upsilon_F M_F}$$

ADIABATIC FLAME TEMPERATURE METHANE/AIR

Adiabatic flame temperature at complete conversion for stoichiometric CH_4/Air mixture at T_u=298 K

$$CH_4 + 2O_2 = CO_2 + 2H_2O$$

$$Q_{\text{ref}} = -(h_{CO_2,m} + 2h_{H_2O,m} - h_{CH_4,m}) = 802.3 \text{ kJ/kg}$$

	CH_4	O_2	N_2	CO_2	H_2O
Unburned	*16*	*64*	*2*3,76*28*	*0*	*0*
Burned	*0*	*0*	*2*3,76*28*	*44*	*36*

$Y_{F,u}$=0,055
Cp=1,4 kJ/Kg
M_F=0,016 Kg/mol

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ADIABATIC FLAME TEMPERATURE METHANE/AIR

Adiabatic flame temperature at complete conversion for stoichiometric CH_4/Air mixture at T_u=298 K

$$CH_4 + 2O_2 = CO_2 + 2H_2O$$

$Y_{F,u}$=0,055
Cp=1,4 kJ/Kg
M_F=0,016 Kg/mol

$$\Delta T_{ad} = T_b - T_u = \frac{Q_{ref} Y_{F,u}}{C_p \upsilon_F M_F}$$

T_b=2260 K

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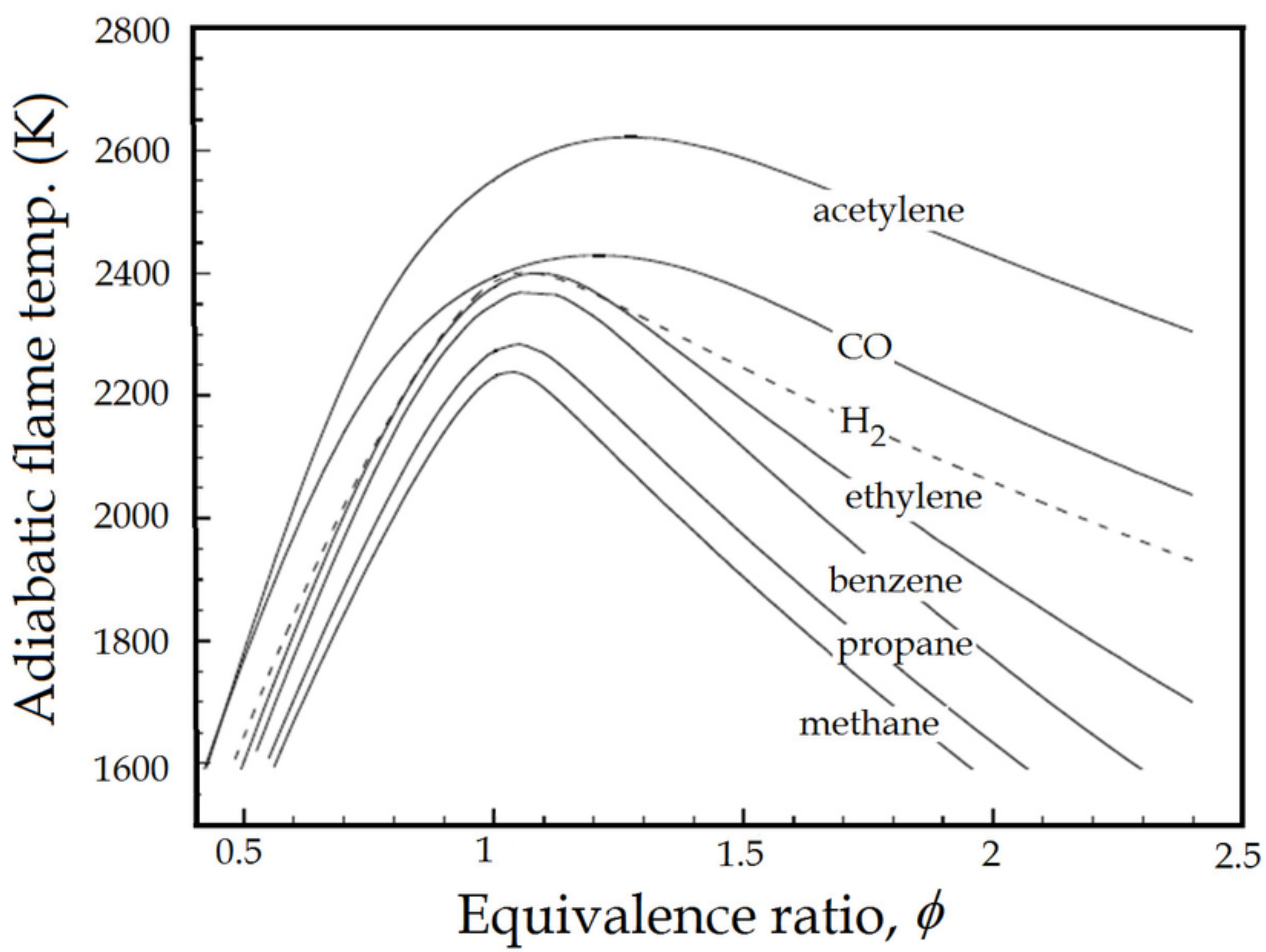
ADIABATIC FLAME TEMPERATURE

FUEL	FLAME TEMPERATURE
acetylene	*2,400 °C*
butane	*1,970 °C*
carbon monoxide	*2,121 °C*
ethane	*1,960 °C*
hydrogen	*2,045 °C*
methane	*1,957 °C*
propane	*1,980 °C*



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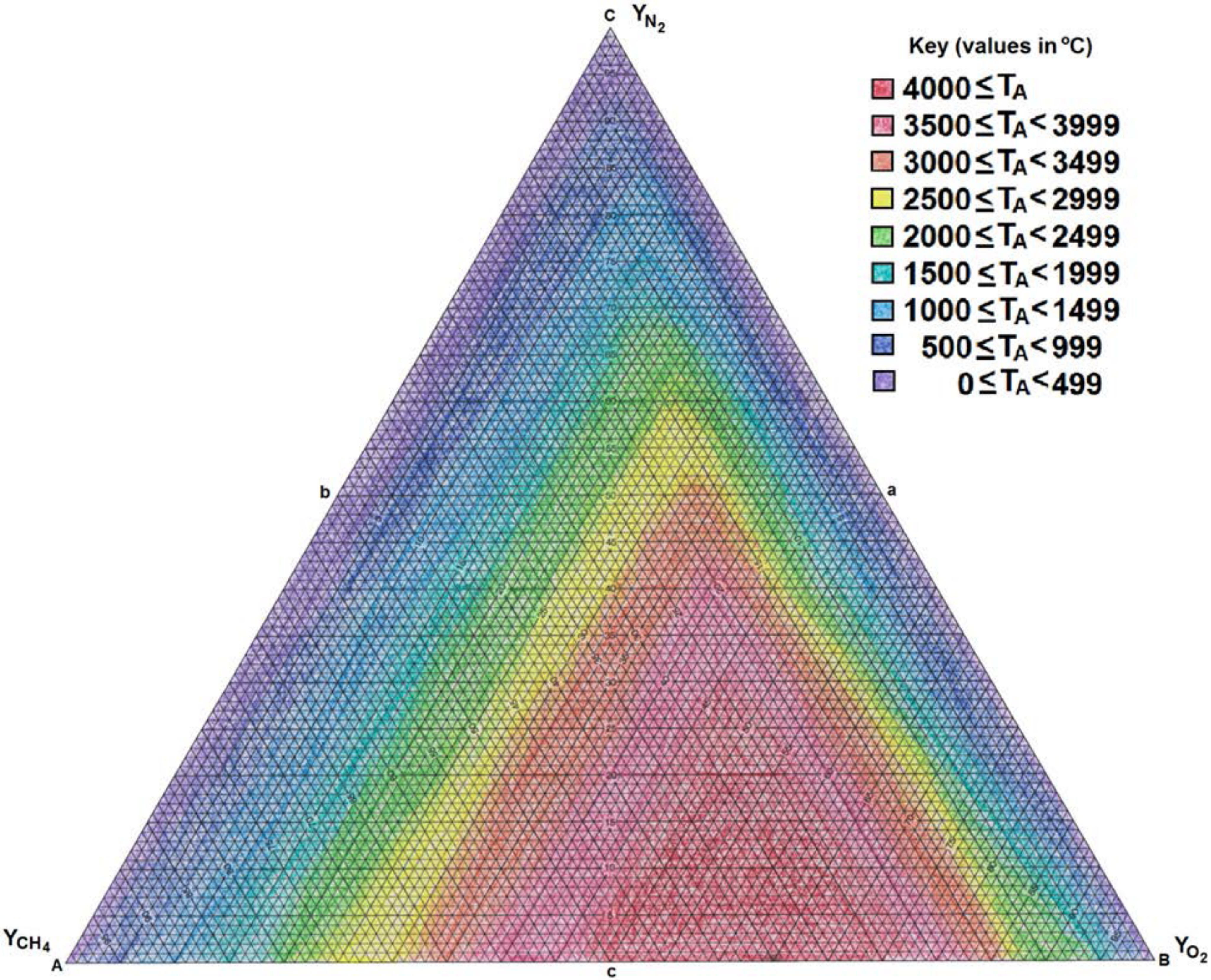
ADIABATIC FLAME TEMPERATURE



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EQUILIBRIUM

Complete combustion is approximation, there is the possibility of dissociation of combustion products

Another important formulation is Chemical Equilibrium

Complete combustion represents the limit of infinitely large equilibrium constant

Chemical equilibrium and complete combustion are valid in the limit of infinitely fast reaction rates only, which is often invalid in combustion systems

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EQUILIBRIUM

Chemical equilibrium assumption over-predicts formation of intermediates such as CO and H_2 for rich conditions by large amounts

Equilibrium assumption represents an exact thermodynamic limit

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ENTROPY

Partial molar entropy $s_{i,m}$ of chemical species in a mixture of ideal gases depends on partial pressure :

$$s_{i,m} = s^0_{i,m} - \mathcal{R} \ln \frac{p_i}{p_0}$$

$$s^0_{i,m} = s^0_{i,m,\mathrm{ref}} + \int_{T_{\mathrm{ref}}}^{T} \frac{c_{\mathrm{p}i,m}}{T} dT$$

values of the reference entropy are listed in tables…

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GIBBS FREE ENERGY

Gibbs Free Energy

$$G = \sum_{i=1}^{n} n_i \, g_{i,m}$$

G=H-T*S $G=G(p,T, n_i)$

is a thermodynamic potential that can be used to calculate the maximum of reversible work that may be performed by a thermodynamic system at a constant temperature and pressure (isothermal, isobaric).

It is the maximum amount of non-expansion work that can be extracted from a thermodynamically closed system. This maximum can be attained only in a completely reversible process.

- **Equilibrium, when Gibbs Free Energy reaches minimum, i.e. dG = 0**

GIBBS EQUATION

$$dG = V\,dp - S dT + \sum_{i=1}^{N} \mu_i dn_i$$

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CHEMICAL POTENTIAL AND GIBBS FREE ENERGY

Gibbs Equation

$$dG = V\,dp - S\,dT + \sum_{i=1}^{N} \mu_i dn_i$$

total differential of $G = G(p, T, n_i)$

$$dG = \left.\frac{\partial G}{\partial p}\right|_{T,\{n_i\}} dp + \left.\frac{\partial G}{\partial T}\right|_{p,\{n_i\}} dT + \sum_{i=1}^{N} \left.\frac{\partial G}{\partial n_i}\right|_{T,p,\{n_{j,i\neq j}\}} dn_i$$

$$\left.\frac{\partial G}{\partial n_i}\right|_{T,p,\{n_{j,i\neq j}\}} = \mu_i$$

Chemical Potential

$$G = \sum_{i=1}^{n} n_i\, g_{i,m} \quad \longrightarrow \quad \mu_i = g_{i,m}$$

Chemical potential is equal to partial molar Gibbs free energy

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LAW OF MASS ACTION

Chemical Potential $\mu_i = h_{i,m} - Ts_{i,m} = \mu_i^0(T) + RT \ln \frac{p_i}{p_0}$

where μ_i^0 is the chemical potential at 1 Atm

Chemical Equilibrium : dG=0

$$\sum_{i=1}^{n} \mu_i dn_i = \sum_{i=1}^{n} \nu_i \mu_i \frac{dn_i}{\nu_i} = 0$$

$$\frac{dn_i}{\nu_i} \sum_{i=1}^{n} \nu_i \mu_i = 0 \qquad \sum_{i=1}^{k} \nu_{il} \mu_i = 0, \quad l = 1, 2, \ldots, r.$$

LAW OF MASS ACTION

By coupling: $$\sum_{i=1}^{k} \nu_{il}\mu_i = 0, \quad l = 1, 2, \dots, r.$$

and

$$\mu_i = h_{i,m} - Ts_{i,m} = \mu_i^0(T) + RT \ln \frac{p_i}{p_0}$$

↓

$$-\sum_{i=1}^{k} \nu_{il}\mu_i^0 = \mathcal{R}T \ln \prod_{i=1}^{k} \left(\frac{p_i}{p_0}\right)^{\nu_{il}}$$

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LAW OF MASS ACTION

Definition of the equilibrium constant K_{pl}:

$$\mathcal{R}T \ln K_{pl} = -\sum_{i=1}^{k} \nu_{il}\mu_i^0$$

Depends only on temperature and thermodynamics, not on composition

law of mass action

↓

$$\prod_{i=1}^{k} \left(\frac{p_i}{p_0}\right)^{\nu_{il}} = K_{pl}(T), \quad l = 1, 2, \ldots, r$$

K_p only depends on temperature

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LAW OF MASS ACTION

EXAMPLE:

A+B=C+D

$$K_p(T) = \frac{p_C \cdot p_D}{p_A \cdot p_B} = \frac{X_C \cdot X_D}{X_A \cdot X_B} \cdot \frac{p_0}{p_0} = \frac{X_C \cdot X_D}{X_A \cdot X_B}$$

K_p determines composition
as a function of temperature: $X_i = f(T)$

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By combining:

$$\prod_{i=1}^{k}\left(\frac{p_i}{p_0}\right)^{\nu_{il}} = K_{pl}(T), \quad l = 1, 2, \ldots, r$$

with the ideal gas law

$$p_i = C_i RT$$

$$\prod_{i=1}^{k} C_i^{\nu_{il}} \cdot \left(\frac{\mathcal{R}T}{p_0}\right)^{\left(\sum_{j=1}^{k}\nu_{jl}\right)} = K_{pl}(T)$$

We can also obtain K_c

$$\prod_{i=1}^{k} C_i^{\nu_{il}} = \frac{K_{pl}(T)}{\left(\frac{\mathcal{R}T}{p_0}\right)^{\left(\sum_{j=1}^{k}\nu_{jl}\right)}} = K_{Cl}(T)$$

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LAW OF MASS ACTION

For Elementary Reactions :

$$\nu_A A + \nu_B B = \nu_C C + \nu_D D$$

$$K_C(T) = \frac{C_C^{\nu_C} C_D^{\nu_D}}{C_A^{\nu_A} C_B^{\nu_B}}$$

At **Equilibrium**:

$$\frac{dC_A}{dt} = k_f C_A^{\nu_A} C_B^{\nu_B} - k_b C_C^{\nu_C} C_D^{\nu_D} = 0$$

$$\frac{k_f}{k_b} = K_C(T)$$

$$K_C(T) = K_p(T) \cdot \left(\frac{p_0}{RT} \right)^{\nu_s}$$

Equilibrium constant determines ratio of forward and reverse rate

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EQUILIBRIUM CONSTANT

$$\nu_A A + \nu_B B = \nu_C C + \nu_D D$$

Magnitude of the Equilibrium Constant

- If $K_c >> 1$, products are favored (rxn nearly complete).
- If $K_c << 1$, reactants are favored (rxn hardly proceeds).
- If K_c is close to 1, the system contains comparable amounts of products and reactants.

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LE CHATELIER'S PRINCIPLE

Le Chatelier's principle states that *if we do something* to a system at equilibrium, *the system will evolve to counteract us*.

Specifically, if we

- add a reactant or product
  - equilibrium will shift to remove it
- remove a reactant or product
  - equilibrium will shift to create it
- decrease the volume (increase the pressure)
  - equilibrium will shift to decrease the pressure
- increase the temperature for an endothermic reaction
  - reaction will go in the forward direction to cool down

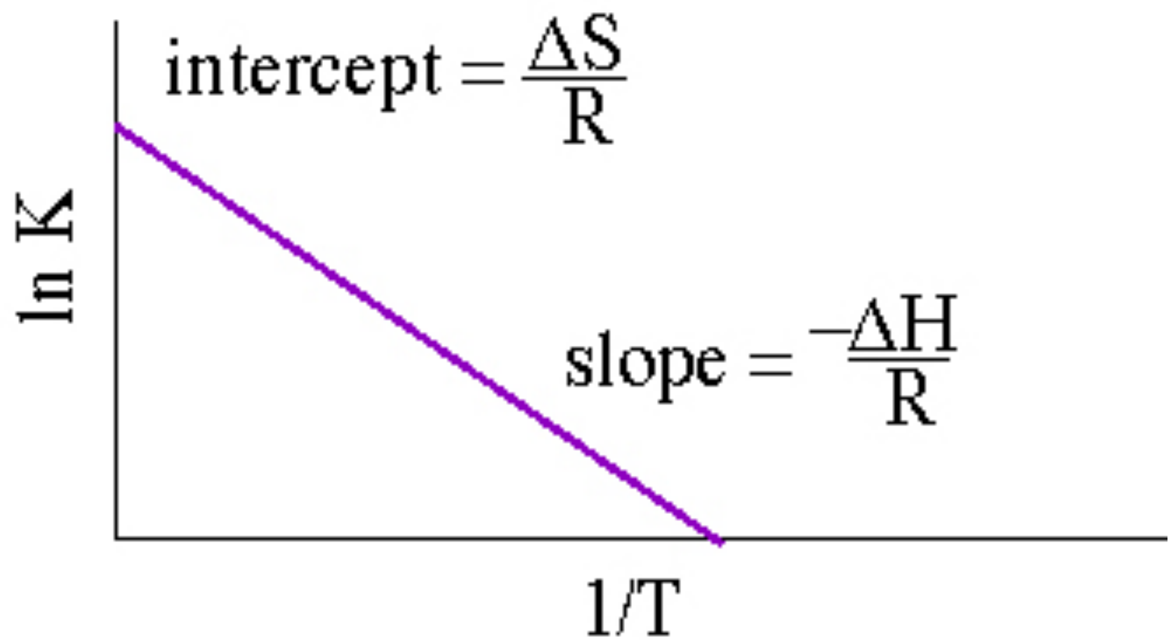
TEMPERATURE DEPENDENCE OF K

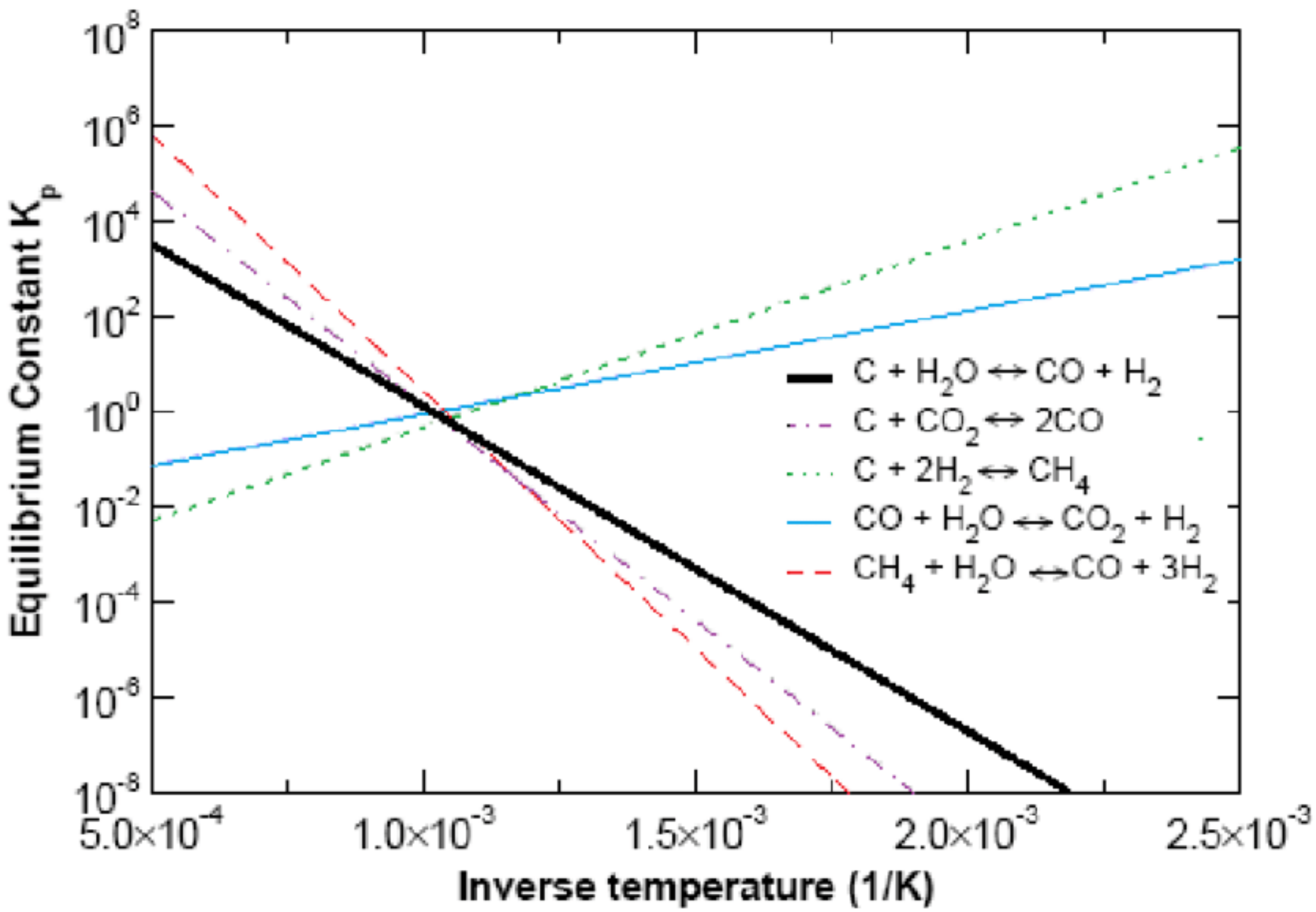
$$\Delta G^0 = -RT \ln K_{eq}$$

$$\Delta G^0 = \Delta H^0 - T\Delta S^0$$

$$-RT \ln K_{eq} = \Delta H^0 - T\Delta S^0$$

$$\ln K_{eq} = -\frac{\Delta H^0}{RT} + \frac{\Delta S^0}{R}$$





Van Hoff's equation establishes the rate of change of the equilibrium constant K with temperature:

$$\frac{d\ell nK}{dT} = \frac{\Delta H_r^\circ}{RT^2} \quad ; \quad T = T_o = 298 \quad K = K_{298}$$

$$\ell n\left(\frac{K_T}{K_{298}}\right) = \frac{\Delta H_r^\circ}{R}\left(\frac{1}{298} - \frac{1}{T}\right)$$

$$K_T = K_{298} e^{\frac{\Delta H_r^\circ}{R}\left(\frac{1}{298} - \frac{1}{T}\right)}$$

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EQUILIBRIUM COMPOSITION

Table 5.2 Equilibrium composition of methane combustion products

	Temperature (K)					
	1400	1600	1800	2000	2200	2400
N_2	0.7149	0.7147	0.7142	0.7127	0.7092	0.7021
H_2O	0.1901	0.1900	0.1894	0.1879	0.1843	0.1768
CO_2	0.0950	0.0949	0.0941	0.0918	0.0862	0.0760
CO	0.0	0.00016	0.00088	0.00307	0.00820	0.0176
O_2	0.0	0.00014	0.00052	0.00168	0.00428	0.00886
H_2	0.0	0.00011	0.00045	0.00135	0.00330	0.00700
OH	0.0	0.00003	0.00018	0.00072	0.00223	0.00558
NO	0.0	0.00005	0.00021	0.00069	0.00179	0.00387
O	0.0	0.0	0.0	0.00003	0.00019	0.00088
H	0.0	0.0	0.00001	0.00006	0.00032	0.00133

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COURSE OVERVIEW

DAY 1

Introduction

a. Definition and relevance of Combustion Science. Applications.
b. Governing equations of multi-component chemically-reacting gas mixtures
c. Thermodynamics, transport, flame temperature and equilibrium

Homogeneous Combustion – AutoIgnition

a. Chain-branching and Thermal Explosions, H_2/O_2 System
b. Auto-ignition. CH_4/O_2 system.
c. Stratified AutoIgnition. Dilution effects.
d. Back-Mixed Ignition. Steady and Unsteady conditions.
e. Heat loss effects. High molecular weight paraffin systems nC_7H_{16}, iC_8H_{18}

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