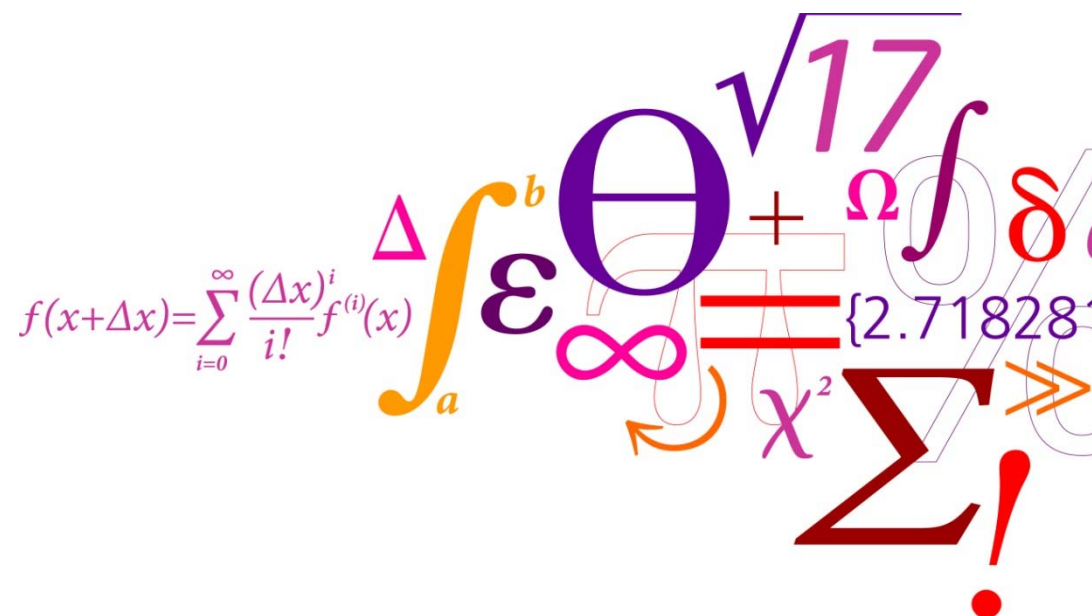


Chemical kinetics

Procida June 2015

Module 1



Module 1

- Introduction to course and teachers (PG, AC)
- Basic concepts about kinetics (PG)
- Introduction to OpenSMOKE++ and pre-processing of kinetic mechanisms (AC)

Teachers

- Peter Glarborg (pgl@kt.dtu.dk)
 - DTU Chemical Engineering
- Alberto Couci (alberto.couci@polimi.it)
 - Politecnico di Milano



The Technical University of Denmark



- Founded in 1829 by the Danish physicist Hans Christian Ørsted
- Moved from Copenhagen to Lyngby in the 1960s
- 6000 students
- 1000 Ph.d. students
- 1250 researchers
- 18 departments



The CHEC Research Center DTU Chemical Engineering

C Combustion
H Harmful
E Emission
C Control

High temperature processes

Production of heat and power
Industrial processes
Production of liquid fuels

Formation and reduction of pollutants

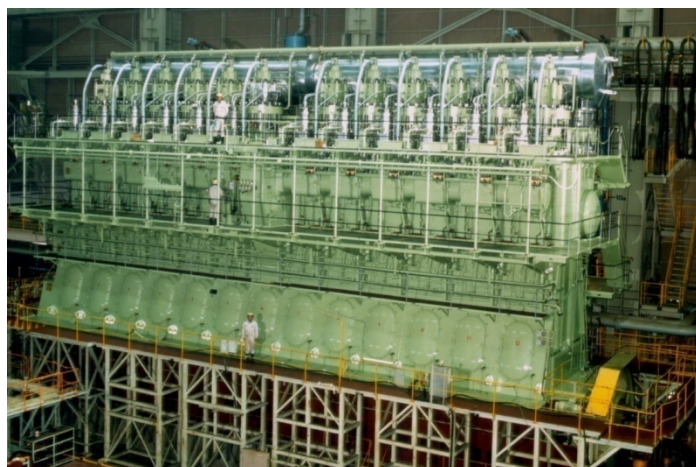
NO_x, SO₂, HCl, CO, PAH
Trace metals
Particles, aerosols

Selected high-temperature processes

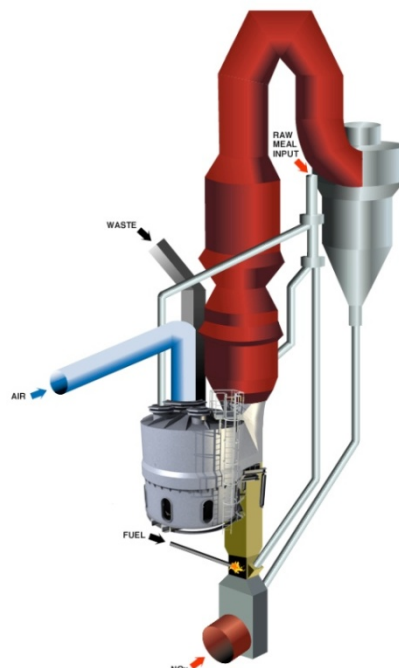
Combustion and incineration



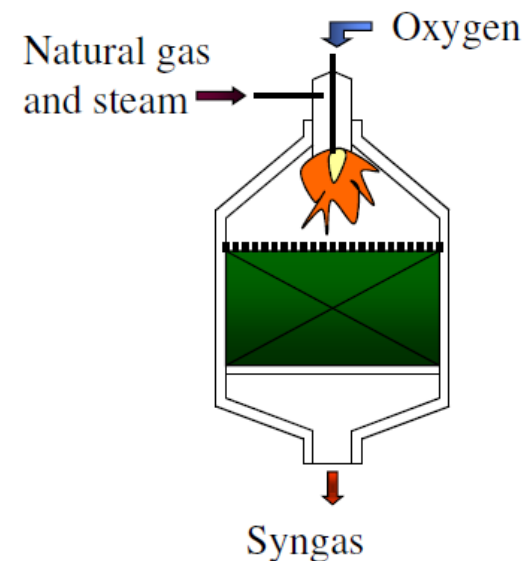
Engine (marine Diesel)



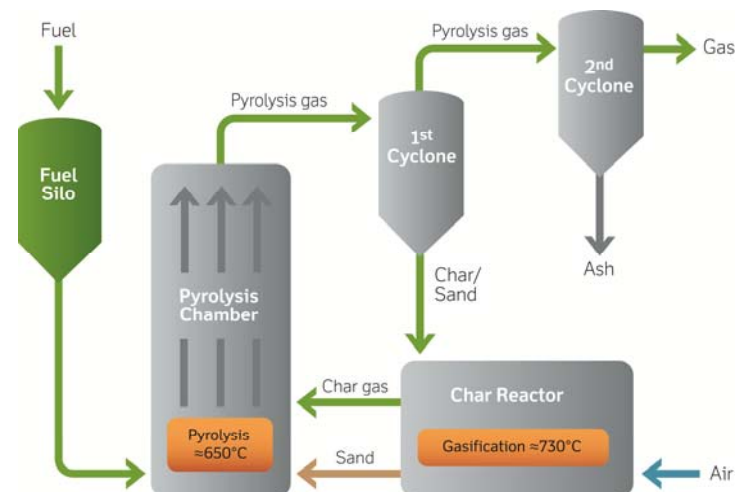
Cement production



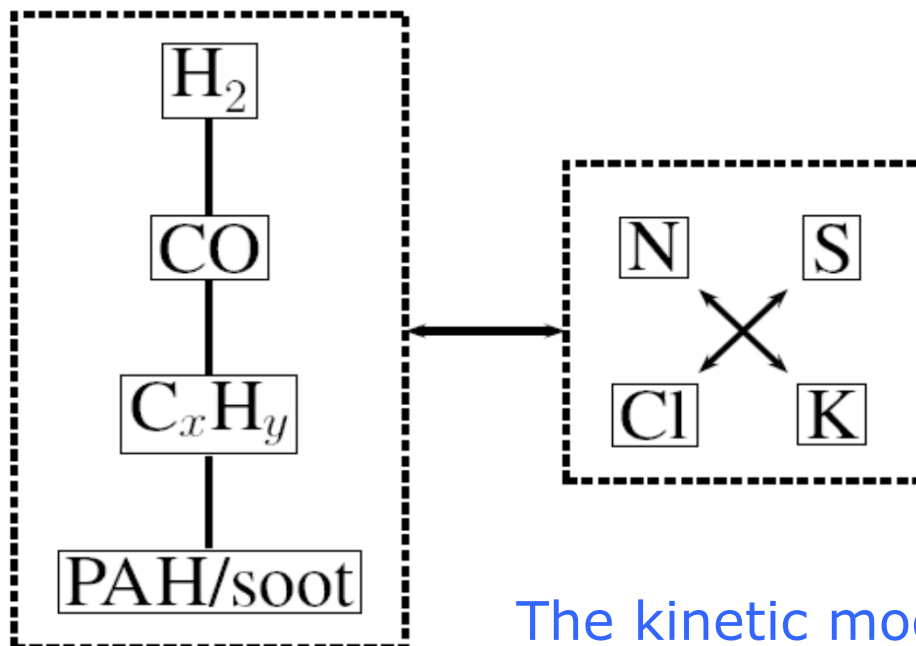
Reforming and fuel synthesis



Pyrolysis and gasification



Combustion chemistry



The kinetic models developed and refined over the years represent to a large extent our accumulated knowledge of combustion chemistry

Pillars of combustion research

- **Fundamental**

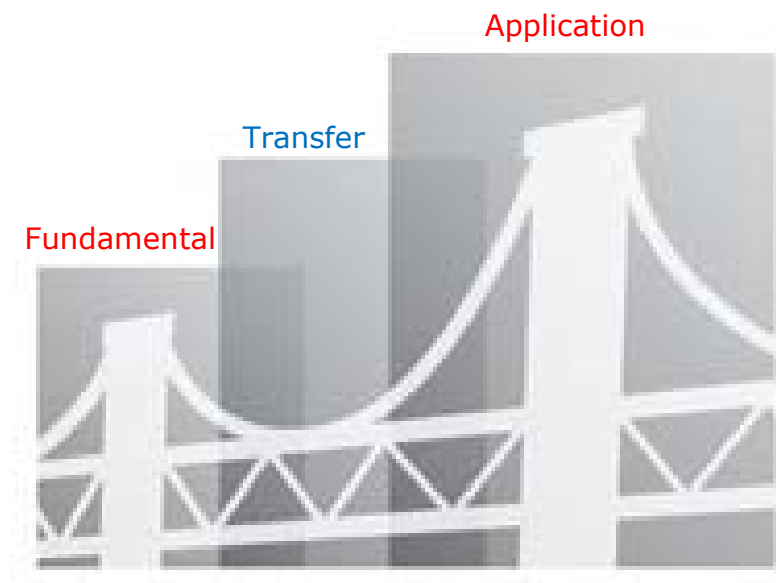
- develop a comprehensive, technology-independent chemical kinetic model for high-temperature gas-phase chemistry
- characterize key gas-solid and gas-to-solid reactions

- **Knowledge transfer**

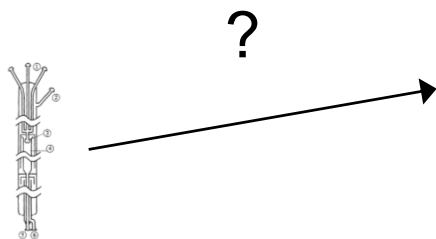
- facilitate industrial use of research results

- **Applied**

- meet the technical challenges of clean and sustainable thermal processes



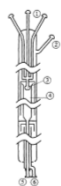
From molecular science to advanced technology



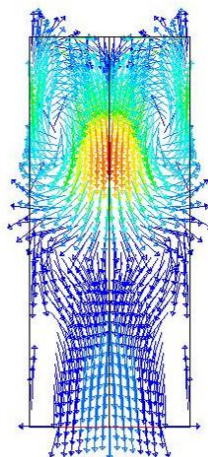
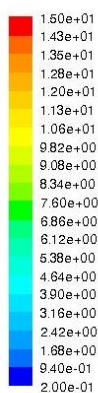
From molecular science to advanced technology



Semi-industrial scale experiments

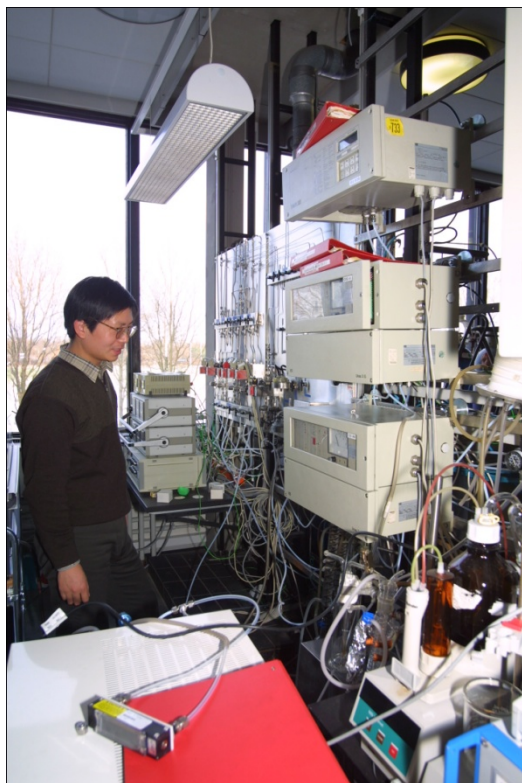


Model (CFD)



How do we work

Laboratory experiments



Pilot scale measurements



Full scale measurements



Model development

Your background?

Course material

- Power point presentations
- Exercise sets
- Note material
 - Excerpts from Kee, Coltrin and Glarborg: Chemically Reacting Flow – Theory and Practice (Wiley, 2000)

Program

Monday June 1

Introduction to course and basic kinetic concepts (PG)

Introduction to OpenSMOKE++ and pre-processing of kinetic mechanisms (AC)

Tuesday June 2

Reaction mechanisms (PG)

Task 1: Oxidation of aromatic compounds (AC)

Thursday June 4

Developing detailed chemical kinetic models (PG)

Task 2: Engine exhaust oxidation of unburned hydrocarbons (AC)

Friday June 5

Challenges in combustion chemistry (PG)

Numerical modeling of reacting flows with detailed kinetic mechanisms: challenges and perspectives (AC)

Task 3: Flame inhibitors (AC)

Objectives

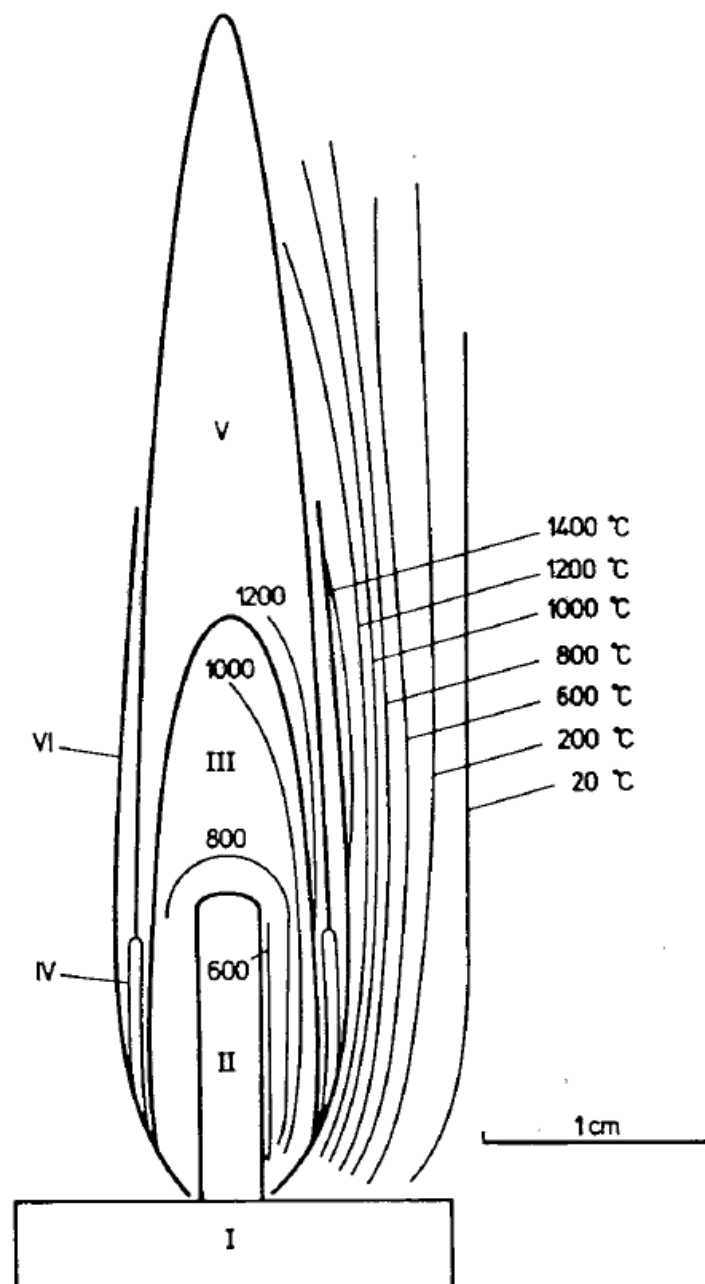
- Theory

- Learn fundamental concepts
- Understand different ways to represent chemistry in reacting flows
- Understand and model complex reactions
- Learn to develop and validate detailed reaction mechanisms

- Practice (hands-on)

- Learn and use OpenSmoke software package
- Solve practical problems using chemical kinetic modeling





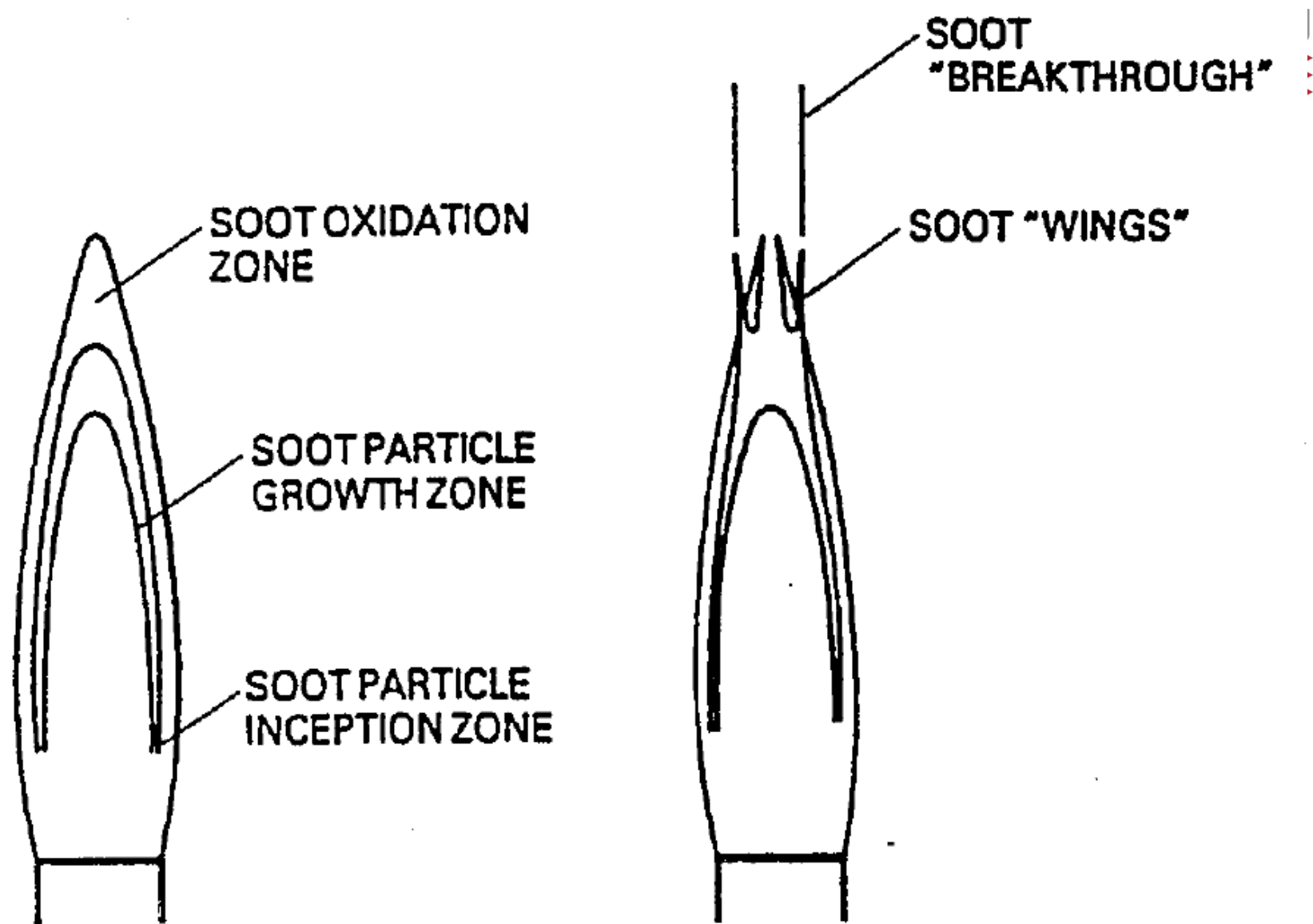
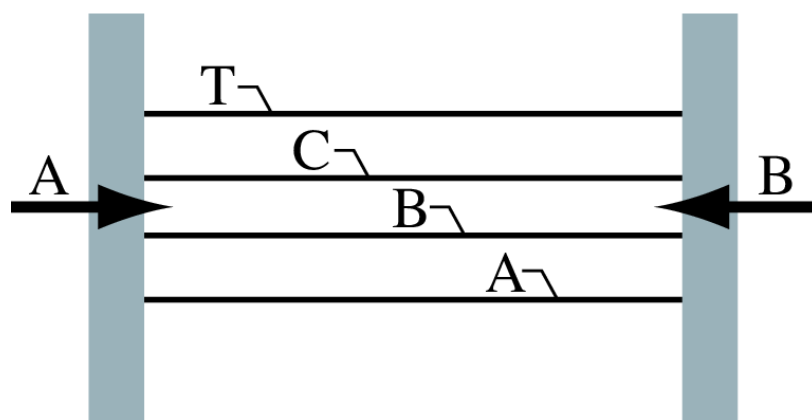


FIGURE 9.5

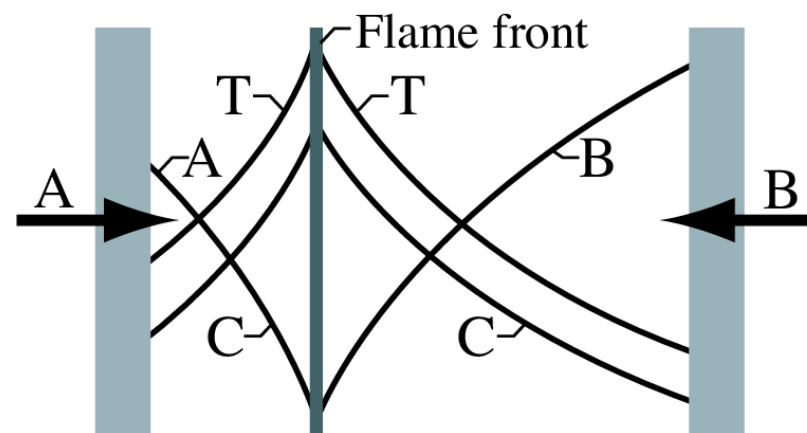
Soot formation and destruction zones in laminar jet flames.

Diffusion or kinetic control?



Kinetically controlled

Finite rate chemistry



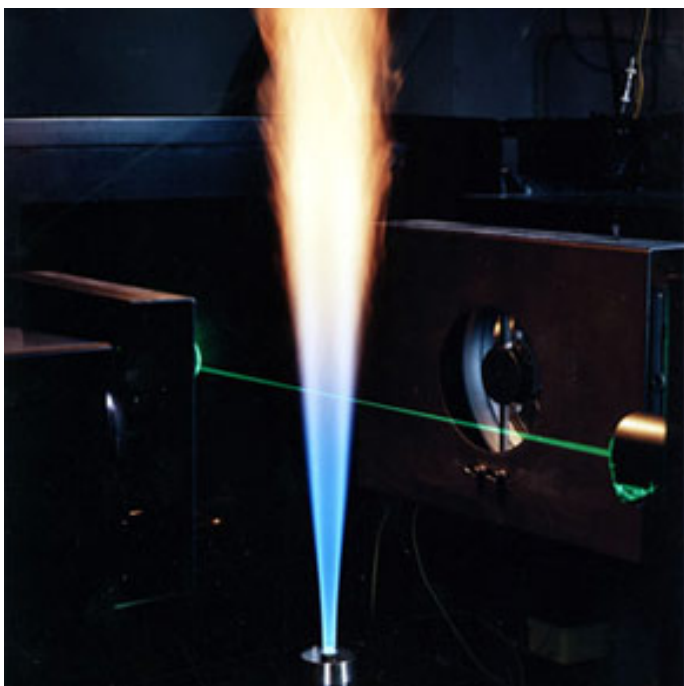
Diffusively controlled

Fast chemistry

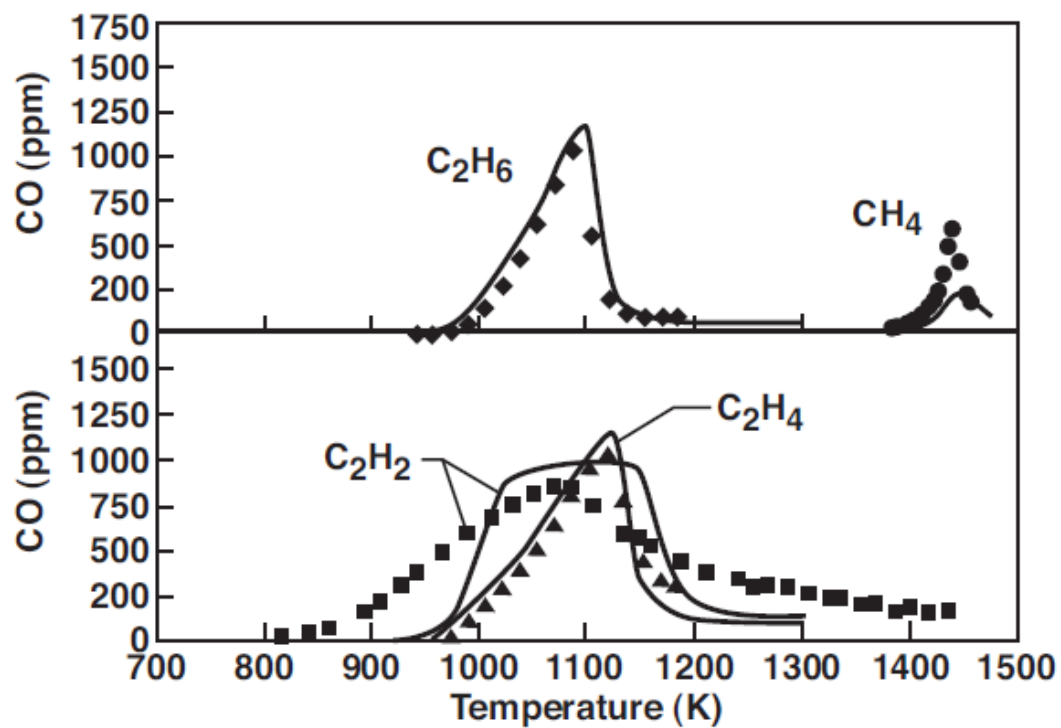
Gas-phase reactions

- Industry
 - Production of heat and power
 - Flue gas cleaning and incineration
 - Production of chemicals
 - Refinery processes
 - Materials synthesis
 - Hazard assessment
- Transportation
 - Engines
 - Turbines
- Atmospheric chemistry

Combustion of natural gas



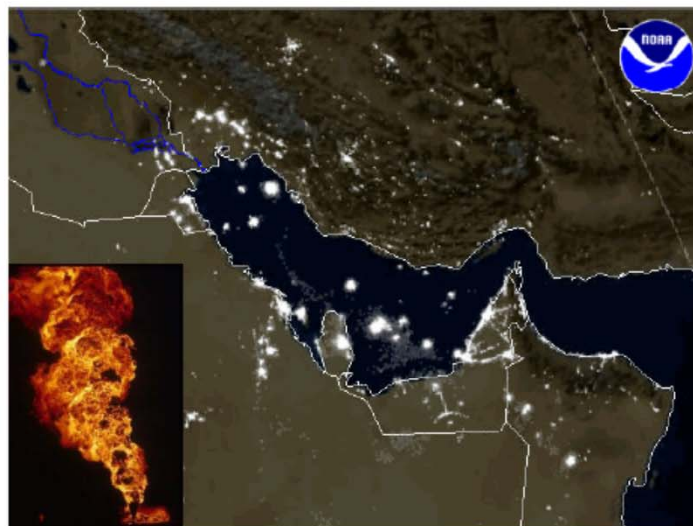
Sandia National Laboratories



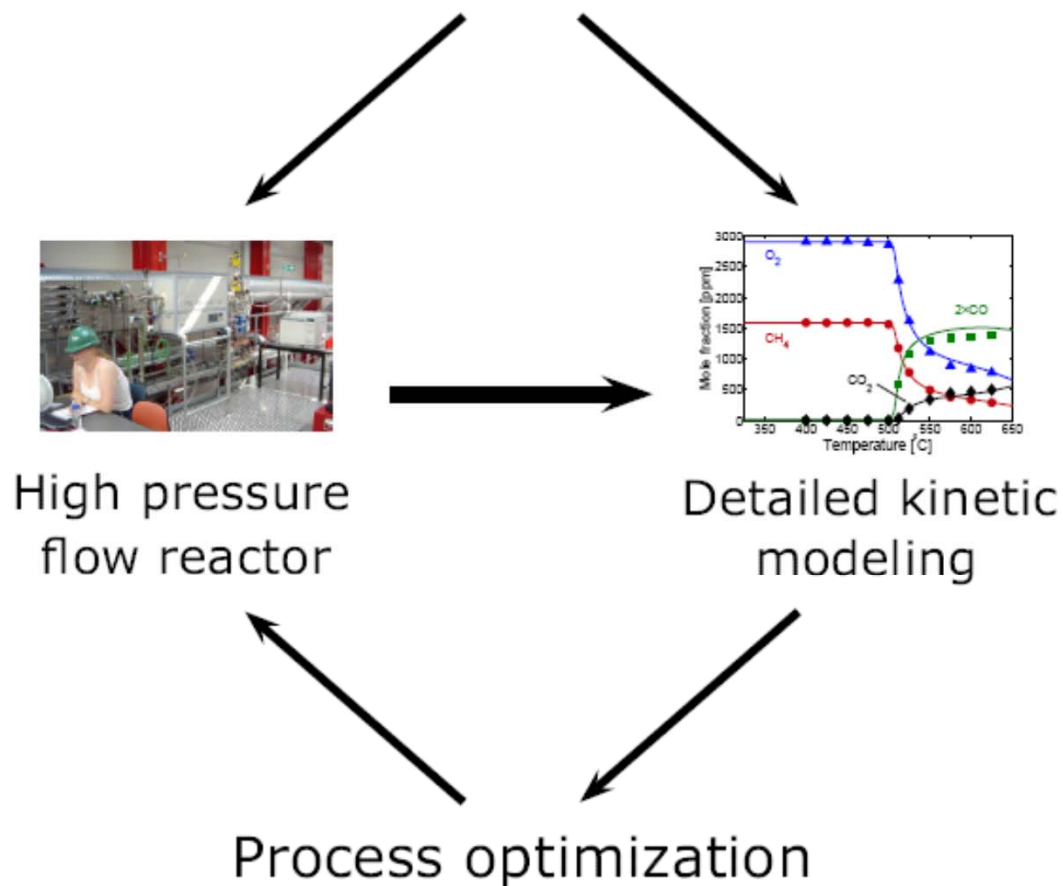
Kee et al. (2000)

GTL processes

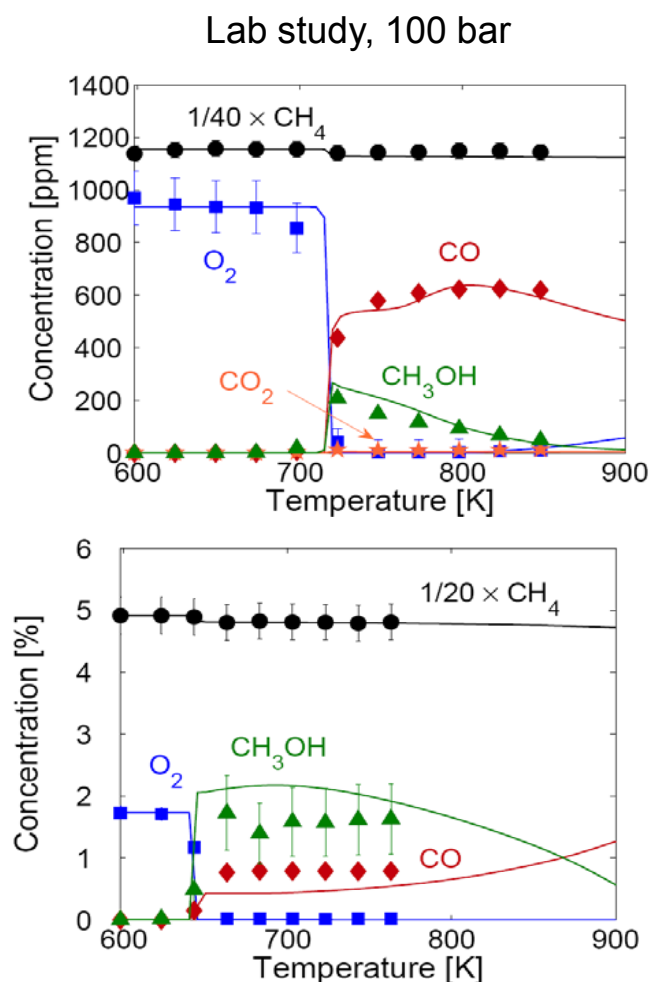
- Conversion of gas to liquid reduces transportation costs
- Direct homogeneous conversion is simple and cheap



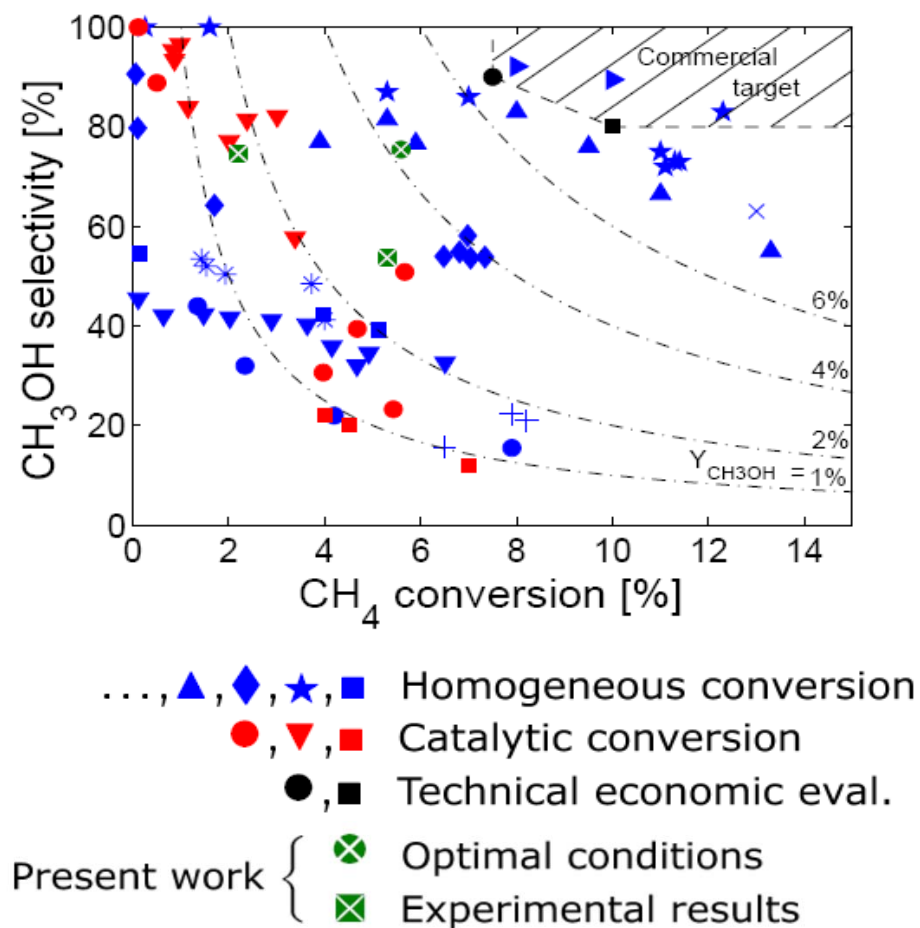
"Direct Partial Oxidation of Natural Gas to Liquid Chemicals"



Direct GTL partial oxidation of CH₄

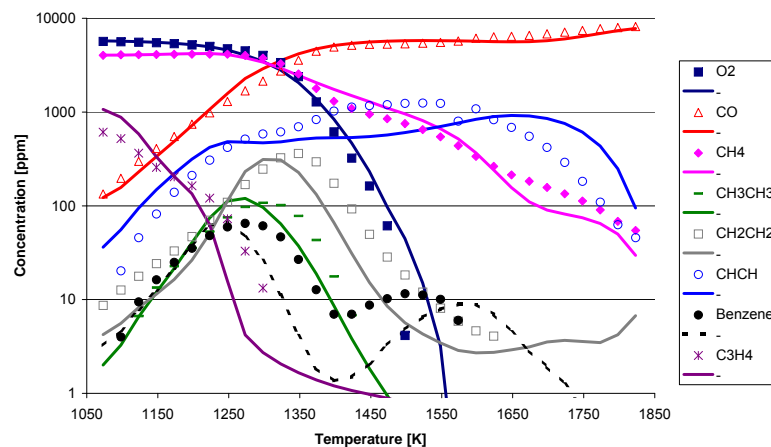
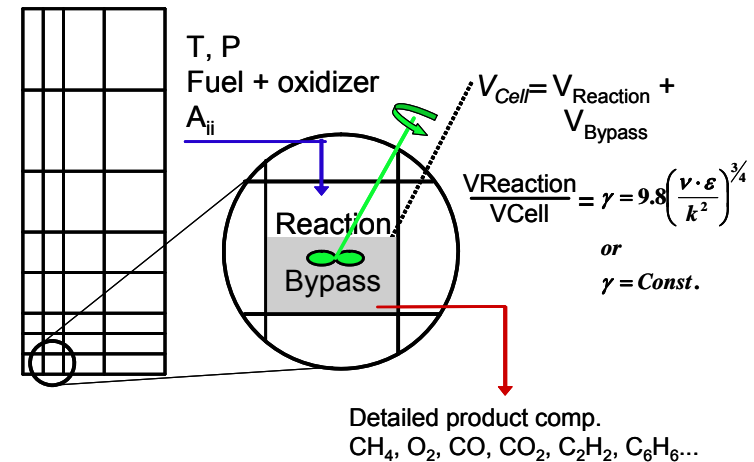
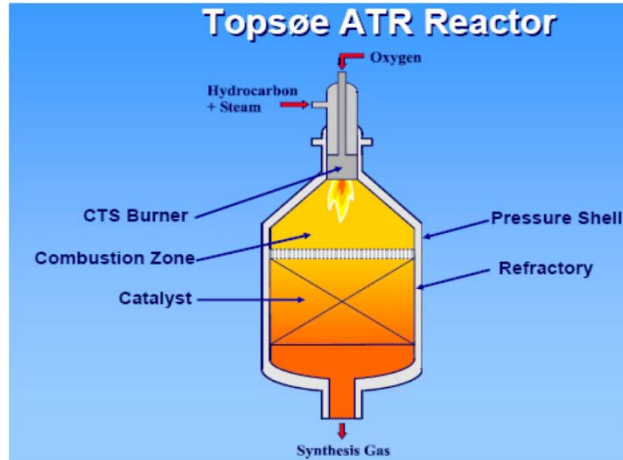


DTU Chemical Engineering, Technical University of Denmark

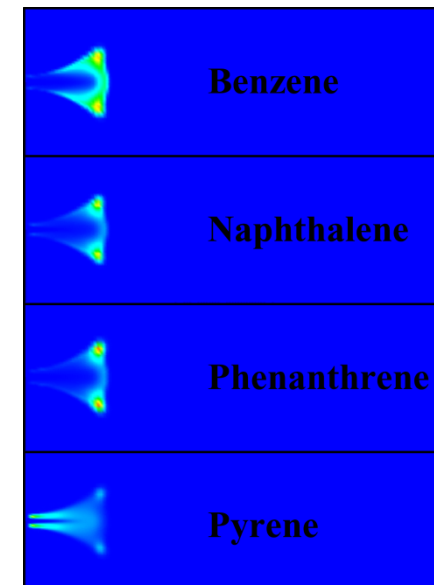


Rasmussen, 2007

Auto-thermal reforming: Prediction of soot propensity



DTU Chemical Engineering, Technical University of Denmark

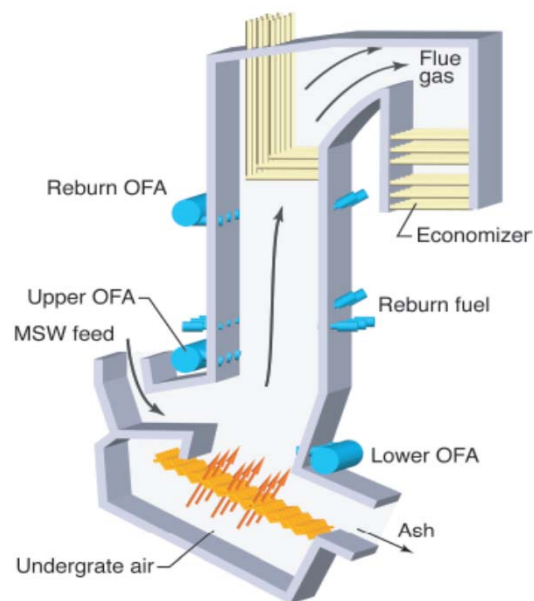


Reburning

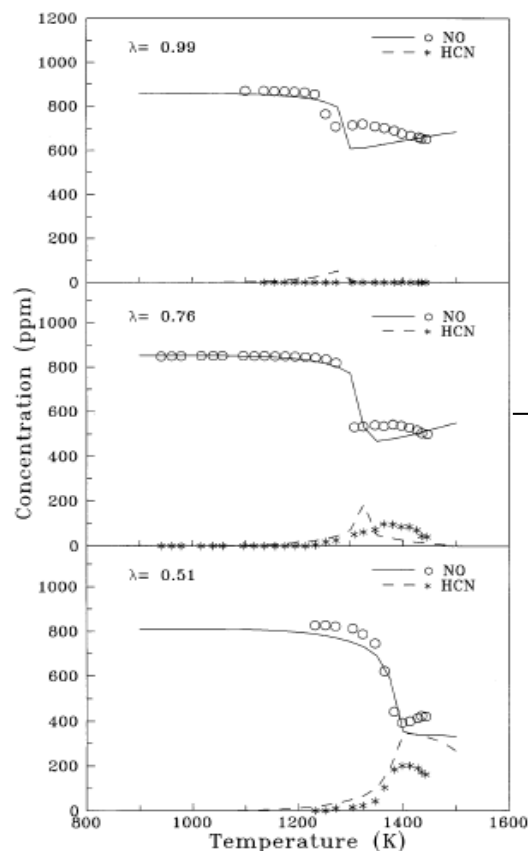
in-situ reduction of NO_x emissions in combustion

Experimental and modeling
study of reburning with CH_4

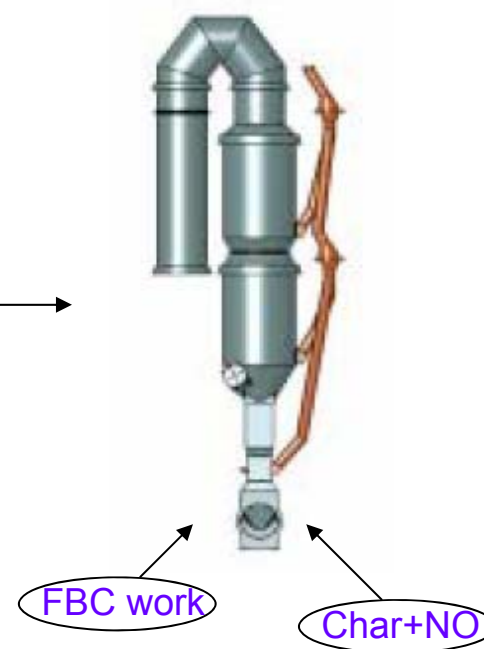
Reburning at SYSAV Municipal Waste Plant



DTU Chemical Engineering, Technical University of Denmark

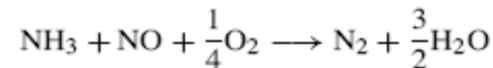


FLS Low- NO_x Calciner

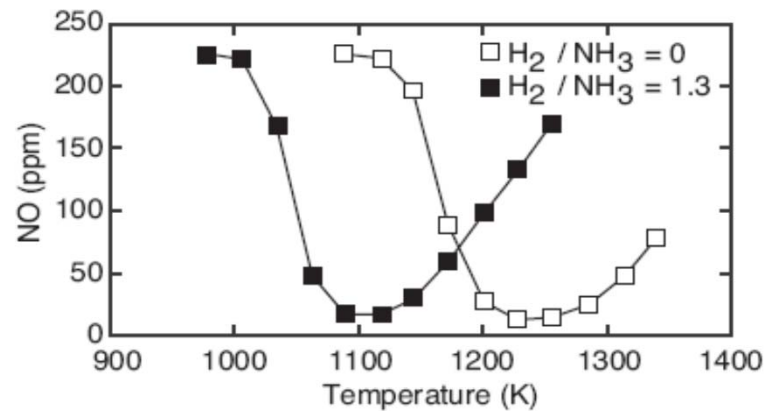


Selective Non-Catalytic Reduction

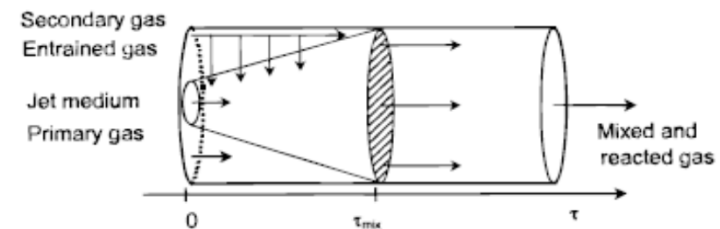
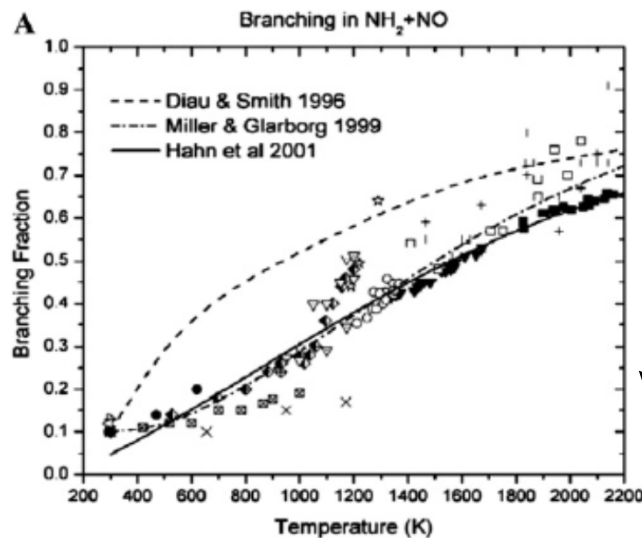
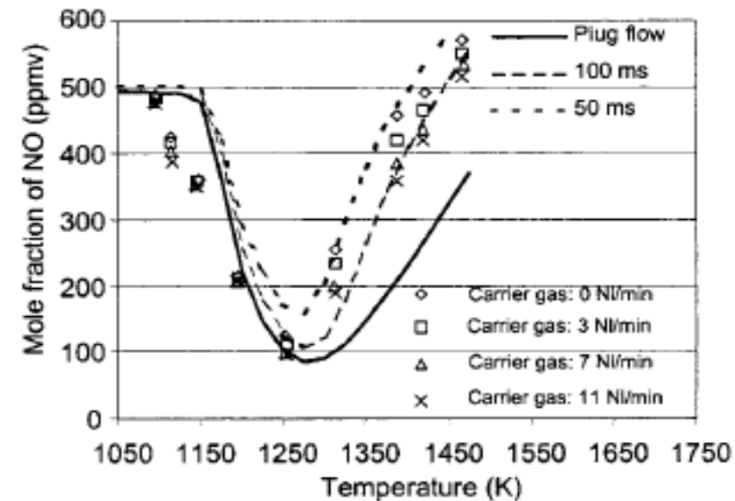
In-situ reduction of NO_x emissions



Lab-scale



Bench scale



Elementary reaction study

Reaction Mechanism: CH₂O Subset

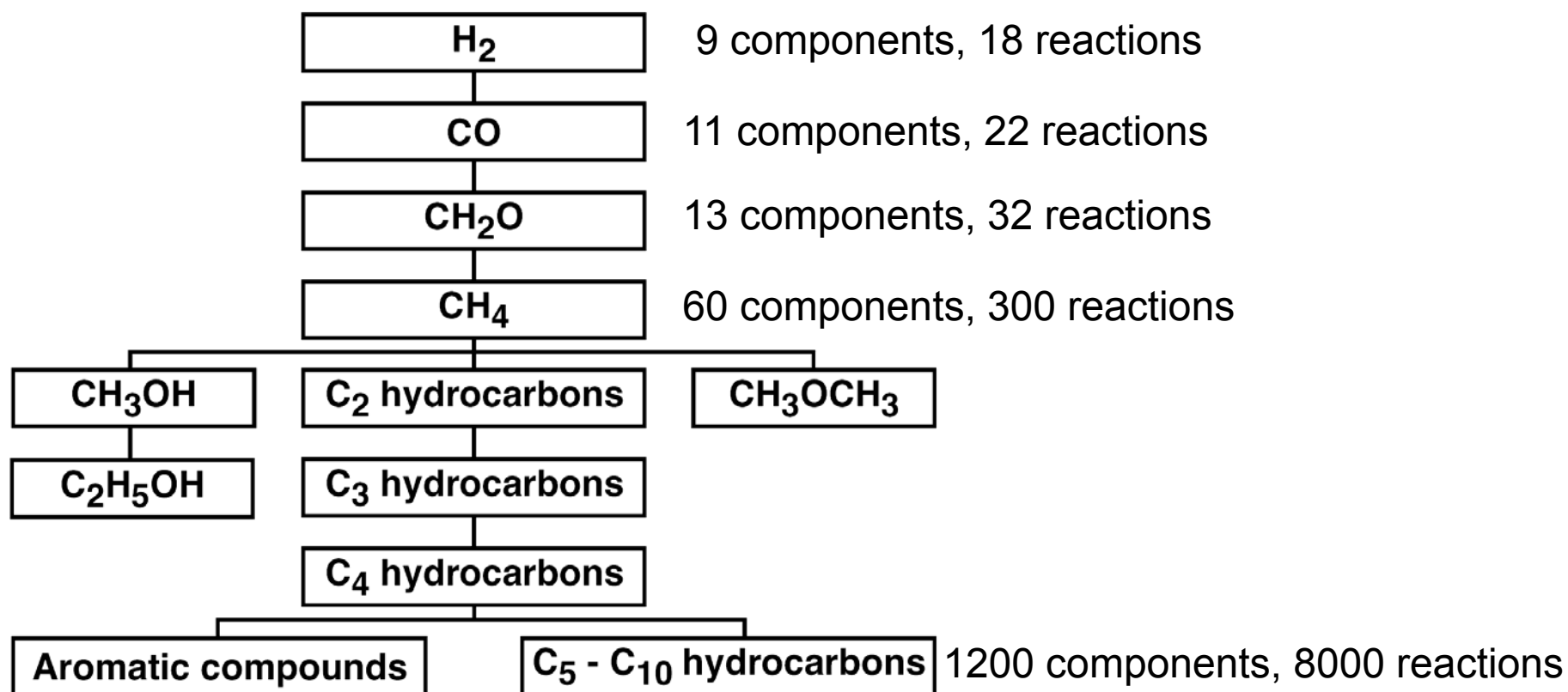
Reaction subset for CH₂O. Rate constants for reactions 21–24 are reported elsewhere [24].

		A [cm, mole, s]	β	E _a [cal/mole]	Source
1.	CH ₂ O + M \rightleftharpoons HCO + H + M ^a	6.1E15	0.00	76900	[28]
2.	CH ₂ O + M \rightleftharpoons CO + H ₂ + M ^a	2.8E15	0.00	63800	[28]
3.	CH ₂ O + H \rightleftharpoons HCO + H ₂	5.7E07	1.90	2740	[5]
4.	CH ₂ O + O \rightleftharpoons HCO + OH	1.8E13	0.00	3080	[31] ^b
5.	CH ₂ O + OH \rightleftharpoons HCO + H ₂ O	3.4E09	1.18	−447	[31] ^b
6.	CH ₂ O + HO ₂ \rightleftharpoons HCO + H ₂ O ₂	4.1E04	2.50	10200	[32]
7.	CH ₂ O + O ₂ \rightleftharpoons HCO + HO ₂	5.0E04	3.00	39000	see text
8.	HCO + M \rightleftharpoons H + CO + M ^a	4.8E17	−1.20	17700	[46]
9.	HCO + H \rightleftharpoons CO + H ₂	1.2E13	0.25	0	[24] ^b
10.	HCO + O \rightleftharpoons CO + OH	3.0E13	0.00	0	[34] ^b
11.	HCO + O \rightleftharpoons CO ₂ + H	3.0E13	0.00	0	[34] ^b
12.	HCO + OH \rightleftharpoons CO + H ₂ O	1.0E14	0.00	0	[34] ^b
13.	HCO + HO ₂ \rightleftharpoons CO ₂ + OH + H	3.0E13	0.00	0	[31]
14.	HCO + O ₂ \rightleftharpoons CO + HO ₂	3.4E12	0.00	0	[45]
15.	HCO + HCO \rightleftharpoons CO + CH ₂ O	3.0E13	0.00	0	[29]
16.	CH ₂ O + NO ₂ \rightleftharpoons HCO + HONO	8.0E02	2.77	13730	[54] ^b
17.	HCO + NO \rightleftharpoons CO + HNO	7.0E13	−0.40	0	[44]
18.	HCO + HNO \rightleftharpoons NO + CH ₂ O	6.0E11	0.00	2000	[54] ^b
19.	HCO + NO ₂ \rightleftharpoons CO + HONO	1.2E23	−3.29	2355	[54] ^b
20.	HCO + NO ₂ \rightleftharpoons H + CO ₂ + NO	8.4E15	−0.75	1930	[54] ^b
25.	NO ₂ + HO ₂ \rightleftharpoons HONO + O ₂	6.3E08	1.25	5000	[48]
26.	HNO + O ₂ \rightleftharpoons NO + HO ₂	2.0E13	0.00	16000	[55]

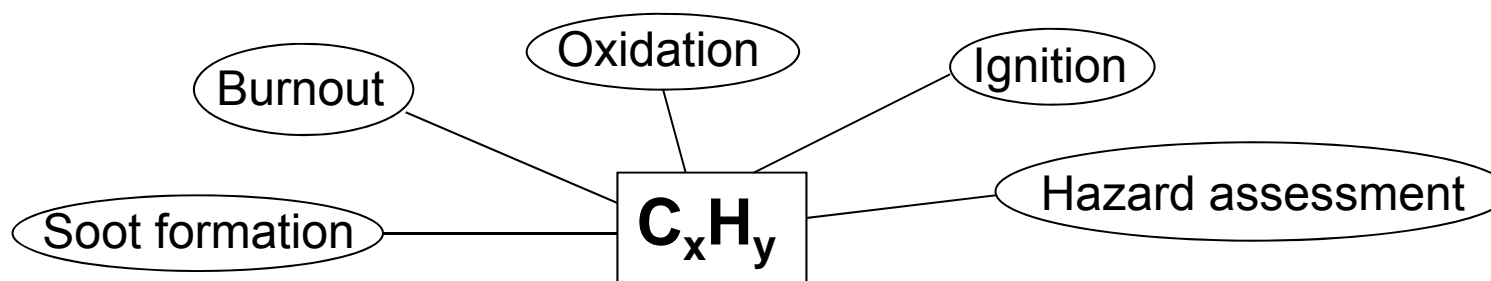
^a Enhanced third-body efficiencies: H₂O = 5.

^b Adopted from Glarborg et al. [24]

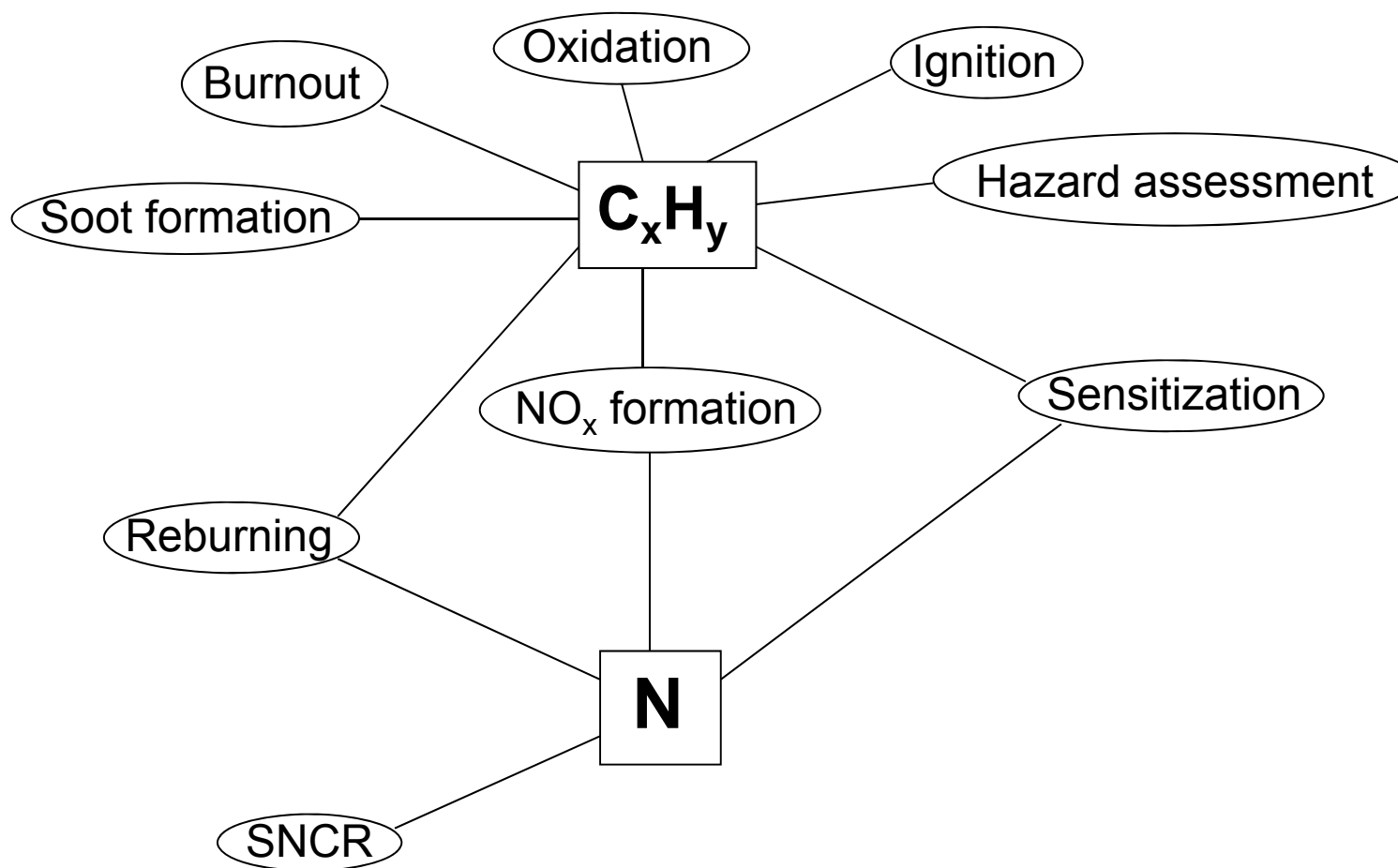
Hierarchical structure of oxidation mechanisms



Hydrocarbon reaction mechanism - comprehensive modeling tool

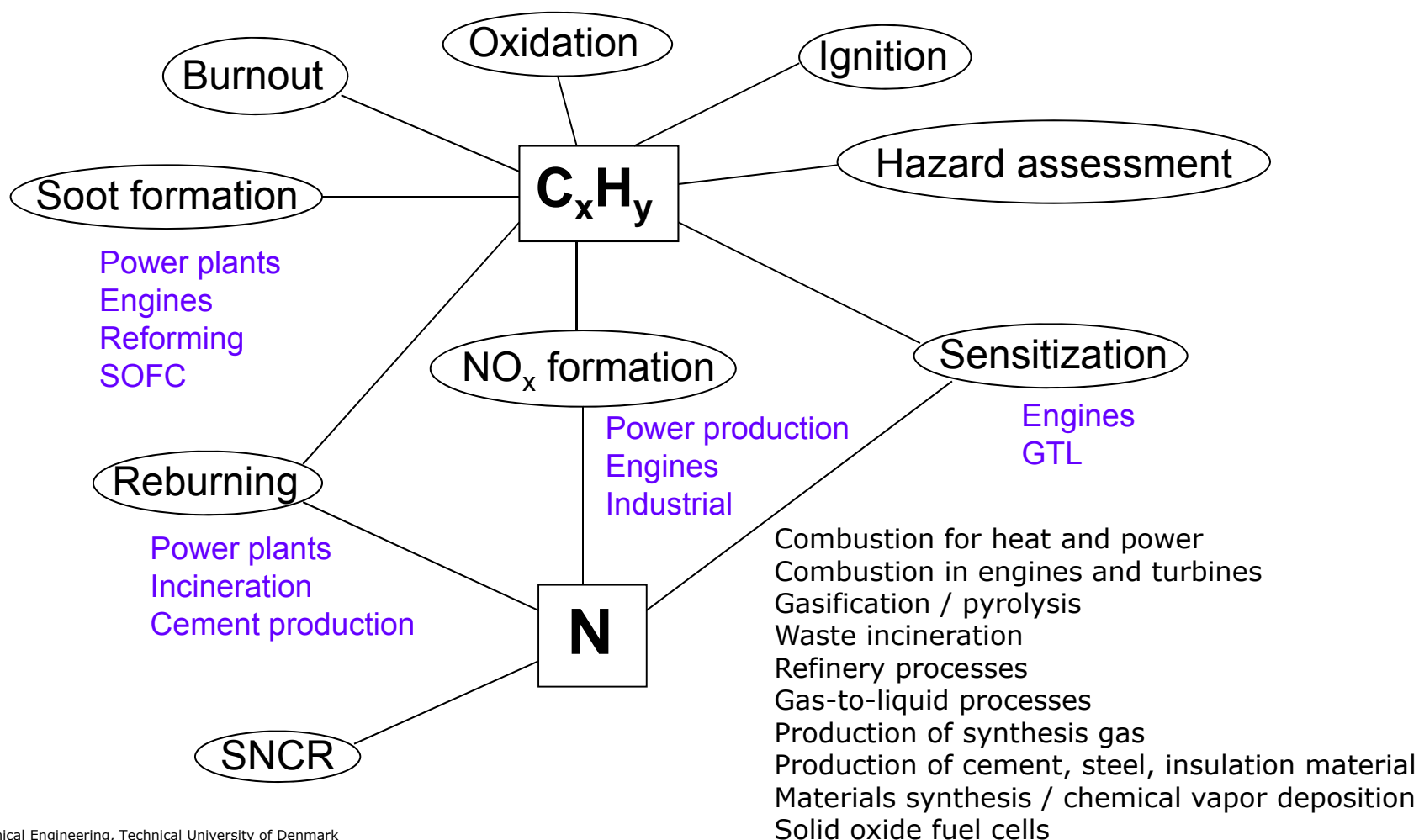


Hydrocarbon/nitrogen reaction mechanism - comprehensive modeling tool



Hydrocarbon/nitrogen reaction mechanism

- technology independent modeling tool



Models of chemical reaction

- Fast chemistry
 - “Mixed is burnt”
 - Chemical equilibrium
- Finite rate chemistry
 - Global reactions
 - Analytically reduced mechanisms
 - Detailed elementary reaction mechanisms

Finite Rate Chemistry

- 2-step global (e.g. Westbrook-Dryer)
 - $\text{CH}_4 + 1.5\text{O}_2 \rightarrow \text{CO} + 2\text{H}_2\text{O}$
 - $\text{CO} + \frac{1}{2}\text{O}_2 \rightleftharpoons \text{CO}_2$
- Reduced mechanism (e.g. Jones-Lindstedt)
 - $\text{CH}_4 + \frac{1}{2}\text{O}_2 \rightarrow \text{CO} + 2\text{H}_2$
 - $\text{CH}_4 + \text{H}_2\text{O} \rightarrow \text{CO} + 3\text{H}_2$
 - $\text{H}_2 + \frac{1}{2}\text{O}_2 \rightleftharpoons \text{H}_2\text{O}$
 - $\text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2$
- Full mechanism
 - E.g., 32 species and 156 reactions

Single-step global rate parameters

TABLE 5.1
Single-step reaction rate parameters for use with Eqn. 5.2. (Adapted from Ref. [6])

Fuel	Pre-exponential factor, A^a	Activation temperature, E_a/R_a (K)	m	n
CH ₄	$1.3 \cdot 10^8$	24,358 ^b	-0.3	1.3
CH ₄	$8.3 \cdot 10^5$	15,098 ^c	-0.3	1.3
C ₂ H ₆	$1.1 \cdot 10^{12}$	15,098	0.1	1.65
C ₃ H ₈	$8.6 \cdot 10^{11}$	15,098	0.1	1.65
C ₄ H ₁₀	$7.4 \cdot 10^{11}$	15,098	0.15	1.6
C ₅ H ₁₂	$6.4 \cdot 10^{11}$	15,098	0.25	1.5
C ₆ H ₁₄	$5.7 \cdot 10^{11}$	15,098	0.25	1.5
C ₇ H ₁₆	$5.1 \cdot 10^{11}$	15,098	0.25	1.5
C ₈ H ₁₈	$4.6 \cdot 10^{11}$	15,098	0.25	1.5
C ₈ H ₁₈	$7.2 \cdot 10^{12}$	20,131 ^d	0.25	1.5
C ₉ H ₂₀	$4.2 \cdot 10^{11}$	15,098	0.25	1.5
C ₁₀ H ₂₂	$3.8 \cdot 10^{11}$	15,098	0.25	1.5
CH ₃ OH	$3.2 \cdot 10^{12}$	15,098	0.25	1.5
C ₂ H ₅ OH	$1.5 \cdot 10^{12}$	15,098	0.15	1.6
C ₆ H ₆	$2.0 \cdot 10^{11}$	15,098	-0.1	1.85
C ₇ H ₈	$1.6 \cdot 10^{11}$	15,098	-0.1	1.85
C ₂ H ₄	$2.0 \cdot 10^{12}$	15,098	0.1	1.65
C ₃ H ₆	$4.2 \cdot 10^{11}$	15,098	-0.1	1.85
C ₂ H ₂	$6.5 \cdot 10^{12}$	15,098	0.5	1.25

^aUnits of A are consistent with concentrations in Eqn. 5.1 expressed in units of gmol/cm³, i.e., $A [=]$ (gmol/cm³)^{1-m-n}/s.

^b $E_a = 48.4$ kcal/gmol.

^c $E_a = 30$ kcal/gmol.

^d $E_a = 40$ kcal/gmol.

Global reaction



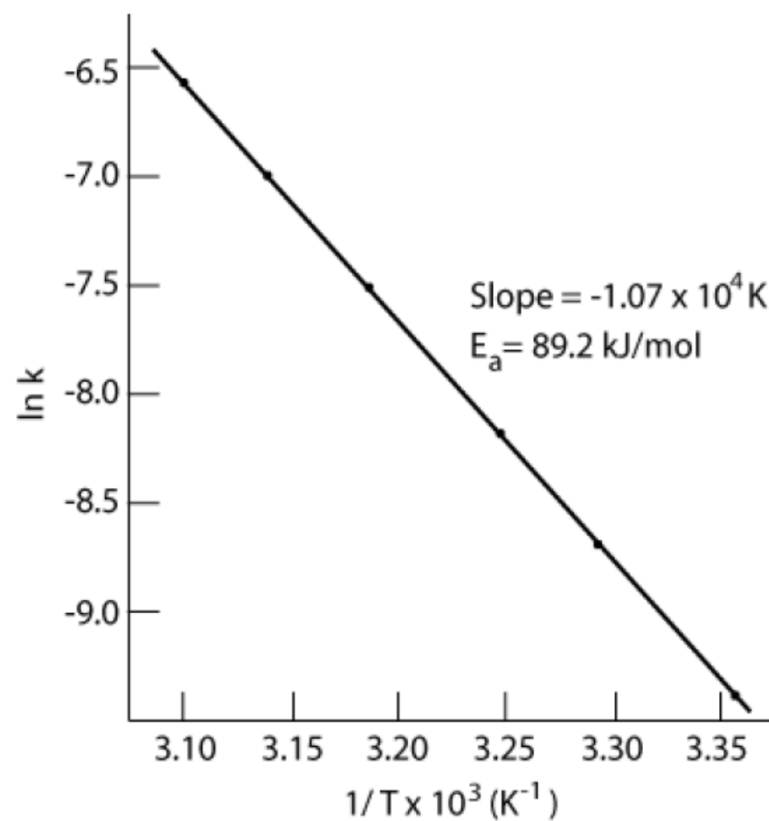
Global rate expression for CO oxidation:

$$-R_{\text{CO}} = k [\text{CO}]^a [\text{O}_2]^b$$

- Rate constant $k = A \exp(-E_a/RT)$ (Arrhenius)
- Reaction order $a+b$
- Parameters k, a, b are empirical

Arrhenius expression

$$k = A \exp(-E_a/RT)$$



Global reaction



Global rate expression for CO oxidation:

$$\begin{aligned} -R_{\text{CO}} &= k [\text{CO}]^a [\text{O}_2]^b \\ &= 1.3 \times 10^{10} \exp(-20130/T) [\text{CO}] [\text{O}_2]^{0.25} [\text{H}_2\text{O}]^{0.5} \end{aligned}$$

Reactor design exercise



1 atm

Global rate expression for CO oxidation:

$$-R_{\text{CO}} = 1.3 \times 10^{10} \exp(-20130/T) [\text{CO}] [\text{O}_2]^{0.25} [\text{H}_2\text{O}]^{0.5}$$

Task: design a high-pressure reactor that ensures oxidation of CO

Reactor design

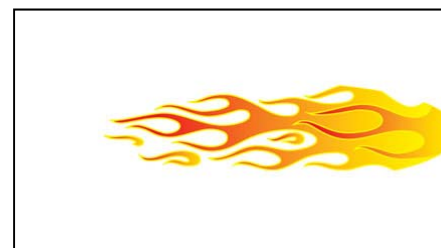


1 atm

$$-R_{\text{CO}} = 1.3 \times 10^{10} \exp(-20130/T) [\text{CO}] [\text{O}_2]^{0.25} [\text{H}_2\text{O}]^{0.5}$$

$$-R_{\text{CO}} \text{ proportional to } [\text{M}]^{1.75} \text{ and thereby } P^{1.75}$$

Design suggestion



10 atm

CO oxidation

Experimental results: effect of pressure

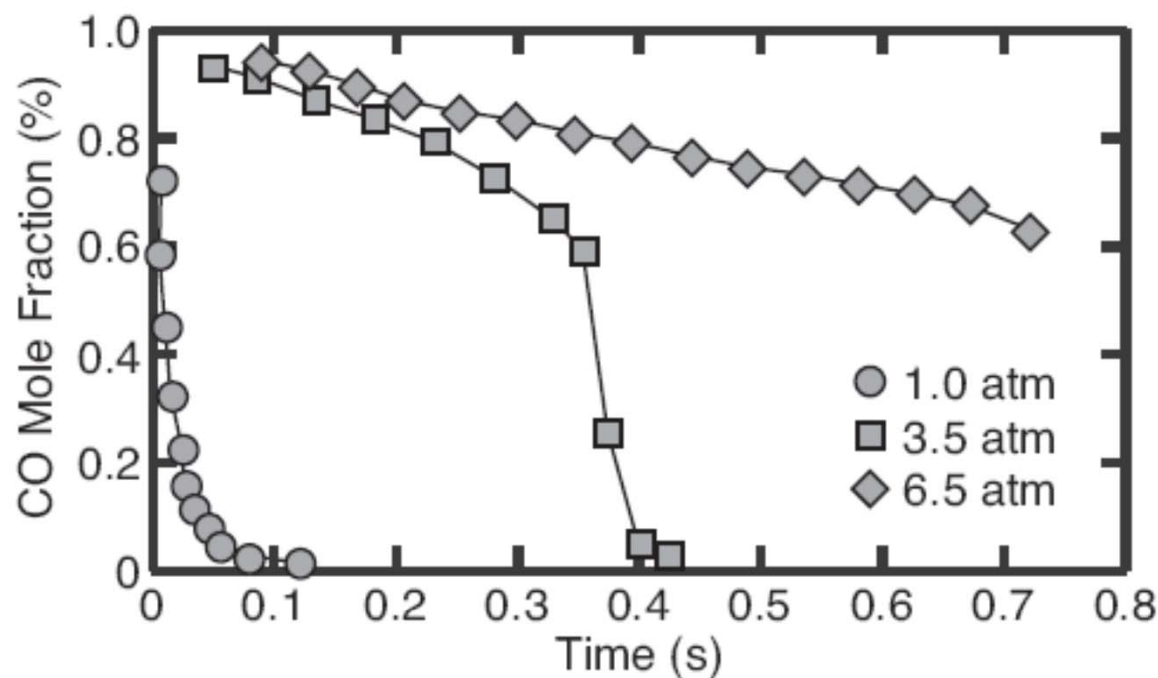


Fig. 13.3 Laboratory flow reactor experiments on carbon monoxide oxidation as function of pressure [226]. The initial temperature is 1040 K and the initial mole fractions are 1.0% CO, 0.5% O₂, and 0.65% H₂O, with the balance N₂.

Reactor design



1 atm

Based on experimental evidence:



10 atm

Elementary reaction



Rate expression for CO oxidation:

$$-R_{\text{CO}} = k [\text{CO}][\text{OH}]$$

- Rate constant $k = A T^{\beta} \exp(-E_a/RT)$
- Bimolecular reaction
- Reactor order according to stoichiometric coefficients
- Parameter k is empirical

Arrhenius plot for CO + OH

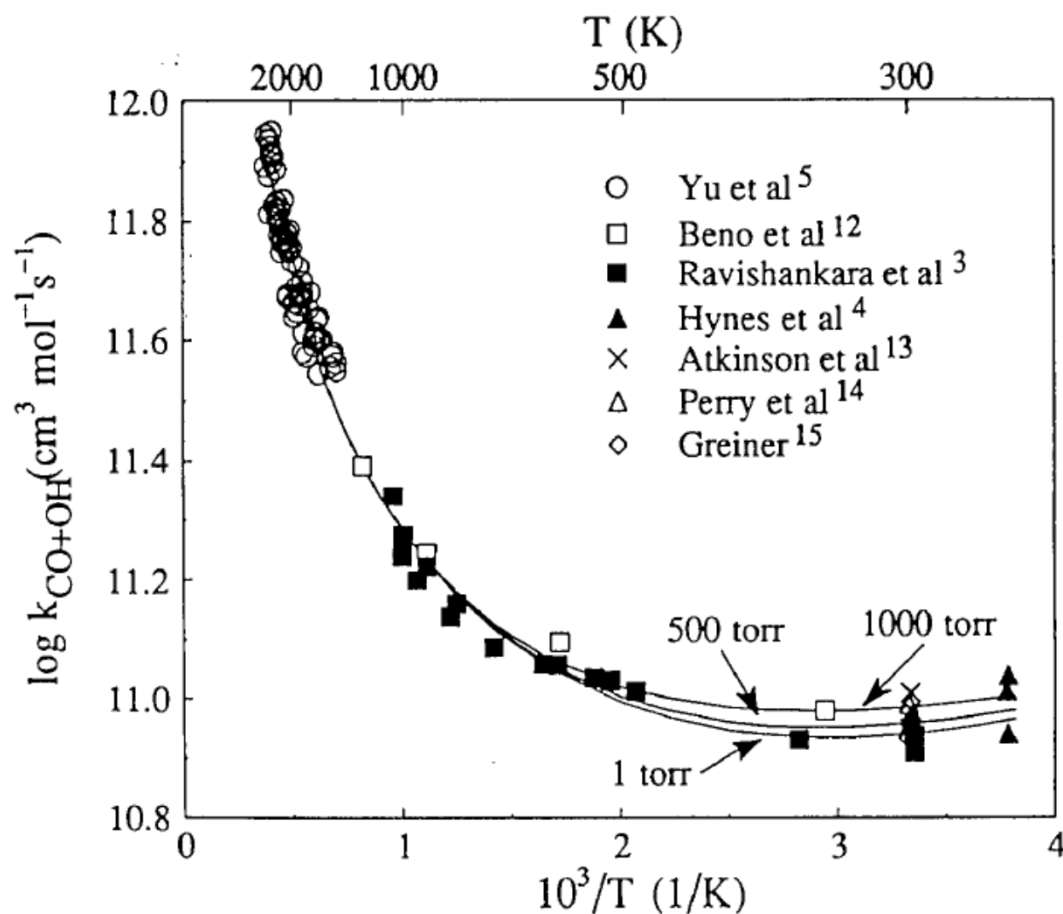


Figure 2. Arrhenius plot for the rate coefficient of reaction CO + OH; buffer gas is argon.

$$k = A T^{\beta} \exp(-E_a/RT)$$

Molecularity of elementary reactions

- Unimolecular (decay) $A \rightarrow P$

$$-\dot{A} = k_1 [A]$$

- Bimolecular (collision) $A + B \rightarrow P$

$$-\dot{A} = k_2 [A] [B]$$

- Termolecular (collision) $A + B + C \rightarrow P$

$$-\dot{A} = k_3 [A] [B] [C]$$

$$-\dot{A} = k_3 [A] [B] [M]$$

Why \dot{A} and not $d[A]/dt$?

CO oxidation

- Global reaction



- Elementary reaction



- Proceeds as written
- As a rule, does not break/form more than one chemical bond
- Seldom involves more than two reactants (may also involve collision partner)

Reaction Mechanism: CH₂O Subset

Reaction subset for CH₂O. Rate constants for reactions 21–24 are reported elsewhere [24].

		A [cm, mole, s]	β	E _a [cal/mole]	Source
1.	CH ₂ O + M \rightleftharpoons HCO + H + M ^a	6.1E15	0.00	76900	[28]
2.	CH ₂ O + M \rightleftharpoons CO + H ₂ + M ^a	2.8E15	0.00	63800	[28]
3.	CH ₂ O + H \rightleftharpoons HCO + H ₂	5.7E07	1.90	2740	[5]
4.	CH ₂ O + O \rightleftharpoons HCO + OH	1.8E13	0.00	3080	[31] ^b
5.	CH ₂ O + OH \rightleftharpoons HCO + H ₂ O	3.4E09	1.18	−447	[31] ^b
6.	CH ₂ O + HO ₂ \rightleftharpoons HCO + H ₂ O ₂	4.1E04	2.50	10200	[32]
7.	CH ₂ O + O ₂ \rightleftharpoons HCO + HO ₂	5.0E04	3.00	39000	see text
8.	HCO + M \rightleftharpoons H + CO + M ^a	4.8E17	−1.20	17700	[46]
9.	HCO + H \rightleftharpoons CO + H ₂	1.2E13	0.25	0	[24] ^b
10.	HCO + O \rightleftharpoons CO + OH	3.0E13	0.00	0	[34] ^b
11.	HCO + O \rightleftharpoons CO ₂ + H	3.0E13	0.00	0	[34] ^b
12.	HCO + OH \rightleftharpoons CO + H ₂ O	1.0E14	0.00	0	[34] ^b
13.	HCO + HO ₂ \rightleftharpoons CO ₂ + OH + H	3.0E13	0.00	0	[31]
14.	HCO + O ₂ \rightleftharpoons CO + HO ₂	3.4E12	0.00	0	[45]
15.	HCO + HCO \rightleftharpoons CO + CH ₂ O	3.0E13	0.00	0	[29]
16.	CH ₂ O + NO ₂ \rightleftharpoons HCO + HONO	8.0E02	2.77	13730	[54] ^b
17.	HCO + NO \rightleftharpoons CO + HNO	7.0E13	−0.40	0	[44]
18.	HCO + HNO \rightleftharpoons NO + CH ₂ O	6.0E11	0.00	2000	[54] ^b
19.	HCO + NO ₂ \rightleftharpoons CO + HONO	1.2E23	−3.29	2355	[54] ^b
20.	HCO + NO ₂ \rightleftharpoons H + CO ₂ + NO	8.4E15	−0.75	1930	[54] ^b
25.	NO ₂ + HO ₂ \rightleftharpoons HONO + O ₂	6.3E08	1.25	5000	[48]
26.	HNO + O ₂ \rightleftharpoons NO + HO ₂	2.0E13	0.00	16000	[55]

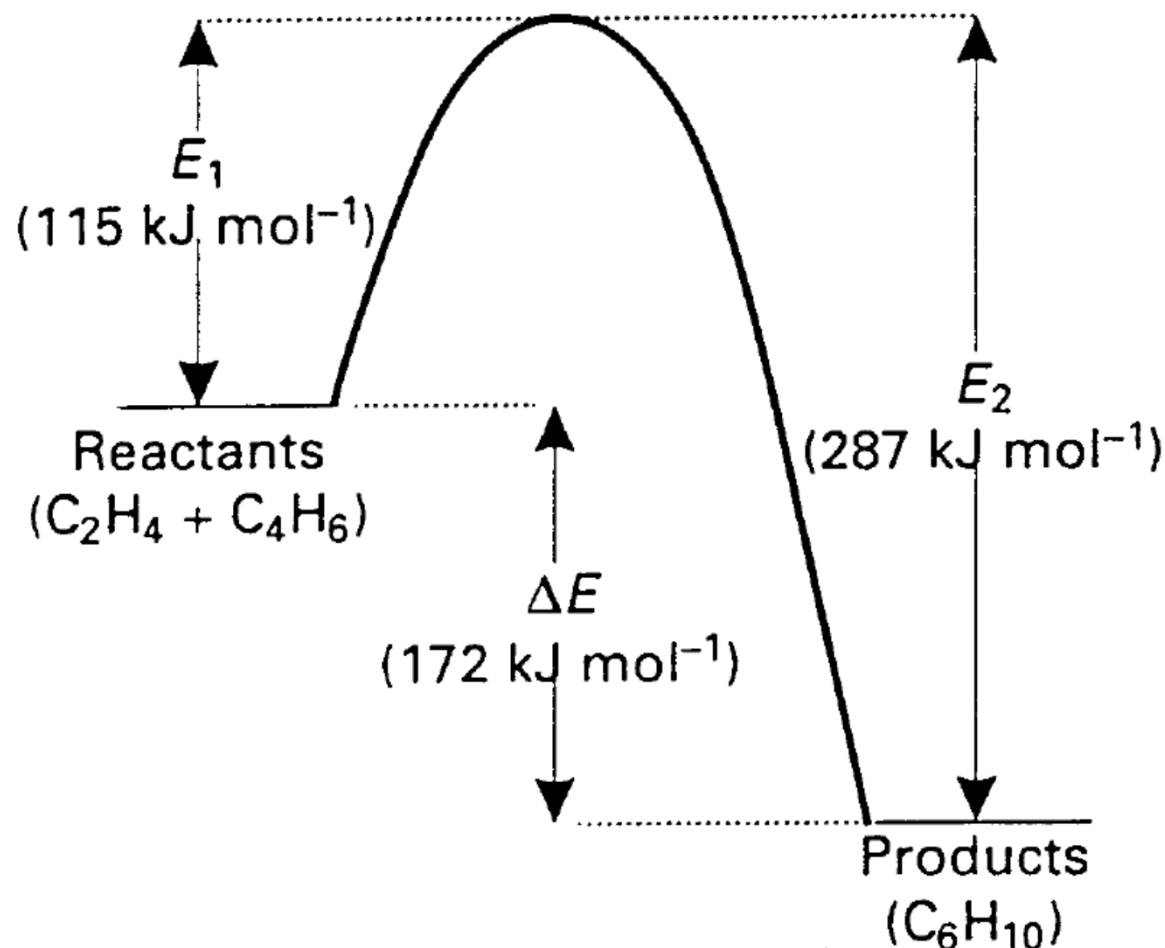
^a Enhanced third-body efficiencies: H₂O = 5.

^b Adopted from Glarborg et al. [24]

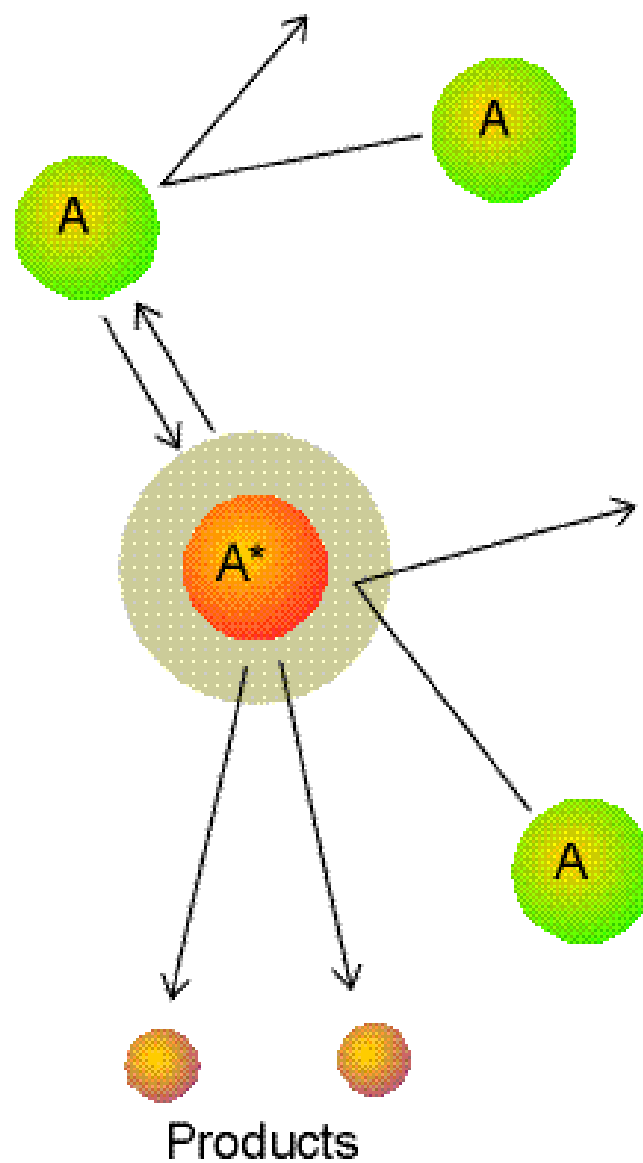
Some fundamentals

- Temperature dependence of reaction
 - Arrhenius expression
$$k = A T^{\beta} \exp(-E_a/RT)$$
- Pressure dependence of reaction rate
 - Lindemann
 - Troe
 - PLOG format
- Kinetics and thermodynamics
$$K_C = k_f / k_r$$

Relationship between forward and reverse activation energies

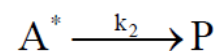
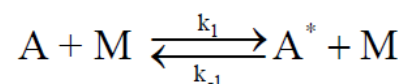


The Lindemann mechanism



Pressure dependent reactions

Lindemann format:



$$k_{\text{uni}} = \frac{k_2 k_1 [M]}{k_{-1} [M] + k_2}$$

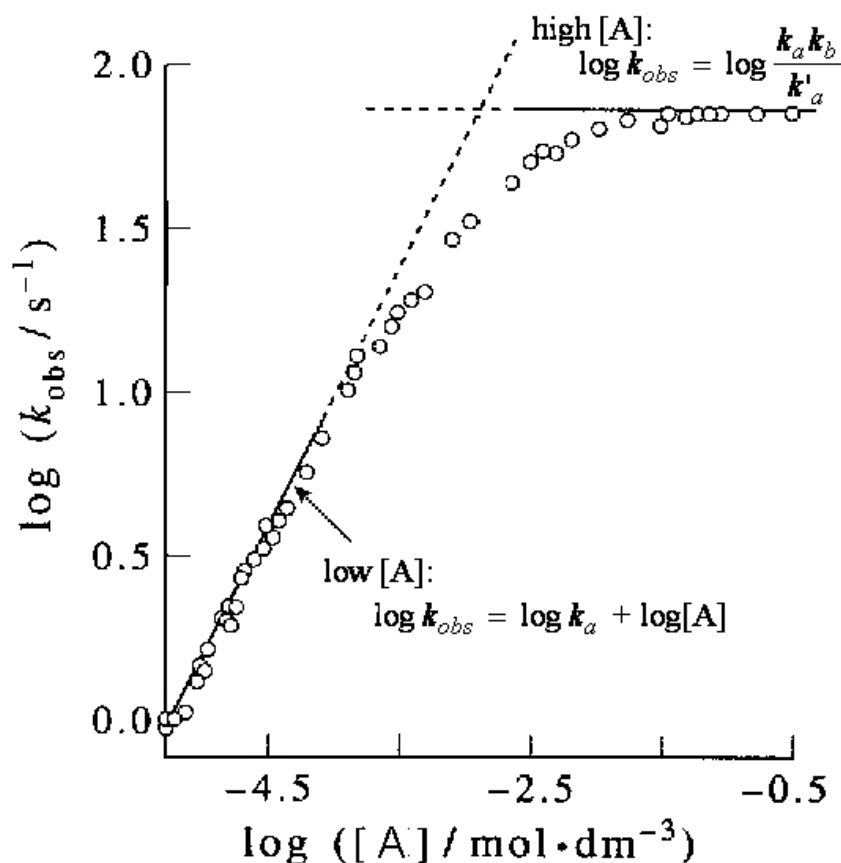
High pressure limit ($[M] \rightarrow \infty$): $k_{\infty} = \frac{k_1}{k_{-1}} k_2$

$$\frac{d[A]}{dt} = k_{\infty} [A] \quad (1. \text{ order})$$

Low pressure limit ($[M] \rightarrow 0$): $k_0 = k_1$

$$\frac{d[A]}{dt} = k_0 [A] [M] \quad (2. \text{ order})$$

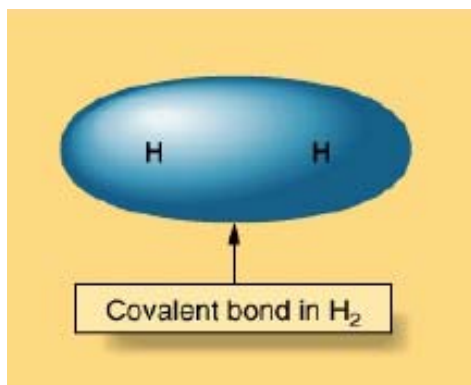
$$k_{\text{uni}} = \frac{k_2 k_1 [M]}{k_{-1} [M] + k_2} = \frac{k_{\infty}}{1 + k_{\infty} / (k_0 [M])}$$



Stable molecules

Hydrogen (H_2):

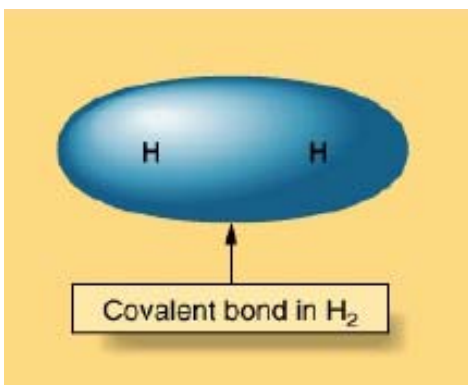
- Stable molecule
- Comparatively unreactive
- Can be stored in a box



Stable molecules and chain carriers

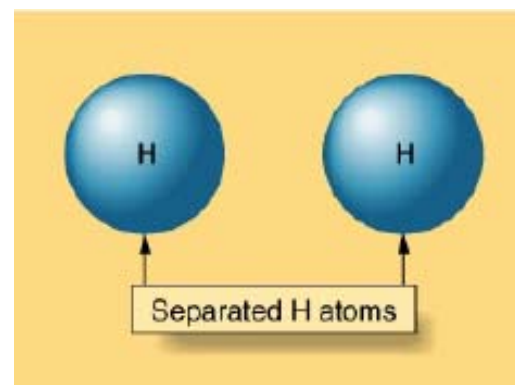
Hydrogen (H_2):

- Stable molecule
- Comparatively unreactive
- Can be stored in a box



Hydrogen atom (H):

- Radical (unpaired electrons)
- Reactive
- Cannot be stored



Chain carrier