Introduction to Chemical Kinetics for Combustion

PART I

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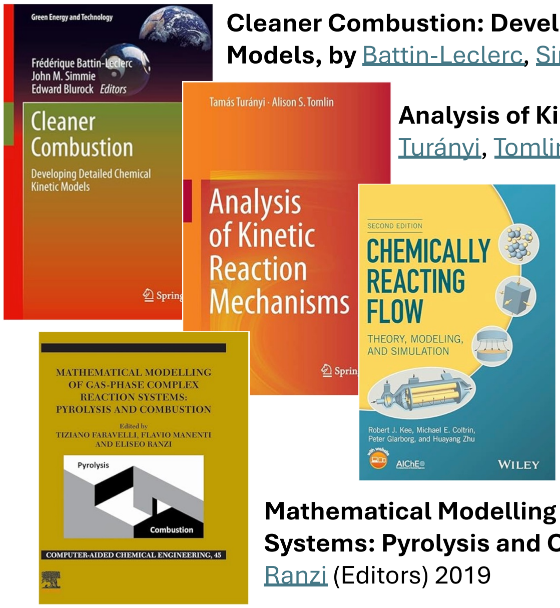
Combustion chemical kinetics is a very rich and complex field

This short course will only be scratching the surface.
More details available in topical textbooks,



Cleaner Combustion: Developing Detailed Chemical Kinetic Models, by Battin-Leclerc, Simmie, Blurock (Editors), 2013

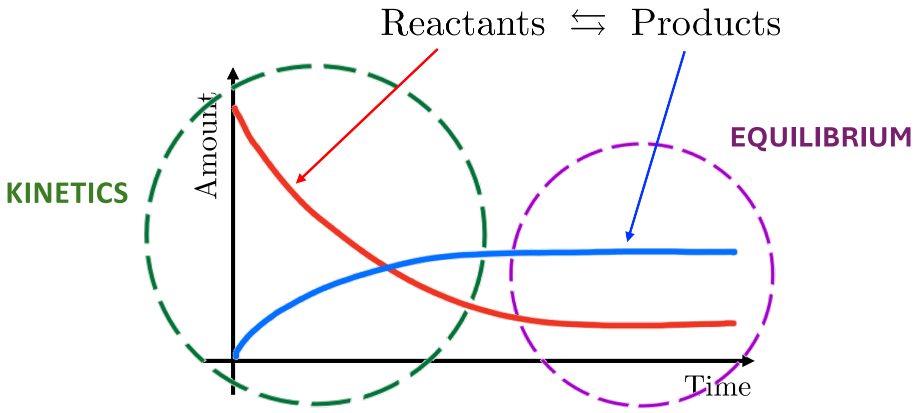
Analysis of Kinetic Reaction Mechanisms, by Turányi, Tomlin (Authors) 2014

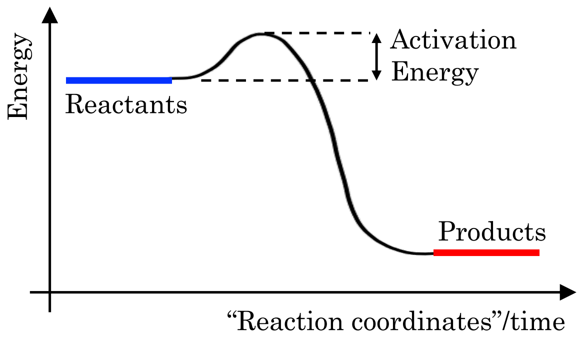
Chemically Reacting Flow: Theory, Modeling, and Simulation, by Kee, Coltrin, Glarborg, Zhu (Authors) 2017

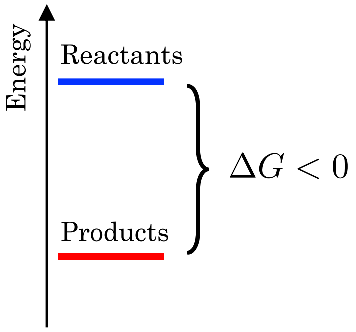
Mathematical Modelling of Gas-Phase Complex Reaction Systems: Pyrolysis and Combustion, by Faravelli, Manenti, Ranzi (Editors) 2019

… and a very large volume of specialized journal articles!

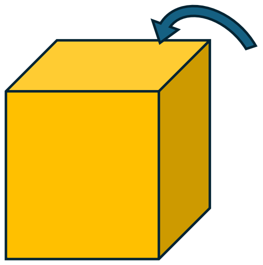
Thermodynamics vs. Kinetics







Part I guiding example – Heptane/Air combustion



Heptane C_7H_{16}
standard air (O_2 and N_2)

Objective: obtain the time evolution of an homogeneous mixture of heptane and air in a box

- ❑ Definitions of variables and initial system characterization
- ❑ What is a chemical kinetic mechanism and what does it contain?
- ❑ Governing equations and challenges associated with their integration
- ❑ Actually obtaining the species and temperature profiles

Part I really is about practical aspects: formalism and modeling framework to simulate the evolution of combustion in an homogenous reactor.

In Part II, we'll go deeper into the associated dynamics and some interesting challenges they create, both from a conceptual and an application point of view.

Definitions and useful relations

Combustion always involves multiple species: $\{ S_i$, with $i = 1$ to $N_s \}$

Molar view

- One mole contains $N_A = 6.0236 \text{ x } 10^{23}$ molecules (Avogadro number)
- Number of moles of species S_i in system : n_i
- Total number of moles in system :

$$n = \sum_{1}^{N_s} n_i$$

- **Mole fraction** of species S_i :

$$X_i \equiv \frac{n_i}{n}$$

By construction,

$$\sum_{1}^{N_s} X_i = 1$$

Definitions and useful relations

Mass viewpoint

- Conversion from moles to mass via the molar mass : M_i
- Mass of all molecules of species S_i in the system : $m_i = M_i n_i$
- Total mass in the system : $m = \sum_{1}^{N_s} m_i$
- **Mass fraction** of species S_i : $Y_i \equiv \frac{m_i}{m}$

By construction, $\sum_{1}^{N_s} Y_i = 1$

- Mean molar mass: $M = \sum_{1}^{N_s} M_i X_i = \frac{1}{\sum_{1}^{N_s} \frac{Y_i}{M_i}}$
- Mole-to-mass fraction conversion : $Y_i = \frac{M_i}{M} X_i$

Definitions and useful relations

Concentration (or partial molar density) viewpoint

- The number of moles of species S_i per volume V is called partial molar density, or more commonly **concentration**:

$$[X_i] = \frac{n_i}{V}$$

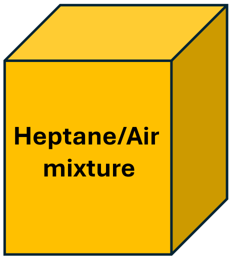
- Total molar density of the system : $\frac{n}{V} = \sum_{1}^{N_s} [X_i]$
- (Mass-based) density of the system : $\rho = \frac{m}{V}$
- Relation between concentrations and mass fractions : $[X_i] = \frac{\rho Y_i}{M_i} = \frac{n}{V} X_i$

Equation of state

- For most combustion applications, the ideal gas law is valid :

$$p = \frac{nRT}{V} = \frac{\rho RT}{M}$$ with the universal gas constant R = 8.3143 J/mol.K

Initial system characterization



- We need to know:
  - Chemical species present
  - How much of each there is
  - Appropriate thermochemical properties
- Convenient to work with **intensive** quantities:
  - Concentrations or mole/mass fractions
  - Only **2** thermochemical properties needed: **P-T, T-rho**

Global reaction/equation

- Characterizes the stoichiometry of a fuel/oxidizer mixture for ideal and complete combustion, aka how much oxygen we need to fully oxidize the fuel.
  - Does not describe an actual molecular process

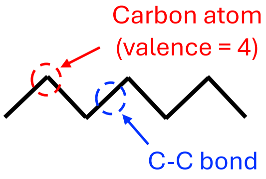
Equivalence ratio ϕ

- Quantifies whether we have too much (lean combustion), just enough (stoichiometric combustion) or not enough (rich combustion) oxygen available to oxidize the fuel

$$\phi = \frac{(X_F/X_{O_2})}{(X_F/X_{O_2})_{\text{stoic}}} = \frac{(Y_F/Y_{O_2})}{(Y_F/Y_{O_2})_{\text{stoic}}}$$

Example: initial composition of an heptane/air mixture at $\phi = 0.9$

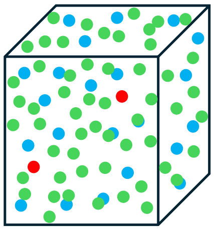
Heptane (NC7)



Global reaction

Note: Elements are conserved during combustion!

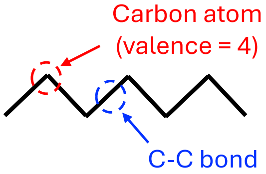
$$C_7H_{16} + 11\ O_2 = 7\ CO_2 + 16\ H_2O$$



● Heptane molecules
● Oxygen molecules
● Nitrogen molecules

Example: initial composition of an heptane/air mixture at $\phi = 0.9$

Heptane (NC7)



Global reaction

Note: Elements are conserved during combustion!

$$C_7H_{16} + 11\ O_2 = 7\ CO_2 + 16\ H_2O$$

❑ 3 unknows: X_{NC7}, X_{O_2}, and X_{N_2}

❑ To solve for them, need 3 equations

1. Equivalence ratio

$$\phi = 0.9 = \frac{(X_{NC7}/X_{O_2})}{(X_{NC7}/X_{O_2})_{\text{stoic}}} = \frac{(X_{NC7}/X_{O_2})}{1/11}$$

$$X_{NC7} = \frac{\phi}{11} X_{O_2}$$

2. Air definition

$$\frac{X_{O_2}}{X_{N_2}} = \left.\frac{X_{O_2}}{X_{N_2}}\right|_{\text{Air}} \approx \frac{0.21}{0.79}$$

3. Property of mole fractions

$$X_{NC7} + X_{O_2} + X_{N_2} = 1$$

To convert into mass fractions, need molar masses for each:

$$\begin{cases} M_{NC7} = 7 \times 12 + 16 = 100 \text{ g/mol} = 0.1 \text{ kg/mol} \\ M_{O_2} = 2 \times 16 = 32 \text{ g/mol} = 0.032 \text{ kg/mol} \\ M_{N_2} = 2 \times 14 = 28 \text{ g/mol} = 0.028 \text{ kg/mol} \end{cases}$$

Description of the kinetics: the chemical mechanism

- ❑ What information do we need to describe how the system evolves in time?
  - ❑ Example mechanism file (YAML format, Cantera software)

List of elements `[N, O, H, C]`

List of species

```
species: [N2, H2, H, O2, O, H2O, OH, H2O2, HO2, CO, CO2, HOCO, CH4,
  CH3, CH2, CH2(S), C, CH, CH3O2H, CH3O2, CH3OH, CH3O, CH2OH, CH2O,
  HCO, HO2CHO, HOCHO, OCHO, C2H6, C2H5, C2H5O2H, C2H5O2, C2H4, C2H3, C2H2,
  C2H, C2H5OH, C2H5O, PC2H4OH, SC2H4OH, C2H4O2H, C2H4O1-2, C2H3O1-2, CH3CHO,
  CH3CO, CH2CHO, CH2CO, HCCO, HCOOH, CH3CO3, CH3CO3H, CH2OHCHO, CHOCHO,
  ...
  NC5H11, NEOC5H12, NEOC5H11, NC5H10, NC5H9-3, B1M2, B1M3, B2M2, CYC5H8,
  C5H7, LC5H8, DIALLYL, RC6H9A, CYC6H8, CYC6H10, RCYC6H9, CYC6H12, CYC6H11,
  NC6H12, NC7H16, NC7H15, NC7H14, NC7H13, IC8H18, IC8H17, IC8H16, DIMEPTD ...]
```

Specific thermochemical data for each species

```
name: NC7H16
composition: {C: 7, H: 16}
thermo:
  model: NASA7
  temperature-ranges: [300.0, 1800.0, 3500.0]
  data:
  - [-2.76912812, 0.0925430866, -6.31219974e-05, 2.21462028e-08, -3.06437509e-12,
    -2.54722127e+04, 42.221823]
  - [31.069612, 0.0173458864, -4.57663884e-07, -1.06280964e-09, 1.59098857e-13,
    -3.76541592e+04, -140.920497]
```

(transport data set aside for now)

Description of the kinetics: the chemical mechanism

- ❑ What information do we need to describe how the system evolves in time?
  - ❑ Example mechanism file (YAML format, Cantera software)

List of reactions

```
reactions:
- equation: H2 + M <=> 2 H + M  # Reaction 1
  type: three-body
  rate-constant: {A: 4.577e+19, b: -1.4, Ea: 1.044e+05}
  efficiencies: {C2H6: 3.0, CH4: 2.0, CO: 1.9, CO2: 3.8, H2: 2.5, H2O: 12.0,
    HE: 0.83}
- equation: H2 + O <=> H + OH  # Reaction 2
  rate-constant: {A: 5.08e+04, b: 2.67, Ea: 6292.0}
- equation: H2 + OH <=> H + H2O  # Reaction 3
  rate-constant: {A: 4.38e+13, b: 0.0, Ea: 6990.0}
- equation: 2 O + M <=> O2 + M  # Reaction 4
  type: three-body
  rate-constant: {A: 6.165e+15, b: -0.5, Ea: 0.0}
  efficiencies: {AR: 0.83, C2H6: 3.0, CH4: 2.0, CO: 1.9, CO2: 3.8, H2: 2.5,
    H2O: 12.0, HE: 0.83}
- equation: H + O2 <=> O + OH  # Reaction 5
  rate-constant: {A: 1.14e+14, b: 0.0, Ea: 1.5286e+04}
  ...
```

Species thermodynamic properties

```
name: NC7H16
composition: {C: 7, H: 16}
thermo:
  model: NASA7
  temperature-ranges: [300.0, 1800.0, 3500.0]
  data:
  - [-2.76912812, 0.0925430866, -6.31219974e-05, 2.21462028e-08, -3.06437509e-12, -2.54722127e+04, 42.221823]
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```

- Thermodynamic variables of interest for S_i: **heat capacity**, **enthalpy** (and **entropy**, see later)
- For ideal gases, those are only a function of temperature T

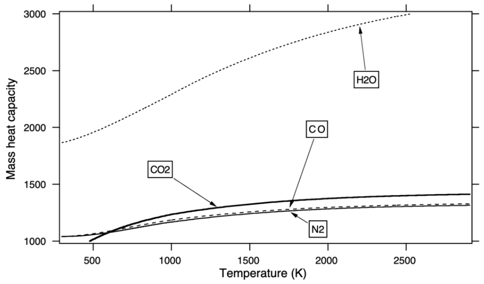
Molar-specific [J/mol]

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

Mass-specific [J/kg]

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

and $h_i^m = M_i h_i$



c_p strongly depends on species and temperature!

Note: Why enthalpy and not internal energy? Both can be used! Which one is most convenient depends on the system of interest. While thermo tables typically encode c_p and h, one can switch easily to internal energy:

$$h_i = u_i + \frac{RT}{M_i}$$

Figure from Poinsot and Veynante, Theoretical and Numerical Combustion

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Species thermodynamic properties

- To capture the temperature dependency properly and conveniently, temperatures are split into low and high ranges, and a polynomial fit is used for each part

Low temperature range

High temperature range

```
name: NC7H16
composition: {C: 7, H: 16}
thermo:
  model: NASA7
  temperature-ranges: [300.0, 1800.0, 3500.0]
  data:
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```

Polynomial coefficients for low temperature fit [a1, a2, a3, a4, a5, a6, a7]

Polynomial coefficients for high temperature fit [A1, A2, A3, A4, A5, A6, A7]

$$\frac{c_p^m}{R} = a_1 + a_2 T + a_3 T^2 + a_4 T^3 + a_5 T^4$$

$$\frac{h_i^m}{RT} = \frac{1}{RT}\int_{T_\mathrm{ref}}^{T} c_p^m dT = a_1 + \frac{a_2}{2}T + \frac{a_3}{3}T^2 + \frac{a_4}{4}T^3 + \frac{a_5}{5}T^4 + \frac{a_6}{T}$$

$$\frac{s^m}{R} = \frac{1}{R}\int_{T_\mathrm{ref}}^{T} \frac{c_p^m}{T} dT = a_1 \ln T + a_2 T + \frac{a_3}{2}T^2 + \frac{a_4}{3}T^3 + \frac{a_5}{4}T^4 + a_7$$

Species thermodynamic properties

- Since we assume an ideal gas, the thermodynamic properties of a multi-component mixture can be evaluated from those of its components:
    - For example, for heat capacity:

Molar-specific (J/mol.K)

$$c^m_{p,\text{mix}} = \sum_1^{N_s} X_i c^m_{p,i}$$

Mass-specific (J/kg.K)

$$c_{p,\text{mix}} = \sum_1^{N_s} Y_i c_{p,i}$$

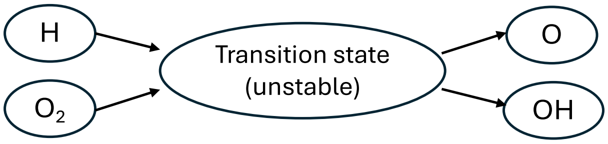
- **Where to find those polynomials (not exhaustive)**
    - Distributed with chemical mechanisms (look for supplemental materials from relevant articles)
    - Burcat database (with ATcT update) : https://respecth.elte.hu/burcat.php
    - Cantera.org : large repository of YAML files with sources covering many species

---

Elementary reactions and law of mass action

```
- equation: H + O2 <=> O + OH  # Reaction 5
  rate-constant: {A: 1.14e+14, b: 0.0, Ea: 1.5286e+04}
```

- This bimolecular reaction happens when one molecule of H collides with one molecule of O_2
- Collision results in the formation of products if it involves enough energy and if the molecules are properly oriented



Rate of consumption of H
= number of molecules per unit time that gets converted into H and OH

Rate should be proportional to amount of H and the amount of O_2 available.

- Introducing stoichiometric coefficients and k_{5f} as proportionality constant, we get the law of mass action :

$$\nu_H H + \nu_{O_2} O_2 \rightarrow \nu_O O + \nu_{OH} OH \qquad (5f)$$

$$\nu_H = \nu_{O_2} = \nu_O = \nu_{OH} = 1$$

Reaction rate (of the “forward” reaction #5)

$$\omega_{5f} = k_{5f}[H][O_2]$$

$$\frac{d[H]}{dt} = -\nu_H \boxed{k_{5f}[H]^{\nu_H}[O_2]^{\nu_{O_2}}}$$

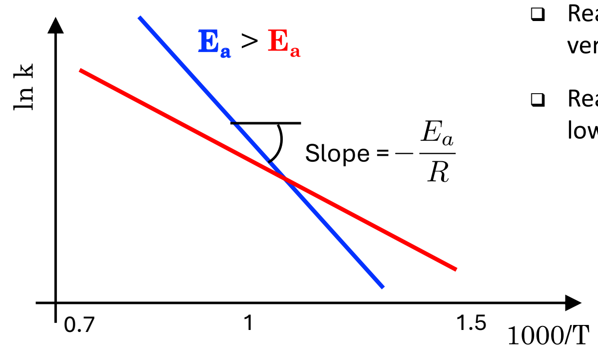
Rate coefficient (of the “forward” reaction #5)

Consumption rate of H
through the “forward” reaction #5)

Closer view of the rate coefficient k

```
- equation: H + O2 <=> O + OH  # Reaction 5
  rate-constant: {A: 1.14e+14, b: 0.0, Ea: 1.5286e+04}
```

- ❑ k is only a function of the temperature, and is usually expressed
  - ❑ In Arrhenius form: $k = Ae^{-\frac{E_a}{RT}}$
  - ❑ In modified Arrhenius form: $k = AT^b e^{-\frac{E_a}{RT}}$
- ❑ Remember that reactions are (mostly) about collisions. That $e^{-\frac{E_a}{RT}}$ comes from the Boltzmann population distribution in the kinetic theory of gases, which describes how the probability for the collision to have enough energy for the reactants to go to products **changes with temperature**.



- ❑ Reactions with high activation energies are very temperature-sensitive
- ❑ Reactions are more temperature-sensitive at low temperatures

Closer view of the rate coefficient k

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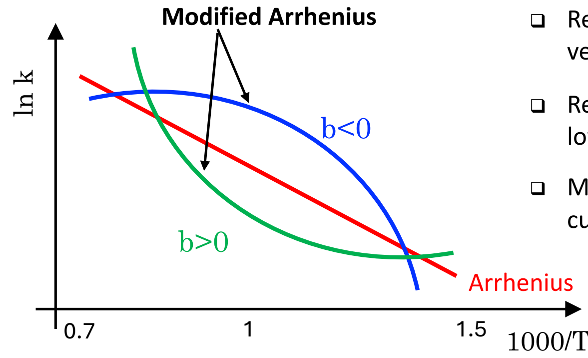
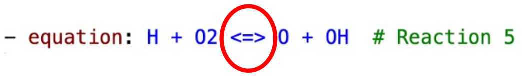


- ❑ Reactions with high activation energies are very temperature-sensitive
- ❑ Reactions are more temperature-sensitive at low temperatures
- ❑ Modified Arrhenius format allows for curvature in ln k vs 1/T space

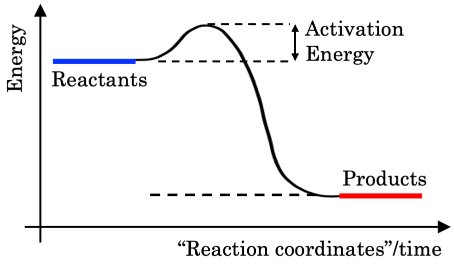
Reverse rate coefficients, equilibrium constants and the principle of microscopic reversibility

- All reactions are reversible



```
- equation: H + O2 <=> O + OH  # Reaction 5
```

  - If a reaction proceeds in one direction, there is a non-zero probability for the products to collide and convert back to reactants
  - **Principle of microscopic reversibility**: the reverse reaction follows the same path as the forward one on the potential energy surface



Reverse rate coefficients, equilibrium constants and the principle of microscopic reversibility

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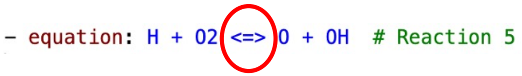


```
- equation: H + O2 <=> O + OH  # Reaction 5
```

  - If a reaction proceeds in one direction, there is a non-zero probability for the products to collide and convert back to reactants
  - **Principle of microscopic reversibility**: the reverse reaction follows the same path as the forward one on the potential energy surface
  - **Forward and backward rate coefficients are not independent from one another!**

$$\frac{k_f(T)}{k_b(T)} = K_c(T) \quad \text{Equilibrium constant in concentration units}$$

$$= \frac{[OH]^{\nu_{OH}}[O]^{\nu_O}}{[H]^{\nu_H}[O_2]^{\nu_{O_2}}}$$

  - K_C is related to the equilibrium constant in pressure units $K_p = \frac{p_{OH}^{\nu_{OH}} p_O^{\nu_O}}{p_H^{\nu_H} p_{O_2}^{\nu_{O_2}}}$ through

$$K_c = \frac{K_p}{(RT)^{\sum \nu_i^{\text{prod}} - \sum \nu_i^{\text{react}}}}$$

    - Where the partial pressure of Si is defined as $p_i = [X_i]RT$

  - K_p is determined from thermodynamic properties

$$K_p = \exp\left(\frac{\Delta S^o}{R} - \frac{\Delta H}{RT}\right)$$

Pressure-dependent reactions

- Some reactions show a dependency on both temperature AND pressure.
  - Example: recombination reaction O + O ⇔ O_2
    - Recombination of 2 radicals liberates a lot of energy. If that energy is not transferred elsewhere, O2 dissociates back immediately. However, O_2 is surrounded by other molecules in the mixture to which that energy can be quickly transferred, which stabilizes it.
    - The more molecules there are close by (high pressure), the better. In that case, **the reaction rate increases when pressure increases**
    - Behavior encoded in reaction coefficient using "*third body*" M

```
- equation: 2 O + M <=> O2 + M  # Reaction 2
  type: three-body
  rate-constant: {A: 1.2e+17, b: -1.0, Ea: 0.0}
  efficiencies: {C2H6: 3.0, CH4: 2.0, CO: 1.75, CO2: 3.6, H2: 2.4, H2O: 15.4}
```

$$\frac{d[O]}{dt} = -2k_f[O]^2[M] = -2AT^b e^{-\frac{Ea}{RT}}[O]^2[M]$$

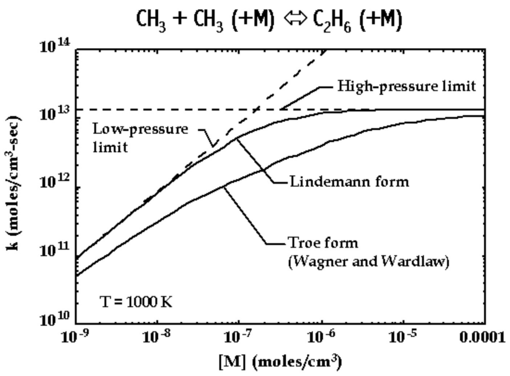
- M can be any molecule in the surrounding. If all molecules are as efficient at removing energy from the O-O system, $[M] = \sum_{i=1}^{N_s}[X_i] = \frac{P}{RT}$
- If some molecules are more efficient,

$$[M] = \sum_{i=1}^{N_s} z_i[X_i]$$ where z_i is the catalytic efficiency (=1 by default)

Pressure-dependent reactions

- Some reactions show a dependency on both temperature AND pressure.
  - Sometimes, the pressure dependency is more complex to capture
  - Example: CH3 + CH3 ⇔ C2H6
    This reaction requires a third body at low pressure, but behaves as a "normal" bi-molecular reaction at high pressure

```
- equation: 2 CH3 (+M) <=> C2H6 (+M)  # Reaction 154
  type: falloff
  low-P-rate-constant: {A: 8.05e+31, b: -3.75, Ea: 981.6}
  high-P-rate-constant: {A: 2.277e+15, b: -0.69, Ea: 174.9}
  Troe: {A: 0.0, T3: 570.0, T1: 1.0000000000000002e+30, T2: 1.0e+30}
  efficiencies: {CO: 2.0, CO2: 3.0, H2O: 5.0}
```



Stewart, Larson, and Golden (1989).

Pressure-dependent reactions

- ❑ Some reactions show a dependency on both temperature AND pressure.
  - ❑ Sometimes, the pressure dependency is more complex to capture
  - ❑ Example: CH3 + CH3 ⇔ C2H6
    This reaction requires a third body at low pressure, but behaves as a "normal" bi-molecular reaction at high pressure
  - ❑ To recover the desired dependency, we need
    - ❑ Low-pressure reaction coefficient

$$k_0 = A_0 T^{\beta_0} \exp(-E_0/R_c T)$$

    - ❑ High pressure reaction coefficient

$$k_\infty = A_\infty T^{\beta_\infty} \exp(-E_\infty/R_c T)$$

    - ❑ A blending function

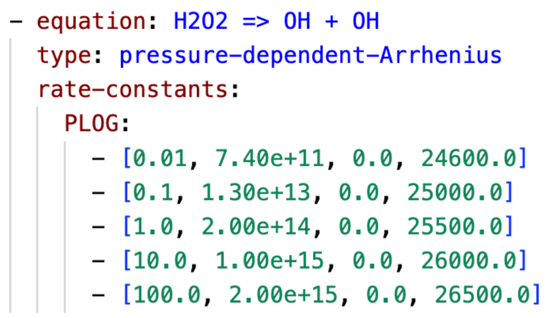
$$k = k_\infty\left(\frac{P_r}{1+P_r}\right)F \qquad \text{with} \qquad P_r = \frac{k_0[M]}{k_\infty}$$

    - ❑ And an expression for F which can be more or less complicated, with or without extra parameters
      - ❑ $F = 1$ (Lindemann)
      - ❑ $\log F = \left[1 + \left[\frac{\log P_r + c}{n - d(\log P_r + c)}\right]^2\right]^{-1} \log F_{\text{cent}}$ (Troe)

$$F_{\text{cent}} = (1-\alpha)\exp(-T/T^{***}) + \alpha\exp(-T/T^{*}) + \exp(-T^{**}/T)$$

Pressure-dependent reactions

- ❑ Some reactions show a dependency on both temperature AND pressure.
  - ❑ When there is a pressure dependency, but a third body is not the best model for it, resort to interpolation between rate coefficients specified at different pressures
  - ❑ PLOG approach



```
- equation: H2O2 => OH + OH
  type: pressure-dependent-Arrhenius
  rate-constants:
    PLOG:
      - [0.01, 7.40e+11, 0.0, 24600.0]
      - [0.1, 1.30e+13, 0.0, 25000.0]
      - [1.0, 2.00e+14, 0.0, 25500.0]
      - [10.0, 1.00e+15, 0.0, 26000.0]
      - [100.0, 2.00e+15, 0.0, 26500.0]
```

$$\log k(T,P) = \log k_1(T) + \left(\log k_2(T) - \log k_1(T)\right)\frac{\log P - \log P_1}{\log P_2 - \log P_1}$$

A note of caution on units

- ❑ The units of a rate coefficient k depends on the nature of the reaction!

Because the consumption or production rates of species are in concentration/time, the units for k must be

Unimolecular	$A \rightarrow \text{Products}$	$\omega = k[A]$	1/time
Bimolecular	$A + A \rightarrow \text{Products}$ $A + B \rightarrow \text{Products}$	$\omega = k[A]^2$ $\omega = k[A][B]$	1/time/concentration)
Trimolecular	$A + A + A \rightarrow \text{Products}$ $A + B + C \rightarrow \text{Products}$	$\omega = k[A]^3$ $\omega = k[A][B][C]$	1/time/concentration²

- ❑ Reasonable chemistry/CFD codes use SI units. Typical YAML chemical kinetic mechanism file starts with

```
units: {length: cm, quantity: mol, activation-energy: cal/mol}
```

What do you think?

Assembling chemical kinetic mechanisms

Combustion kinetics is quite complex, even when the fuel is a simple molecule.

- ❑ **How are thermodynamic data obtained?**
  - ❑ Experimentally through combustion calorimetry (limited, expensive)
  - ❑ Ab initio quantum chemistry (Gaussian, VASP etc.)
  - ❑ Group additivity: molecule property estimated based its structure, using contributions from its atoms and their bonding partners, with correction for long range effects (THERM, NIST database, THERGAS, CRANIUM)
    - ❑ Recently, effort to generalize with machine learning approach
- ❑ **How are k's obtained?**
  - ❑ Experimentally, when there is a way to isolate the reaction
  - ❑ Numerically, from first principles (rate theory equations, relies extensively on)
  - ❑ When those are not possible, approximations of varying accuracy can be obtained using rate rules
    - ❑ Relate reaction to others, usually simpler ones for which k is known
- ❑ **How are all those reactions put together?**
  - ❑ Manually, using a modular approach
  - ❑ Increasingly with the help of computers and automated approaches
    - ❑ Example: RMG
      https://github.com/ReactionMechanismGenerator/RMG-Py

Governing equations – Conservation of mass

- ☐ Variables of interest: mass fractions Y_i, Temperature
  Constant volume (box!) so density is constant.
  Pressure can be obtained from EOS
- ☐ Net rate of reaction of reaction j $$\omega_j = k_{f,j}\Pi_{i=1}^{N_s}[X_i]^{\nu'_{i,j}} - k_{b,j}\Pi_{i=1}^{N_s}[X_i]^{\nu''_{i,j}}$$
- ☐ Molar production of species S_i $$\frac{d[X_i]}{dt} = \sum_{j=1}^{N_r} \nu_{i,j}\omega_j$$

With $\nu_{i,j} = -\nu'_{i,j}$ for reactants (consumption of species)
and $\nu_{i,j} = \nu''_{i,j}$ for products (production of species)

- ☐ Conversion to mass fractions: $$[X_i] = \frac{\rho Y_i}{M_i}$$
- ☐ Final equation for mass fraction Y_i: $$\frac{dY_i}{dt} = \frac{M_i}{\rho}\sum_{j=1}^{N_r} \nu_{i,j}\omega_j$$
- ☐ Question: is mass indeed conserved? How to we check?

Governing equations – Conservation of energy

- ☐ First Law of thermodynamics
  (System = box, adiabatic, no friction work) $$dE = \delta Q + \delta W = 0$$
- ☐ Time derivative of specific energy u : $$\frac{du}{dt} = 0$$

$$u = \sum_{i=1}^{N_s} u_i Y_i$$

$$\frac{du}{dt} = 0 = \frac{d}{dt}\left(\sum_{i=1}^{N_s} u_i Y_i\right) = \sum_{i=1}^{N_s} \frac{d}{dt}(u_i Y_i)$$

$$0 = \sum_{i=1}^{N_s}\left(u_i \frac{dY_i}{dt} + Y_i \bigcirc\!\!\!\!\!\frac{du_i}{dt}\right) \longrightarrow \boxed{\frac{du_i}{dT}\frac{dT}{dt} = c_{v,i}\frac{dT}{dt}}$$

$$0 = \sum_{i=1}^{N_s} u_i \frac{dY_i}{dt} + \frac{dT}{dt}\sum_{i=1}^{N_s} c_{v,i} Y_i \longrightarrow \boxed{c_v \text{ of mixture}}$$

$$\frac{dT}{dt} = \frac{1}{c_v}\left[-\sum_{i=1}^{N_s} u_i \frac{dY_i}{dt}\right]$$

Thermochemistry expressed in terms of c_p and h!

$$c_{p,i} = c_{v,i} + \frac{R}{M_i}$$

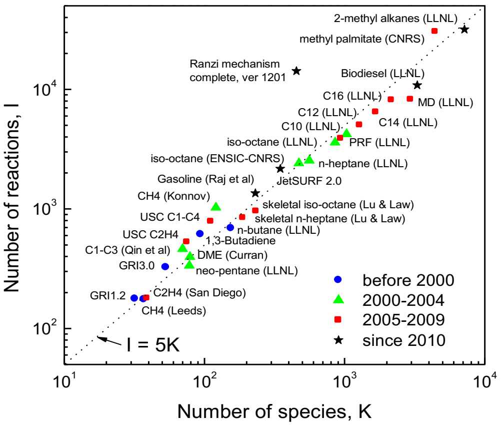
$$u_i = h_i - \frac{RT}{M_i}$$

$$\boxed{\frac{dT}{dt} = -\frac{1}{c_v - \frac{R}{M}}\left[\sum_{i=1}^{N_s}\left(h_i - \frac{RT}{M_i}\right)\frac{dY_i}{dt}\right]}$$

How tricky is the system of equations we are trying to solve, really?

- ☐ **The dimensionality issue**

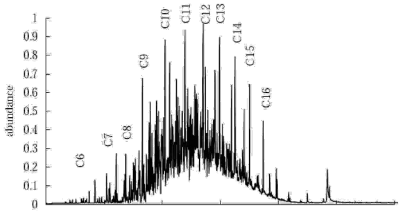
  Chemistry of even simple pure fuels involves thousands of Reactions.



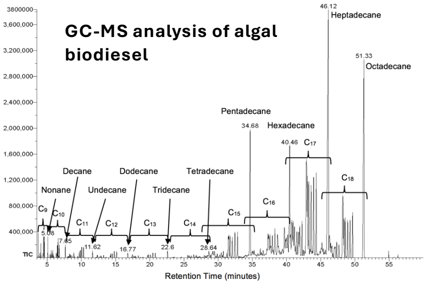
Size of selected detailed and skeletal mechanisms for hydrocarbon fuels superimposed with colors indicating the approximate time when the mechanisms were compiled.

Reproduced from Law & Lu, 2008, 2012

Realistic fuels involves hundreds of compounds



Jet A ion chromatogram
J. Shepherd et al, 1997

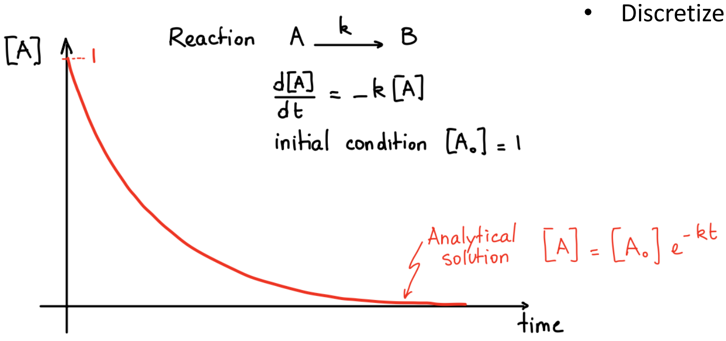


GC-MS analysis of algal biodiesel

How tricky is the system of equations we are trying to solve, really?

The stiffness issue

Consider a very simple example



Reaction $A \xrightarrow{k} B$

$$\frac{d[A]}{dt} = -k[A]$$

initial condition $[A_0] = 1$

Analytical solution $[A] = [A_0]\, e^{-kt}$

Numerical integration of the ODE is discrete

- Proceeds in discrete time intervals Δt
- Discretized equation using forward Euler

$$[A] \equiv y$$

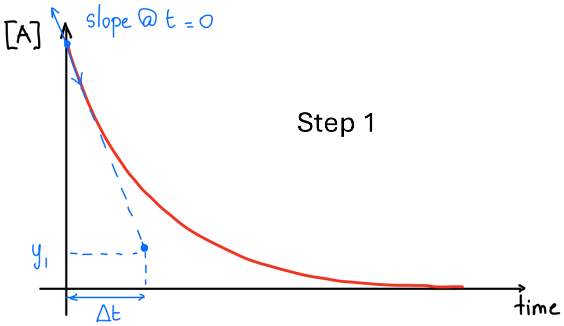
$$\frac{y_{i+1} - y_i}{\Delta t} = -k y_i$$

$$y_{i+1} = (1 - k\Delta t)\, y_i$$

How tricky is the system of equations we are trying to solve, really?

The stiffness issue

Consider a very simple example



Step 1

Numerical integration of the ODE is discrete

- Proceeds in discrete time intervals Δt
- Discretized equation using forward Euler

$$[A] \equiv y$$

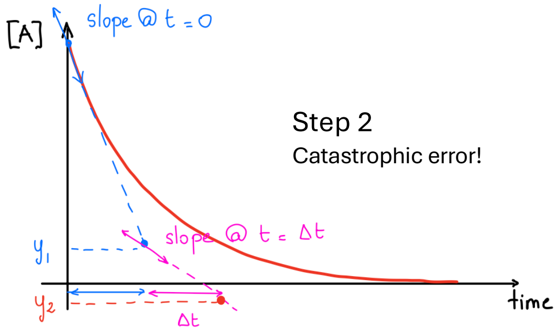
$$\frac{y_{i+1} - y_i}{\Delta t} = -k y_i$$

$$y_{i+1} = (1 - k\Delta t)\, y_i$$

How tricky is the system of equations we are trying to solve, really?

The stiffness issue

Consider a very simple example



Step 2

Catastrophic error!

Numerical integration of the ODE is discrete

- Proceeds in discrete time intervals Δt
- Discretized equation using forward Euler

$$[A] \equiv y$$

$$\frac{y_{i+1} - y_i}{\Delta t} = -k y_i$$

$$y_{i+1} = (1 - k\Delta t)\, y_i$$

How to choose Δt to get a stable solution?

- Introduce a disturbance at ti, and look at its evolution in time.
  If $\left|\frac{\varepsilon_{i+1}}{\varepsilon_i}\right| > 1$, the integration scheme is unstable
- With a touch of algebra and some Taylor expansion, we can show that $\left|\frac{\varepsilon_{i+1}}{\varepsilon_i}\right| = |1 - k\Delta t|$
  that is, the criterion for stability is $\Delta t < \frac{1}{k}$

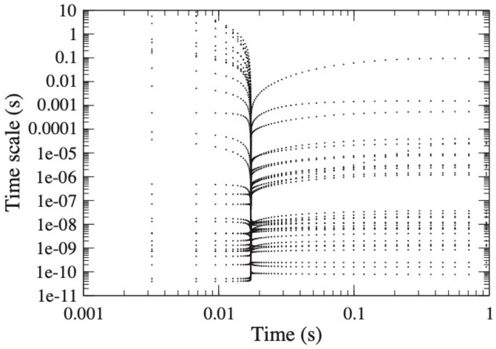
How tricky is the system of equations we are trying to solve, really?

What does it have to do with our chemical kinetics?

- $1/k$ in our previous example is the characteristic time scale of the dynamic system.
- For the more complex system associated with a detailed chemical kinetic mechanism, we can calculate characteristics time scales by computing the eigenvalues of the Jacobian matrix (partial derivative of the chemical source term with respect to the state variables)
    - Each eigenvalue λ is associated with a stability constraint of the type $|1 - \lambda \Delta t| < 1$
    - The largest eigenvalue, ie the fastest time step, controls the time step.

Typical homogeneous combustion case

Caudal et al. PROCI 2012



Time scale of interest – 1 s

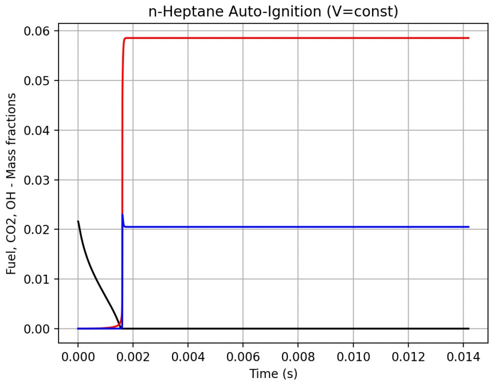
Fastest time scale in the system – 1e-10 s

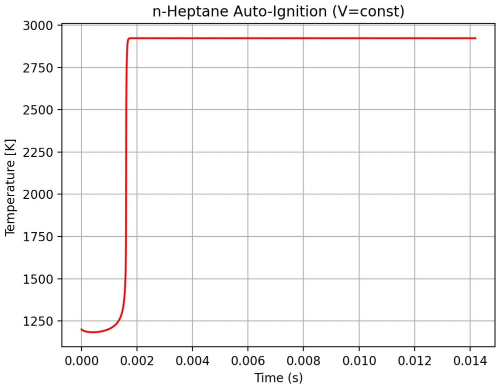
How tricky is the system of equations we are trying to solve, really?

- A system is NOT stiff if the local accuracy requires to take time steps of the same order of magnitude as the smallest time scale
- A system IS stiff when stability requirements require to take much smaller time steps than what accuracy requirements would allow us
    - Integrating chemical kinetics equations require the use of efficient implicit solvers
        - DVODE, CVODE, ODE23s in Matlab
    - Those solvers (which involve inverting large matrices) come at a very large additional computational cost compared to simple, explicit or semi-explicit methods
    - Active area of research to develop methods to reduce stiffness

What about results?

- We now know or have:
  - A chemical kinetic mechanism containing all necessary thermochemistry and reactions
  - Governing equations for mass and energy
  - Methods to integrate those equations in time
  - Just need a solver! You can write your own (fun, but 100% would not recommend) or use one of many software available: Cantera, FlameMaster, Chemkin (commercial) etc.


n-Heptane Auto-Ignition (V=const)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