



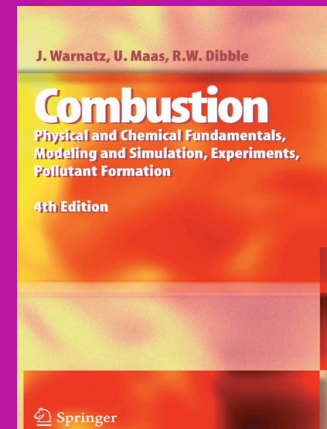
Aalto University  
School of Engineering

# AAE-E3030 – Numerical Modeling of Multiphase Flows

## Lecture 4: Combustion Chemistry

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# Upcoming Sessions

- Lecture 3: Thermodynamics of Combustion
- Python tutorial : Basics of Python
- Lecture 4: Combustion Chemistry
- Exercise 2: Second Exercise of Combustion Course
- MyCourses web interface for discussions and questions:  
<https://mycourses.aalto.fi/>

# Why Combustion Chemistry?

- To accurately model combustion phenomenon we need to capture two main features of the system:
  - Complex in-cylinder **flow structures**: DNS and LES over conventional RANS models
  - **Combustion properties** of the system such as ignition delay time, laminar flame speed, final temperature, emissions and etc.
- We may propose a useful combustion model for a specific modeling need only and only when we have a correct understanding of the phenomenon and only then we may use simpler models.
- No model is perfect

# Collision Theory

- Molecules must collide before they can react
- Consider a simple reaction as below:



- If molecules A and B want to react, their initial bonds must be disrupted. This is done by collision of molecules
- The frequency of collisions between A and B in a gas will be proportional to the concentration of each:

$$\text{Rate of reaction} = [A][B]$$

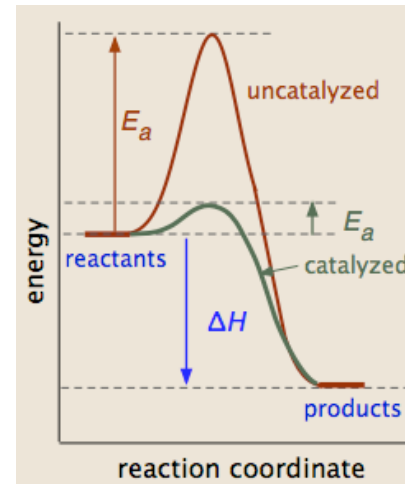
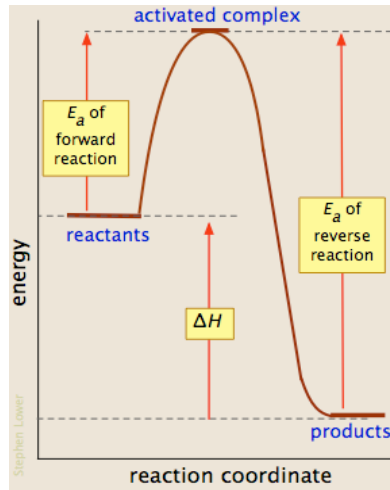
- But, **not all collisions are equal**
- **Collisions energetic enough to disrupt the initial bonds of molecules are called successful collisions**

# Collision Theory

- Now, consider temperature effects on reactions
- Higher the temperature, higher the reaction rate e.g. milk in room temperature
- Thermal energy (temperature) relates direction to motion at the molecular level
- As the temperature rises, molecules move faster and collide more vigorously
- **Increasing temperature will then increase the probability of more successful collisions**
- In more complex molecules, sometimes the **orientation of collision** becomes important as well
- Due to high randomization of gas and liquids, there are always enough correct orientations to happen however, **this reduces the number of successful collisions**

# Activation Energy

- Successful collision (reaction) cannot take place at all until species have acquired the energy needed to stretch, bend, or otherwise distort one or more bonds. This critical energy is known as the **activation energy** of the reaction.
- Activation energy might be different for different pathways (e.g. catalyst effect)



# Arrhenius Law

- By 1890 it was common knowledge that higher temperatures speed up reactions, but the reasons for this were not clear. Finally, in 1899, the Swedish chemist Svante Arrhenius (1859-1927) combined the concepts of activation energy and the Boltzmann distribution law into one of the most important relationships in physical chemistry:

$$k = A e^{-E_a / (RT)}$$

k: Rate constant

T: Absolute temperature [K]

A: Pre-exponential factor, defines the rate due to frequency of collisions in the correct orientation

$E_a$ : Activation energy [J/mol]

R: Universal gas constant, 8.314 [J/K-mol]



# Modified Arrhenius Law

- The pre-exponential factor has been observed to be affected by the temperature as well. Nowadays, this effect is explicitly mentioned in the **modified Arrhenius law**.

$$k = AT^n e^{-E_a/(RT)}$$

- So to calculate a rate constant, one needs A, n and  $E_a$ .
- The modified Arrhenius law is the one we will use in combustion community.
- Rate of reaction for A in the  $aA + bB \rightarrow cC + dD$  reaction is calculated as follow:

$$\text{Rate of reaction of A} = (0 - a) [k_{\text{forward}} [A]^a [B]^b - k_{\text{backward}} [C]^c [D]^d]$$

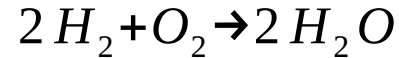
Coefficient of A at product side

Coefficient of A at reactants side



# Global Reactions

- Global (One-step) reaction for H<sub>2</sub>:



- Two molecules collide and produce two molecules of water
- Reactants transform to products simultaneously
- The rate of this reaction follows one single Arrhenius law
- Simple and understandable
- Fast computations

This is not the real story!!!

# The Real Story

- $\text{H}_2$  and  $\text{O}_2$  are broken into H and O radicals (Initiation reaction)
- Now, we have  $\text{H}_2$ , H,  $\text{O}_2$  and O in the system
- All species try to react with each other in all possible combinations
- New species/radicals are produced: OH,  $\text{HO}_2$ ,  $\text{H}_2\text{O}_2$
- Radicals are highly reactive (have unpaired electron)
- Once we have big enough radical pool the ignition happens
- The final products are just then being created
- Including all the chemistry details of the all species involved in a reaction is called Detailed Chemistry

		A	n	E	Reference
<b><i>H<sub>2</sub>/O<sub>2</sub> Chain Reactions</i></b>					
1.	H + O <sub>2</sub> = O + OH	3.55 × 10 <sup>15</sup>	-0.41	16.6	Hessler [16]
2.	O + H <sub>2</sub> = H + OH	5.08 × 10 <sup>4</sup>	2.67	6.29	Sutherland et al. [44]
3.	H <sub>2</sub> + OH = H <sub>2</sub> O + H	2.16 × 10 <sup>8</sup>	1.51	3.43	Michael et al. [45]
4.	O + H <sub>2</sub> O = OH + OH	2.97 × 10 <sup>6</sup>	2.02	13.4	Sutherland et al. [46]
<b><i>H<sub>2</sub>/O<sub>2</sub> Dissociation/Recombination Reactions</i></b>					
5.	H <sub>2</sub> + M = H + H + M <sup>a</sup>	4.58 × 10 <sup>19</sup>	-1.40	104.38	Tsang et al. [47]
	H <sub>2</sub> + Ar = H + H + Ar	5.84 × 10 <sup>18</sup>	-1.10	104.38	Tsang et al. [47]
	H <sub>2</sub> + He = H + H + He	5.84 × 10 <sup>18</sup>	-1.10	104.38	See text
6.	O + O + M = O <sub>2</sub> + M <sup>a</sup>	6.16 × 10 <sup>15</sup>	-0.50	0.00	Tsang et al. [47]
	O + O + Ar = O <sub>2</sub> + Ar	1.89 × 10 <sup>13</sup>	0.00	-1.79	Tsang et al. [47]
	O + O + He = O <sub>2</sub> + He	1.89 × 10 <sup>13</sup>	0.00	-1.79	See text
7.	O + H + M = OH + M <sup>a</sup>	4.71 × 10 <sup>18</sup>	-1.0	0.00	Tsang et al. [47]
8.	H + OH + M = H <sub>2</sub> O + M <sup>b</sup>	3.8 × 10 <sup>22</sup>	-2.00	0.00	See text
<b><i>Formation and Consumption of HO<sub>2</sub></i></b>					
9.	H + O <sub>2</sub> + M = HO <sub>2</sub> + M <sup>c</sup>	k <sub>O</sub> 6.37 × 10 <sup>20</sup>	-1.72	0.52	Michael et al. [19] (M = N <sub>2</sub> )
	H + O <sub>2</sub> + M = HO <sub>2</sub> + M <sup>d</sup>	k <sub>O</sub> 9.04 × 10 <sup>19</sup>	-1.50	0.49	Michael et al. [19] (M = Ar or He)
		k <sub>∞</sub> 1.48 × 10 <sup>12</sup>	0.60	0.00	Cobos et al. [48]
10.	HO <sub>2</sub> + H = H <sub>2</sub> + O <sub>2</sub>	1.66 × 10 <sup>13</sup>	0.00	0.82	Mueller et al. [1]
11.	HO <sub>2</sub> + H = OH + OH	7.08 × 10 <sup>13</sup>	0.00	0.30	Mueller et al. [1]
12.	HO <sub>2</sub> + O = OH + O <sub>2</sub>	3.25 × 10 <sup>13</sup>	0.00	0.00	Baulch et al. [34]
13.	HO <sub>2</sub> + OH = H <sub>2</sub> O + O <sub>2</sub>	2.89 × 10 <sup>13</sup>	0.00	-0.50	Baulch et al. [34]
<b><i>Formation and Consumption of H<sub>2</sub>O<sub>2</sub></i></b>					
14.	HO <sub>2</sub> + HO <sub>2</sub> = H <sub>2</sub> O <sub>2</sub> + O <sub>2</sub> <sup>e</sup>	4.20 × 10 <sup>14</sup>	0.00	11.98	Hipler et al. [49]
	HO <sub>2</sub> + HO <sub>2</sub> = H <sub>2</sub> O <sub>2</sub> + O <sub>2</sub>	1.30 × 10 <sup>11</sup>	0.00	-1.63	
15.	H <sub>2</sub> O <sub>2</sub> + M = OH + OH + M <sup>f</sup>	k <sub>O</sub> 1.20 × 10 <sup>17</sup>	0.00	45.5	Warnatz [50]
		k <sub>∞</sub> 2.95 × 10 <sup>14</sup>	0.00	48.4	Brouwer et al. [51]
16.	H <sub>2</sub> O <sub>2</sub> + H = H <sub>2</sub> O + OH	2.41 × 10 <sup>13</sup>	0.00	3.97	Tsang et al. [47]
17.	H <sub>2</sub> O <sub>2</sub> + H = H <sub>2</sub> + HO <sub>2</sub>	4.82 × 10 <sup>13</sup>	0.00	7.95	Tsang et al. [47]
18.	H <sub>2</sub> O <sub>2</sub> + O = OH + HO <sub>2</sub>	9.55 × 10 <sup>6</sup>	2.00	3.97	Tsang et al. [47]
19.	H <sub>2</sub> O <sub>2</sub> + OH = H <sub>2</sub> O + HO <sub>2</sub> <sup>e</sup>	1.00 × 10 <sup>12</sup>	0.00	0.00	Hipler et al. [52]
	H <sub>2</sub> O <sub>2</sub> + OH = H <sub>2</sub> O + HO <sub>2</sub>	5.8 × 10 <sup>14</sup>	0.00	9.56	

# Mechanism

- The **mechanism** of a chemical reaction is the **sequence of actual events that take place as reactant molecules are converted into products**.
- Each of these events constitutes an elementary step (elementary reaction) that can be represented as collision or as the breaking-up of a molecule (dissociation) into simpler units.
- The molecular entity that emerges from each step may be a final product of the reaction, or it might be an intermediate — a species that is created in one elementary step and destroyed in a subsequent step, and therefore does not appear in the net reaction equation.
- We solve modified Arrhenius equation (let's call it Arrhenius from now) for each elementary reaction in a mechanism
- $[M]$  is called a third body reaction: all species contribute to that to some extent (heavy molecules usually have bigger effects)

# Mechanism File

- A mechanism is usually available in **Chemkin** format. (You can google it)
  - Chemkin format provides a mechanism in three separate files
  - The first file is **Input file** which provides data regarding all the species and elementary reactions in that mechanism. It provides also all the Arrhenius equation related coefficients which are  $A$ ,  $n$  and  $E_a$
  - The second file is **Thermo file** which provides data for the NASA polynomials (JANAF)
  - The third file is **Transport file** which provides data for viscosity, thermal conductivity and diffusion coefficients
  - In general, **viscosity** and **conductivity** are expressed in terms of **binary diffusion coefficients**
  - As **diffusivity** is not an intrinsic property, the binary diffusion coefficients must be evaluated from Lennard-Jones potentials of the two considered species, which in turn permits a generally valid tabulation of transport properties.
-

# Mechanism File

- In practical computations, the Lennard-Jones potentials are evaluated for the specific mixture and the transport properties are fitted for each species  $i$  to a polynomial form  
(Lennard-Jones potentials  $\rightarrow$  Binary diffusion coefficients  $\rightarrow$  Fitting polynomials)

# Input File

```
! GRI-Mech Version 3.0 7/30/99 CHEMKIN-II format
! See README30 file at anonymous FTP site unix.sri.com, directory gri;
! WorldwideWeb home page http://www.me.berkeley.edu/gri_mech/ or
! through http://www.gri.org , under 'Basic Research',
! for additional information, contacts, and disclaimer
ELEMENTS
O H C N AR
END
SPECIES
H2      H      O      O2      OH      H2O      HO2      H2O2
C       CH      CH2     CH2(S)  CH3     CH4      CO       CO2
HCO     CH2O    CH2OH   CH3O    CH3OH   C2H      C2H2     C2H3
C2H4    C2H5    C2H6    HCCO    CH2CO   HCCOH    N        NH
NH2     NH3     NNH     NO      NO2     N2O      HNO      CN
HCN     H2CN    HCNN    HCNO    HOCN    HNCO     NCO      N2
AR      C3H7    C3H8    CH2CHO  CH3CHO
END
!THERMO
! Insert GRI-Mech thermodynamics here or use in default file
!END
REACTIONS
2O+M<=>O2+M                      1.200E+17  -1.000  .00
H2/ 2.40/ H2O/15.40/ CH4/ 2.00/ CO/ 1.75/ CO2/ 3.60/ C2H6/ 3.00/ AR/ .83/
O+H+M<=>OH+M                      5.000E+17  -1.000  .00
H2/2.00/ H2O/6.00/ CH4/2.00/ CO/1.50/ CO2/2.00/ C2H6/3.00/ AR/ .70/
O+H2<=>H+OH                        3.870E+04  2.700  6260.00
O+HO2<=>OH+O2                      2.000E+13  .000  .00
O+H2O2<=>OH+HO2                    9.630E+06  2.000  4000.00
O+CH<=>H+CO                         5.700E+13  .000  .00
O+CH2<=>H+HCO                       8.000E+13  .000  .00
O+CH2(S)<=>H2+CO                    1.500E+13  .000  .00
O+CH2(S)<=>H+HCO                    1.500E+13  .000  .00
O+CH3<=>H+CH2O                      5.060E+13  .000  .00
O+CH4<=>OH+CH3                      1.020E+09  1.500  8600.00
O+CO(+M)<=>CO2(+M)                  1.800E+10  .000  2385.00
LOW/ 6.020E+14  .000  3000.00/
H2/2.00/ O2/6.00/ H2O/6.00/ CH4/2.00/ CO/1.50/ CO2/3.50/ C2H6/3.00/ AR/ .50/
O+HCO<=>OH+CO                       3.000E+13  .000  .00
O+HCO<=>H+CO2                       3.000E+13  .000  .00
O+CH2O<=>OH+HCO                     3.900E+13  .000  3540.00
O+CH2OH<=>OH+CH2O                   1.000E+13  .000  .00
O+CH3O<=>OH+CH2O                    1.000E+13  .000  .00
O+CH3OH<=>OH+CH2OH                  3.880E+05  2.500  3100.00
O+CH3OH<=>OH+CH3O                    1.300E+05  2.500  5000.00
O+C2H<=>CH+CO                       5.000E+13  .000  .00
O+C2H2<=>H+HCCO                     1.350E+07  2.000  1900.00
O+C2H2<=>OH+C2H                     4.600E+19  -1.410  28950.00
O+C2H2<=>CO+CH2                     6.940E+06  2.000  1900.00
O+C2H3<=>H+CH2CO                    3.000E+13  .000  .00
```

# Thermo File

```
THERMO
  300.000 1000.000 5000.000
! GRI-Mech Version 3.0 Thermodynamics released 7/30/99
! NASA Polynomial format for CHEMKIN-II
! see README file for disclaimer
O          L 1/900  1          G  200.000  3500.000  1000.000  1
  2.56942078E+00-8.59741137E-05 4.19484589E-08-1.00177799E-11 1.22833691E-15  2
  2.92175791E+04 4.78433864E+00 3.16826710E+00-3.27931884E-03 6.64306396E-06  3
-6.12806624E-09 2.11265971E-12 2.91222592E+04 2.05193346E+00                4
O2         TPIS890  2          G  200.000  3500.000  1000.000  1
  3.28253784E+00 1.48308754E-03-7.57966669E-07 2.09470555E-10-2.16717794E-14  2
-1.08845772E+03 5.45323129E+00 3.78245636E+00-2.99673416E-03 9.84730201E-06  3
-9.68129509E-09 3.24372837E-12-1.06394356E+03 3.65767573E+00                4
H          L 7/88H  1          G  200.000  3500.000  1000.000  1
  2.50000001E+00-2.30842973E-11 1.61561948E-14-4.73515235E-18 4.98197357E-22  2
  2.54736599E+04-4.46682914E-01 2.50000000E+00 7.05332819E-13-1.99591964E-15  3
  2.30081632E-18-9.27732332E-22 2.54736599E+04-4.46682853E-01                4
H2         TPIS78H  2          G  200.000  3500.000  1000.000  1
  3.33727920E+00-4.94024731E-05 4.99456778E-07-1.79566394E-10 2.00255376E-14  2
-9.50158922E+02-3.20502331E+00 2.34433112E+00 7.98052075E-03-1.94781510E-05  3
  2.01572094E-08-7.37611761E-12-9.17935173E+02 6.83010238E-01                4
OH         RUS 780  1H  1          G  200.000  3500.000  1000.000  1
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-3.88113333E-09 1.36411470E-12 3.61508056E+03-1.03925458E-01                4
H2O        L 8/89H  20  1          G  200.000  3500.000  1000.000  1
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-3.00042971E+04 4.96677010E+00 4.19864056E+00-2.03643410E-03 6.52040211E-06  3
-5.48797062E-09 1.77197817E-12-3.02937267E+04-8.49032208E-01                4
H2O2       L 5/89H  10  2          G  200.000  3500.000  1000.000  1
  4.01721090E+00 2.23982013E-03-6.33658150E-07 1.14246370E-10-1.07908535E-14  2
  1.11856713E+02 3.78510215E+00 4.30179801E+00-4.74912051E-03 2.11582891E-05  3
-2.42763894E-08 9.29225124E-12 2.94808040E+02 3.71666245E+00                4
H2O2       L 7/88H  20  2          G  200.000  3500.000  1000.000  1
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-2.15770813E-08 8.62454363E-12-1.77025821E+04 3.43505074E+00                4
C          L11/88C  1          G  200.000  3500.000  1000.000  1
  2.49266888E+00 4.79889284E-05-7.24335020E-08 3.74291029E-11-4.87277893E-15  2
  8.54512953E+04 4.80150373E+00 2.55423955E+00-3.21537724E-04 7.33792245E-07  3
-7.32234889E-10 2.66521446E-13 8.54438832E+04 4.53130848E+00                4
```



# Transport File

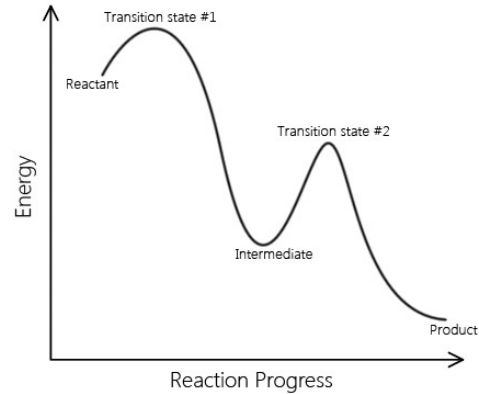
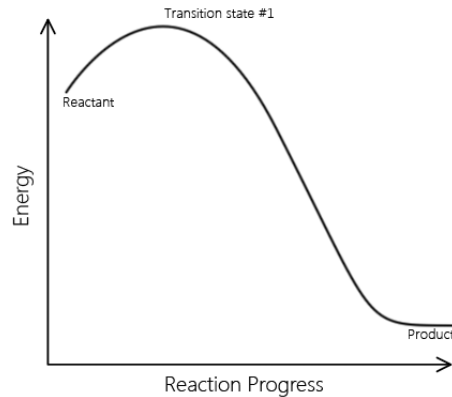
AR	0	136.500	3.330	0.000	0.000	0.000	
C	0	71.400	3.298	0.000	0.000	0.000	! *
C2	1	97.530	3.621	0.000	1.760	4.000	
C2O	1	232.400	3.828	0.000	0.000	1.000	! *
CN2	1	232.400	3.828	0.000	0.000	1.000	! OIS
C2H	1	209.000	4.100	0.000	0.000	2.500	
C2H2	1	209.000	4.100	0.000	0.000	2.500	
C2H20H	2	224.700	4.162	0.000	0.000	1.000	! *
C2H3	2	209.000	4.100	0.000	0.000	1.000	! *
C2H4	2	280.800	3.971	0.000	0.000	1.500	
C2H5	2	252.300	4.302	0.000	0.000	1.500	

## 1. Transport inputs: Transport database *trandat* (optional)

AR	0	136.500	3.330	0.000	0.000	0.000	
C	0	71.400	3.298	0.000	0.000	0.000	! *
C2	1	97.530	3.621	0.000	1.760	4.000	
C2O	1	232.400	3.828	0.000	0.000	1.000	! *
CN2	1	232.400	3.828	0.000	0.000	1.000	! OIS

species      molecular index      L-J potential well depth      L-J collision diameter      dipole moment      polarizability      rotational relaxation collision number

# Elementary Reactions



- The first type of categorization of elementary reactions is based on number of species involved in reactants



Unimolecular reaction



Bimolecular reaction



Termolecular reaction

# Elementary Reactions

Even a unimolecular reaction needs a collision first

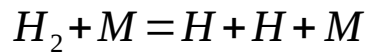
**Table 1:** The three known types of elementary reactions:

Molecularity	Elementary Step	Rate Law	Example
Unimolecular	$A \rightarrow \text{Products}$	$\text{rate} = k[A]$	$N_2O_{4(g)} \rightarrow 2NO_{2(g)}$
Bimolecular	$A + A \rightarrow \text{Products}$	$\text{rate} = k[A]^2$	$2NOCl \rightarrow 2NO_{(g)} + CO_{2(g)}$
	$A + B \rightarrow \text{Products}$	$\text{rate} = k[A][B]$	$CO_{(g)} + NO_{3(g)} \rightarrow NO_{2(g)} + CO_{2(g)}$
Termolecular	$A + A + A \rightarrow \text{Products}$	$\text{rate} = k[A]^3$	
	$A + A + B \rightarrow \text{Products}$	$\text{rate} = k[A]^2[B]$	$2NO_{(g)} + O_{2(g)} \rightarrow 2NO_{2(g)}$
	$A + B + C \rightarrow \text{Products}$	$\text{rate} = k[A][B][C]$	$H + O_{2(g)} + M \rightarrow HO_{2(g)} + M$

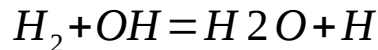
# Elementary Reactions

- The second type of categorization of elementary reactions is based on their role in the reaction progress:

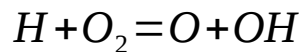
1) **Chain initiation:** The reactants have no radicals but, it will produce radicals



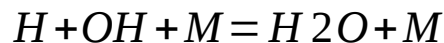
2) **Chain carrying:** The reactant side has one radical but product side will have a different radical



3) **Chain propagation:** The reactant side has one radical and product side will have two different radicals



4) **Chain termination:** Reactant side has radical/s but, no radical is created as product



# Governing Equations in Reactive Flows

- All fluid mechanics is based on **conservation of mass, momentum and energy**
- **In reactive flows**, the conservation of mass is complemented by **conservation of species mass fractions** for all the calculated species

$$\frac{\partial (\rho Y_i)}{\partial t} + \nabla (\rho \vec{u} Y_i) + \nabla (\rho \vec{V}_i Y_i) = \dot{\omega}_i + S_{Y_i}$$

Temporal term      Convection term      Diffusion velocity      Chemical source term      Liquid source term on species

- We also have equation of state in the form of ideal gas law:

$$P = \rho R T$$

- We need thermodynamic and transport properties which are dependent of temperature and pressure but, pressure dependency can be neglected with a good accuracy

# Governing Equations in Reactive Flows

- For a multicomponent mixture (more than one specie in the mixture) we may use the mass averaging as bellow where  $N_s$  is the number of species and  $i$  refers to “i”th specie:

$$c_p = \sum_{i=1}^{N_s} Y_i c_{p,i}$$

$$c_p/R_u = a_1 + a_2 T + a_3 T^2 + a_4 T^3 + a_5 T^4$$

$$S/R_u = a_1 \ln T + a_2 T + a_3 T^2/2 + a_4 T^3/3 + a_5 T^5/4 + a_7$$

$$H_T/R_u = a_1 T + a_2 T^2/2 + a_3 T^3/3 + a_4 T^4/4 + a_5 T^5/5 + a_6$$

- Also we need to calculate the viscosity as a function of temperature using Sutherlands Law, Wilke correlation (1950) or polynomial coefficients:

$$\ln \mu_k = \sum_{n=1}^N a_n k (\ln T)^{n-1}$$

- The polynomials coefficients for **viscosity**, **thermal conductivity** and **diffusion coefficients** are calculated by the available data in Thermo and Transport files which are included in the mechanism file

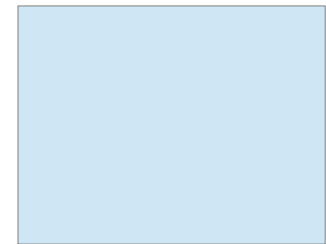
# Homogeneous Reactor

- Consider a box very very small, we define it in a form which the composition of the system is homogeneous everywhere.
- If we have  $\Phi = 1$ , i.e. stoichiometric condition, then in the whole domain we have the same condition
- We want to solve this system in **zero dimension (0D): no velocity in the system**
- Also we assume that there is no heat transfer happening at the walls
- Also we assume that there is no inlet nor outlet in the system
- To setup the system we need two independent intensive thermodynamic properties and composition of the system, e.g.

$T = 700 \text{ K}$

$p = 5 \text{ Mpa}$

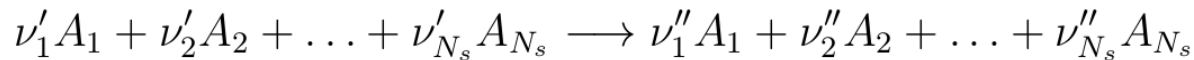
$\Phi = \text{Stoichiometric methane and air}$



Homogeneous reactor

# Chemistry Modeling

- The chemical source term  $\omega_i$  in the introduced conservation equations accounts for the mass conversion of species creation or consumption due to chemical reactions and is the only explicit link of the flow quantities and combustion chemistry.



$$\sum_{i=1}^{N_s} \nu'_{i,l} A_i \rightleftharpoons \sum_{i=1}^{N_s} \nu''_{i,l} A_i, \quad \text{with } l = 1 \dots N_r$$

$$q_l = k_l^f \prod_{i=1}^{N_s} c_i^{\nu'_{i,l}} - k_l^r \prod_{i=1}^{N_s} c_i^{\nu''_{i,l}}$$

$$\omega_i = W_i \sum_{l=1}^{N_r} (\nu''_{i,l} - \nu'_{i,l}) q_l$$

$c = n/V$ , Molar concentration

$k_1^f$ : Forward reaction rate

$k_1^r$ : Reverse reaction rate

$\nu''_{i,l}$ : Stoichiometric coefficient on product side

$\nu'_{i,l}$ : Stoichiometric coefficient on reactant side

$\omega_i$ : Chemical source term

$$\frac{\partial (\rho Y_i)}{\partial t} + \nabla (\rho \vec{u} Y_i) + \nabla (\rho \vec{V}_i Y_i) = \dot{\omega}_i + S_i$$



# Chemistry Modeling

	Reaction	$A$	$n$	$E_a$	Ref.
H <sub>2</sub> /O <sub>2</sub> Chain Reactions					
1	$\dot{\text{H}} + \text{O}_2 = \dot{\text{O}} + \dot{\text{O}}\text{H}$	$1.91 \times 10^{14}$	0.00	16.44	[39]
2	$\dot{\text{O}} + \text{H}_2 = \dot{\text{H}} + \dot{\text{O}}\text{H}$	$5.08 \times 10^4$	2.67	6.292	[40]
3	$\dot{\text{O}}\text{H} + \text{H}_2 = \dot{\text{H}} + \text{H}_2\text{O}$	$2.16 \times 10^8$	1.51	3.43	[41]
4	$\dot{\text{O}} + \text{H}_2\text{O} = \dot{\text{O}}\text{H} + \dot{\text{O}}\text{H}$	$2.97 \times 10^6$	2.02	13.4	[42]

Let's solve for the specie "O" in a e.g. four reaction mechanism (not a real mechanism) to calculate the chemical source term

$$\frac{\partial(\rho Y_o)}{\partial t} = \frac{Y_o^{t+1} - Y_o^t}{t_2 - t_1} = \omega_i$$

# Ignition Delay Time

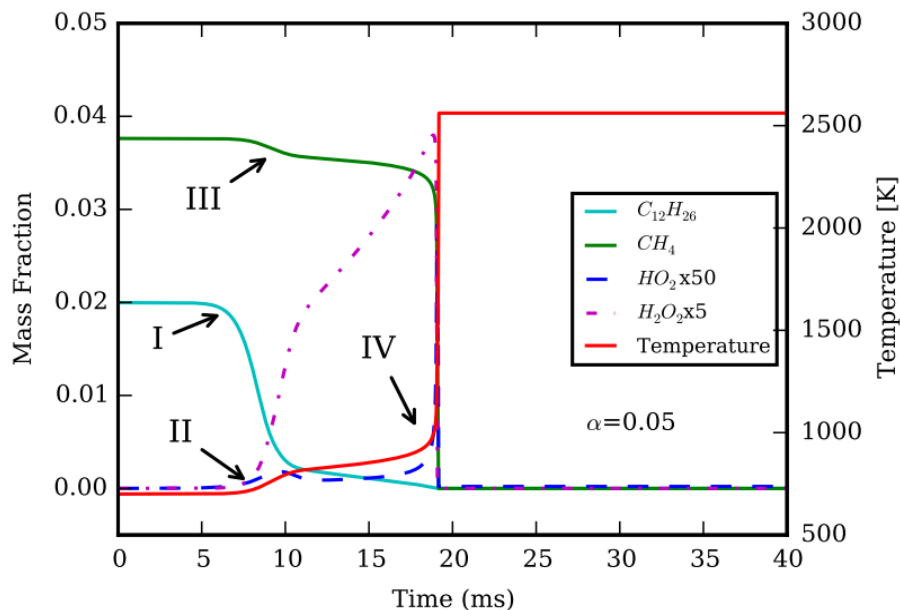
- Ignition delay time (IDT) is the time when combustion initiates in your system
- There are different ways to define the IDT e.g. the time when we have 90% of  $T_{max}$  or  $\text{Max}([\text{OH}][\text{O}])$  or  $P_{max}$  in the system and etc.
- Always always **mention the definition of IDT** that you are using in your calculations
- This is an important property of combustion as we are interested to know when ignition happens in the system e.g. internal combustion engines
- Now let's see the effect of different parameters on IDT of a system

# Role of Radicals in Combustion

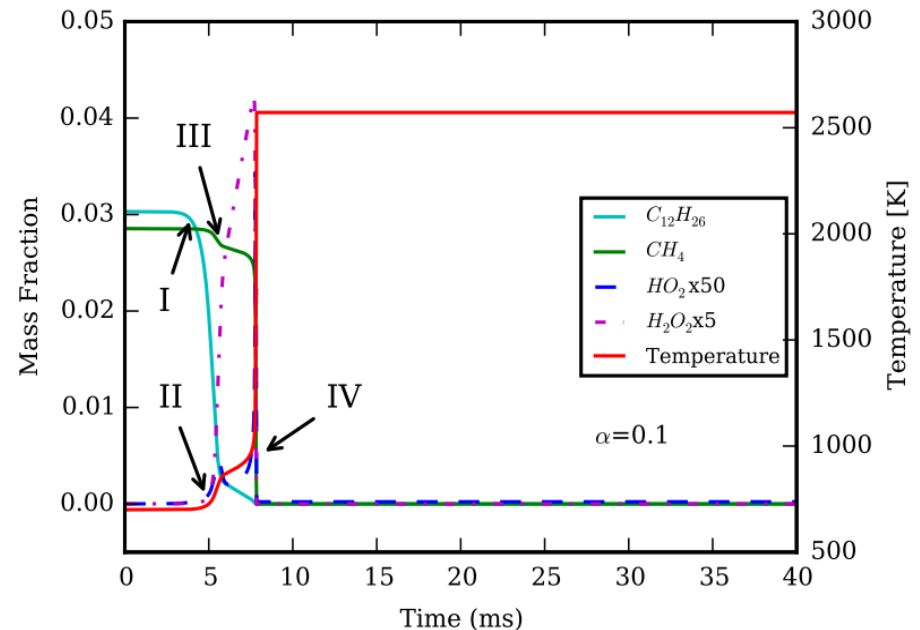
- We run stoichiometric methane and air at  $T=700\text{K}$  and  $p=5\text{ Mpa}$ .

No ignition till 40ms!!!

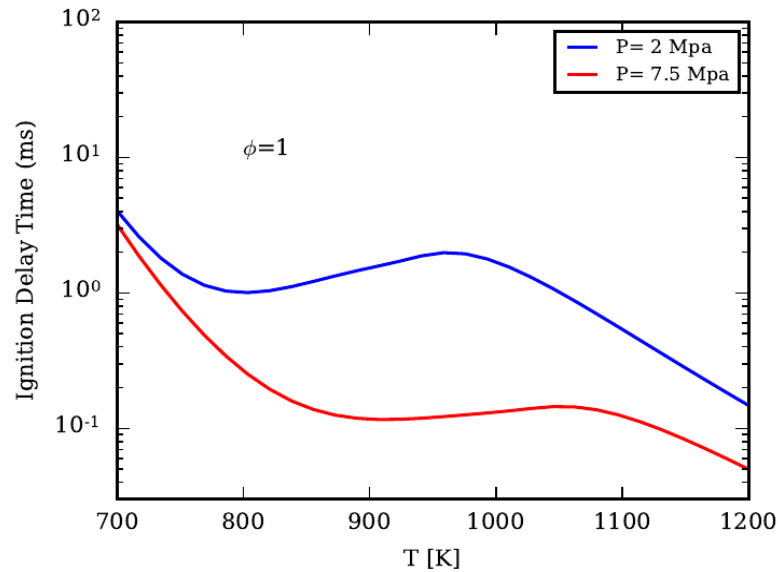
## Add n-dodecane



## Add more n-dodecane

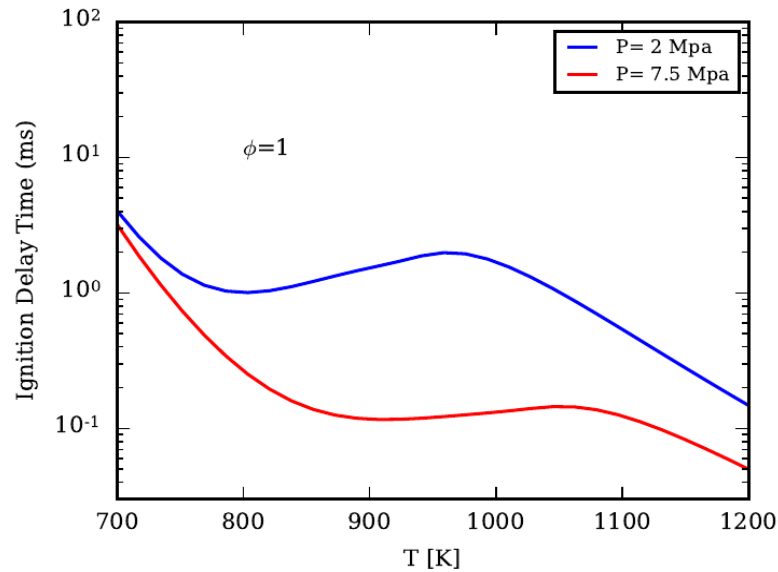


# Temperature & Pressure Effect on IDT



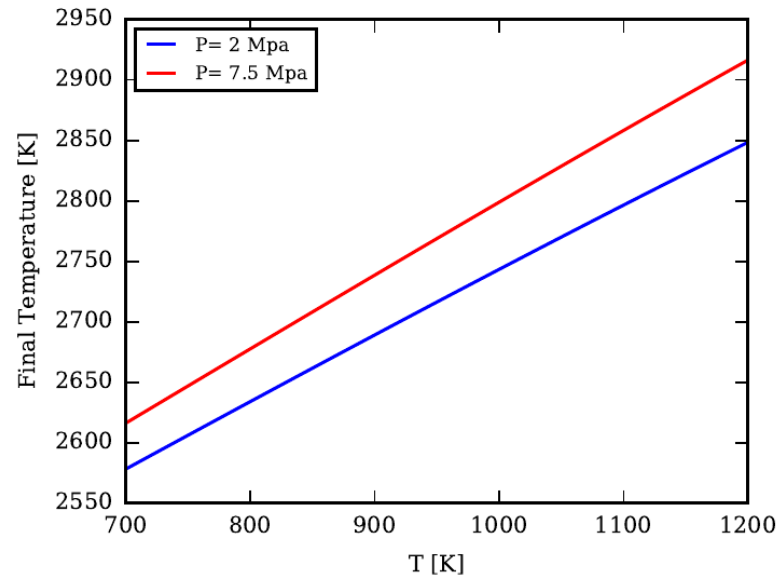
- Increasing temperature of mixture reduces the IDT of a system in general
- Higher temperature means higher random motion of molecules leading to more successful collisions in the system
- Negative Temperature Coefficient (NTC) behavior refers to the condition when increasing the temperature increases the IDT which is shown in some species

# Temperature & Pressure Effect on IDT



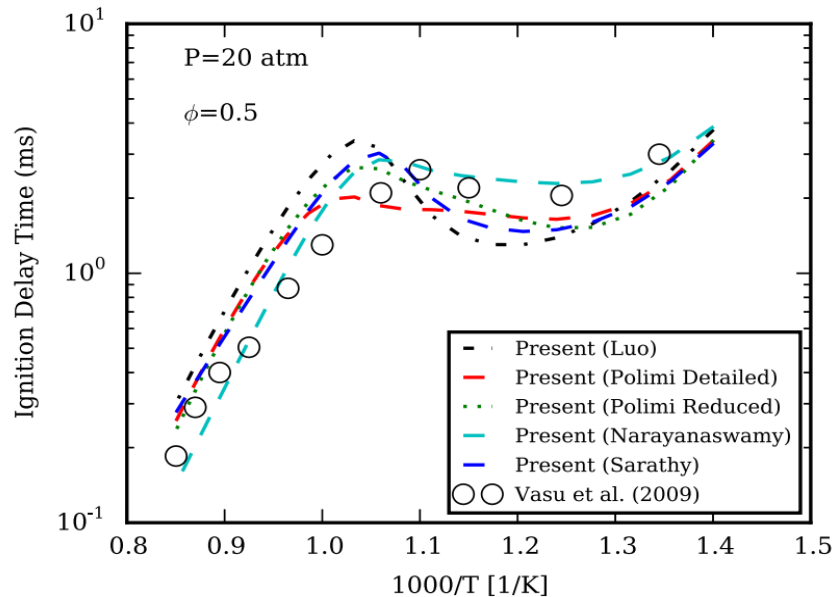
- Increasing pressure of mixture reduces the IDT of a system as it increases the collisions in the system by making the system more compact
- This could be not true for special cases such as H<sub>2</sub> as by increasing P, the collision of termolecular reactions becomes more and more important changing system pathways
- **Higher pressure usually** leads to **more successful collisions** in the system

# Temperature Effect on Final Temperature



- Increasing initial temperature or pressure constantly increases the final temperature of the system

# Mechanisms Perform Differently



- Mechanisms are detailed (original huge number of species and reactions), reduced (originated from one of the detailed ones) or skeletal (modified for a certain purpose e.g. IDT for a specific range)
- Even the detailed ones are different with each other as they have different species, reactions and also different thermal properties so, we should be careful when choosing a mechanism

# Cantera Software

- Open source software similar to Chemkin for problems involving chemical kinetics, thermodynamics, and/or transport processes.
- Cantera can be used from Python and Matlab interfaces
- In this course we use the Python interface
- We solve for time history of homogeneous reactors
- We setup each single case by two independent intensive thermodynamic properties in addition the composition of the system
- Here I show simple cases how to setup cases in Cantera/Python interface
- **We may use in linux terminal the command:**

```
ck2cti --input=chem.inp --thermo=therm.dat --transport=tran.dat --permissive
```

With this we may download any mechanism and turn it into "cti" format which can be read by Cantera software



# Cantera Software

```
import cantera as ct          # This imports cantera package into python
import numpy as np           # This imports numpy which has many ready-made functions similar to Matlab into Python
gas1 = ct.Solution('gri30.xml') # We upload a mechanism "gri30.xml" into a variable gas1 (.xml/.cti files)
gas1()
#This is setting the temperature, pressure and mole fraction (X). We could set mass fraction (Y) instead of mole fraction.
gas1.TPX= 1200 (this is Kelvin), 101325 (this is in Pascal), 'CH4': 1, 'O2': 2, 'N2':7.52
or
gas1.TPY= 1200 (this is Kelvin), 101325 (this is in Pascal), 'CH4': 0.0551863, 'O2': 0.220149, 'N2':0.724665
```

```
gri30:
  temperature      1200 K
  pressure         101325 Pa
  density          0.280629 kg/m^3
  mean mol. weight 27.6332 amu

           1 kg          1 kmol
-----
enthalpy      861943      2.382e+07 J
internal energy 500879      1.384e+07 J
entropy       8914.3      2.463e+05 J/K
Gibbs function -9.83522e+06 -2.718e+08 J
heat capacity c_p 1397.26    3.861e+04 J/K
heat capacity c_v 1096.38    3.03e+04 J/K

           X          Y          Chem. Pot. / RT
-----
O2         0.190114    0.220149    -28.7472
CH4        0.095057    0.0551863   -35.961
N2         0.714829    0.724665    -25.6789
[ +50 minor] 0          0
```

# Cantera: Useful commands

- **Try these commands:**

```
gas1.species_name
```

```
gas1.n_species
```

```
gas1.n_reactions
```

```
gas1.species_index('CH4')
```

```
gas1.Y[gas1.species_index('CH4')]
```

```
gas1.set_equivalence_ratio(0.5, 'CH4', 'O2:1.0, N2:3.76')
```

```
gas1.TP=1000, 10*ct.one_atm
```

```
gas1.X
```

```
gas1.Y
```

```
gas1.T
```

```
gas1.P
```

# Cantera: Equilibrium

```
>>> import cantera as ct
>>> g = ct.Solution('gri30.xml')
>>> g.TPX = 300.0, ct.one_atm, 'CH4:0.95,O2:2,N2:7.52'
>>> g.equilibrate('TP')
```

- The above statement sets the state of object g to the state of chemical equilibrium holding temperature and pressure fixed. Alternatively, the specific enthalpy and pressure can be held fixed:

```
>>> g.TPX = 300.0, ct.one_atm, 'CH4:0.95,O2:2,N2:7.52'
>>> g.equilibrate('HP')
```

- This is giving us equilibrium based on the Gibbs free energy as it was discussed in previous session
- Now we want to run our homogeneous reactor for a certain time and record the time history

# Time History

- You may look at the code provided for the second session in the course material

[runTest\\_timeHistory.py](#) : This script runs a single homogeneous reactor and saves the data in a txt file. We may change the initial conditions and see how combustion is delayed or accelerated (Remember this is a methane ignition case which means we have to start with big initial temperatures such as 900K)

[postProcessingtest\\_timeHistory.py](#) : This script reads the txt file created by previous script. Just remember that if you change initial conditions (T, P or phi) in the first script you have to change them here as well

**Thank you for your attention!**