Modeling of Partial Oxidation of Acetaldehyde in Cool Flame

Alexandre V. Chirokov

- Description of Modeling Case
- Gas Dynamics Modeling
- Chemistry Kinetics Modeling

Project Framework

Gas-Phase Reactions Mechanism

CHEMKIN

Proved, Enhanced and Reduced Gas-Phase Reactions Mechanism

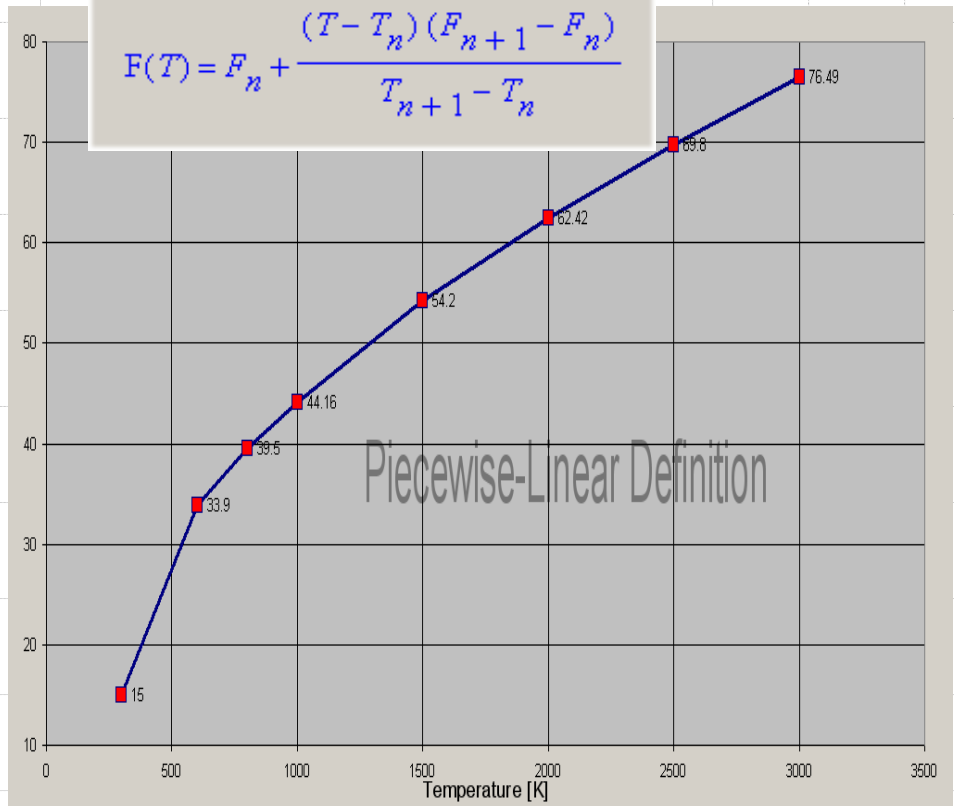
FLUENT

Database of Physical Properties for Reacting flow with Heat/Mass Transfer

Physical Properties for Reacting flow

- Density
- Viscosity
- Formation Enthalpies
- Heat Capacity
- Thermal Conductivity
- Mass Diffusion Coefficient

$$F(T) = F_n + \frac{(T - T_n)(F_{n+1} - F_n)}{T_{n+1} - T_n}$$

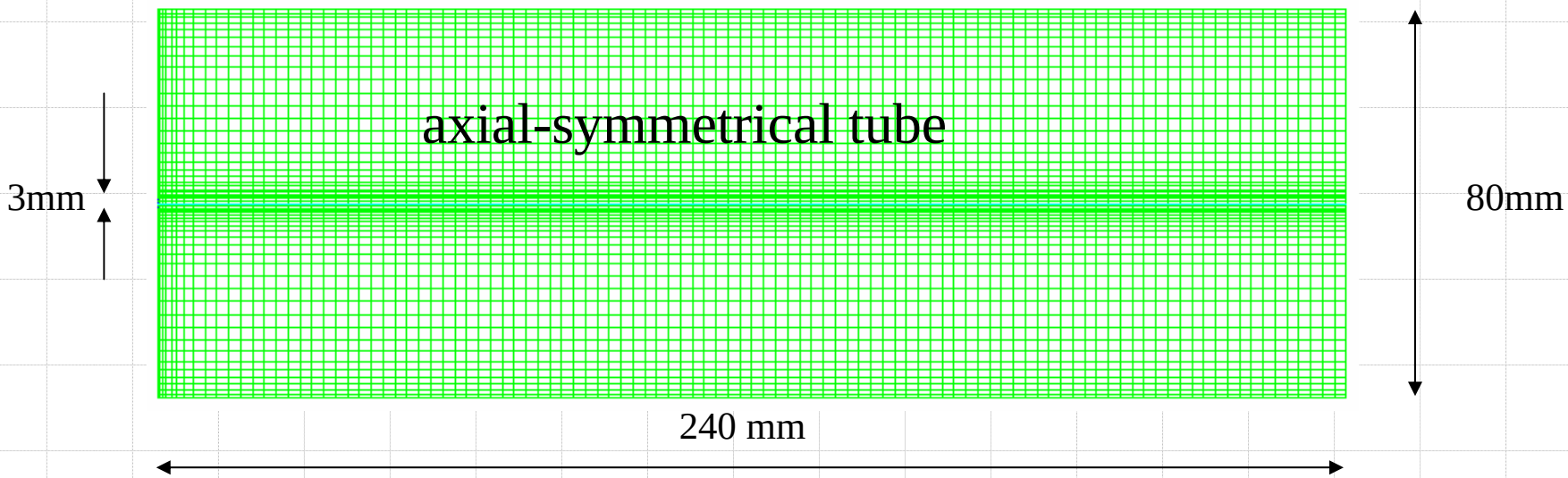


300	600	800	1000	1500	2000	2500	3000	K

13 Species → 5 Physical Properties → at 8 Temperature points

Piecewise-Linear Variation with Temperature

Gas Dynamics Modeling



We solve Gas Dynamics equations on 2D axial-symmetrical non-uniform Grid.
We vary the following parameters:

- Gas Mixture inlet velocity **0.2 .. 50** [m/sec]
- Temperature boundary conditions on Tube walls **600 .. 1200**[K]

and we try **adiabatic walls**.

We kept constant the following parameters:

- Gas Mixture composition **1:8** [O2:CH3CHO] molar fractions
- Gas Mixture inlet temperature **300** [K]

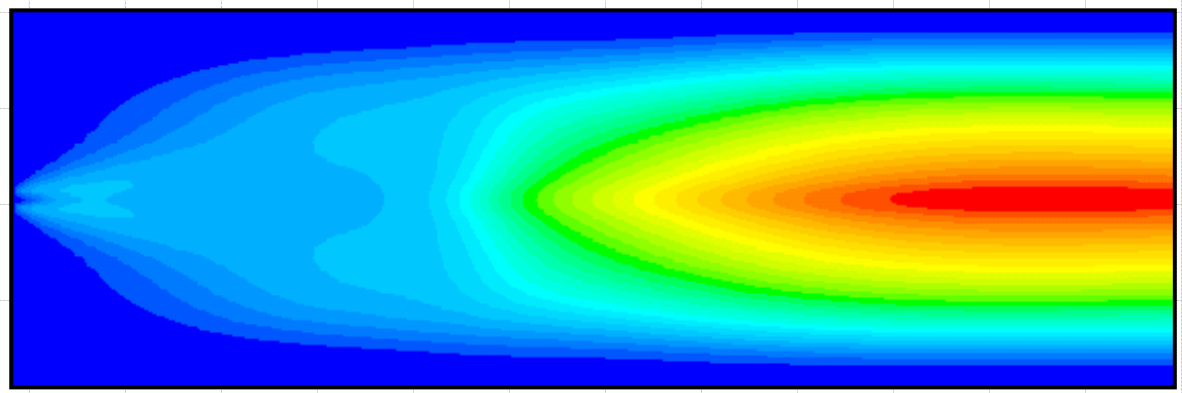
Tube

Tube Parameters

Length	=	**240**	[mm]
Inner diameter	=	**80**	[mm]
Outlet diameter	=	**80**	[mm]
Inlet diameter	=	**3**	[mm]

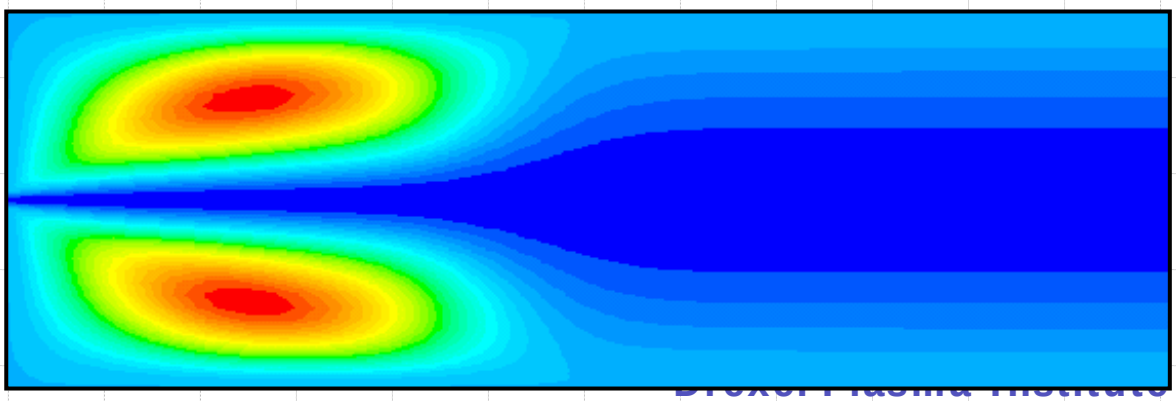
Gas Dynamics Modeling

Effective Viscosity of Gas Mixture **1.8E-05 .. 0.35E-3** [KG/M-S]

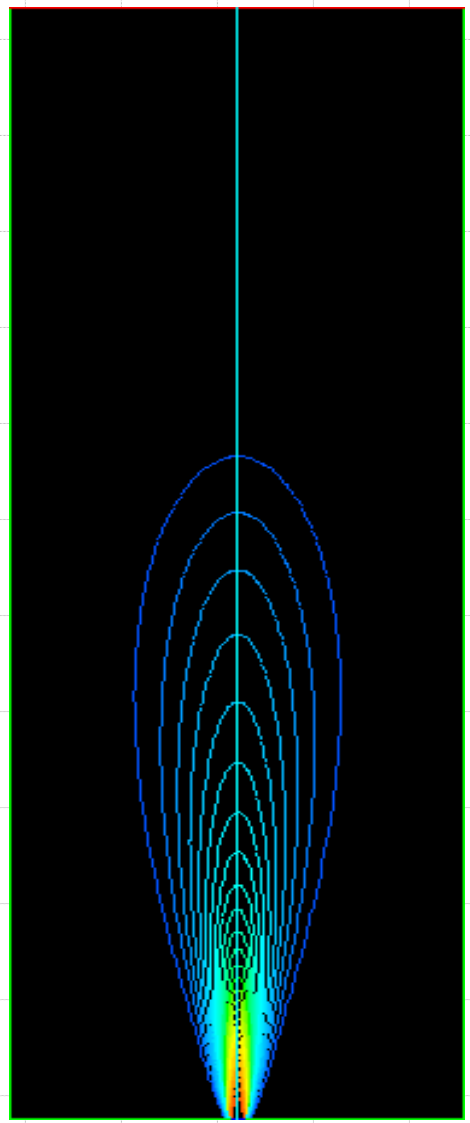


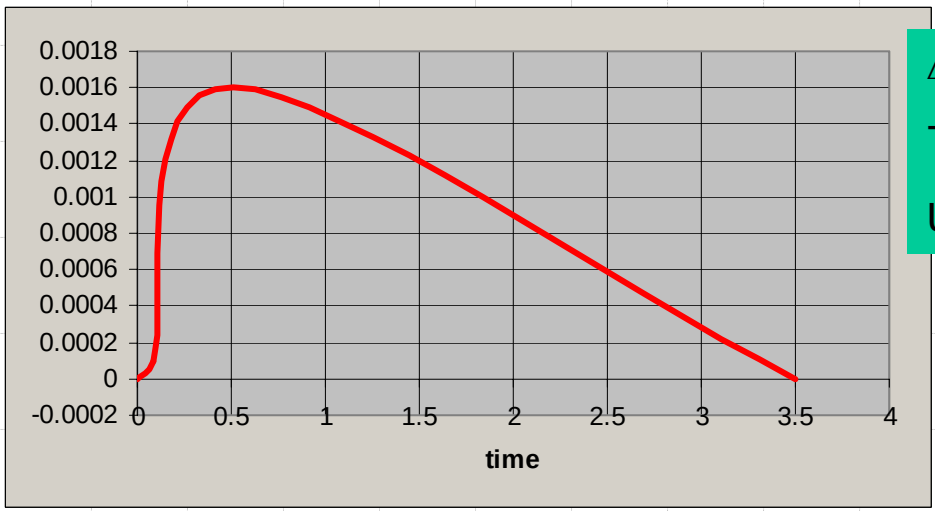
U =**0.6** [m/sec]
Tw=**600** [K]
Tg=**300** [K]

Stream Function of Gas Mixture **0.0 .. 2.65E-05** [M3/S]



Gas Dynamics Modeling

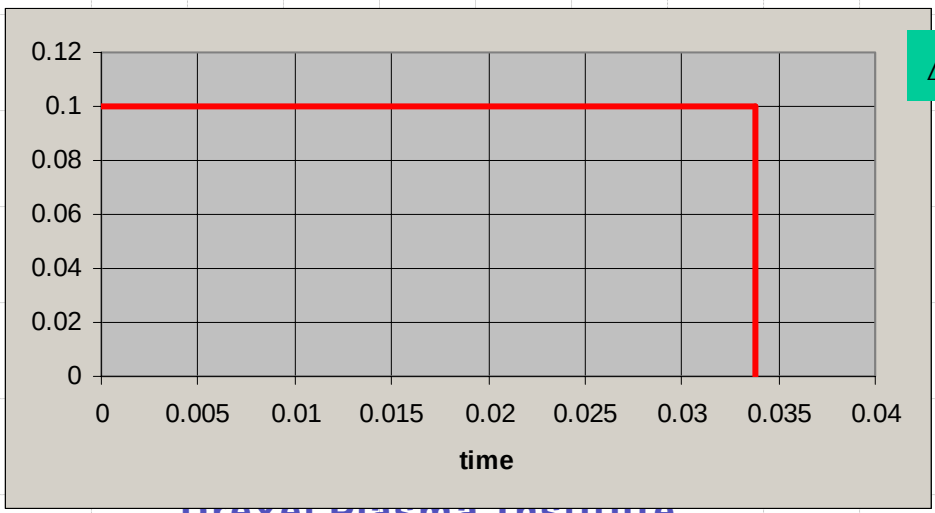




ΔT = **3.5** sec

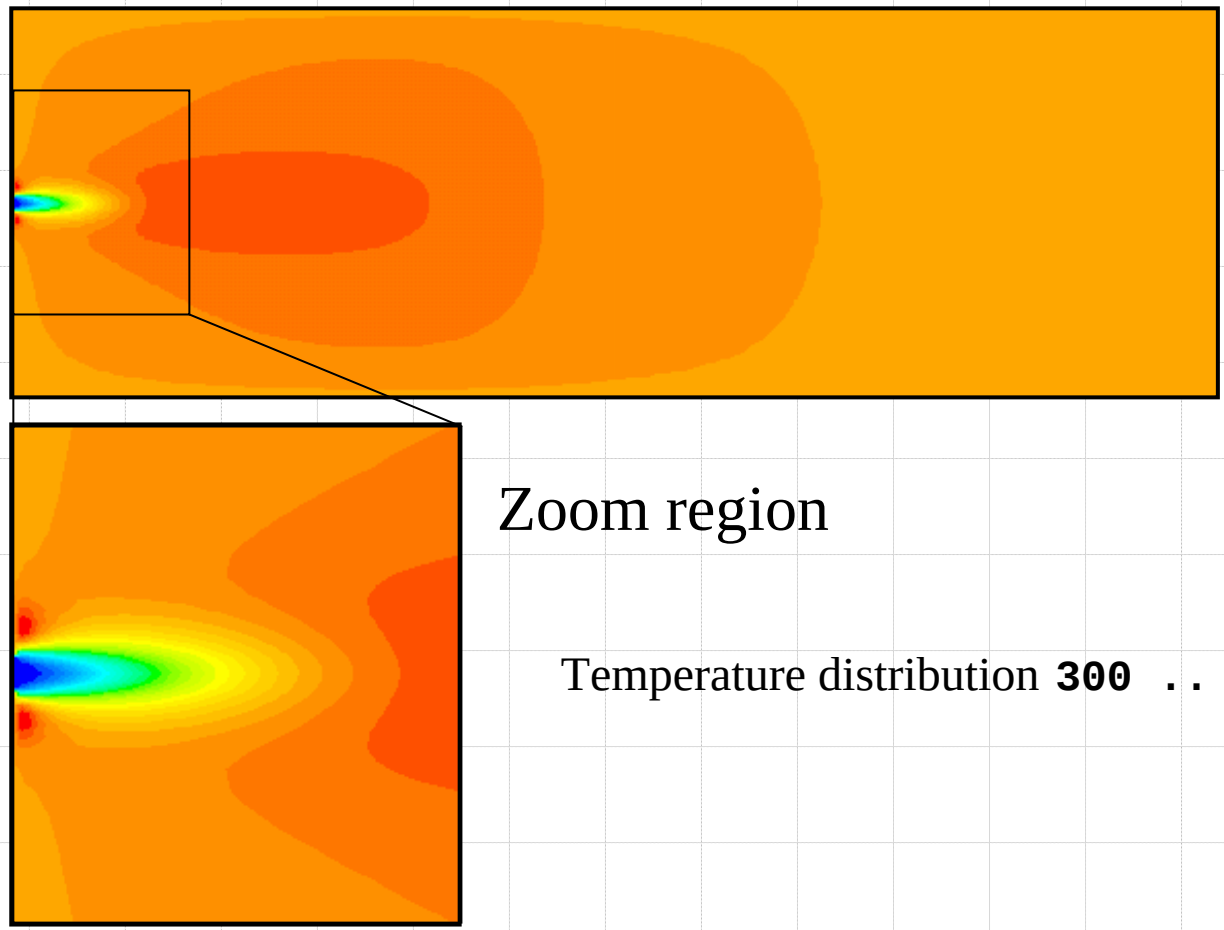
Tm = **0.5** sec

U = **50** m/sec



ΔT =**0.0338** sec

Temperature Distribution



U = **0.6** [m/sec]

Tw = **600** [K]

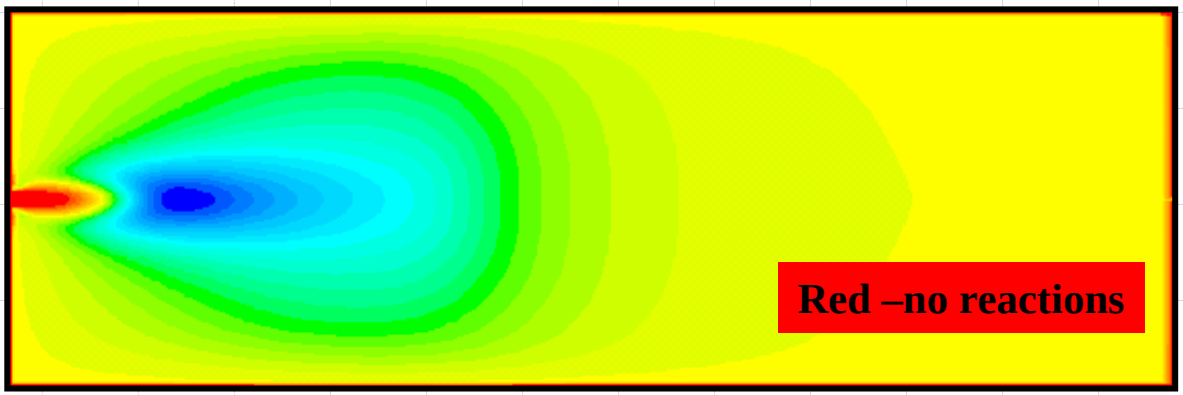
Tg = **300** [K]

Zoom region

Temperature distribution **300 .. 650** [K]

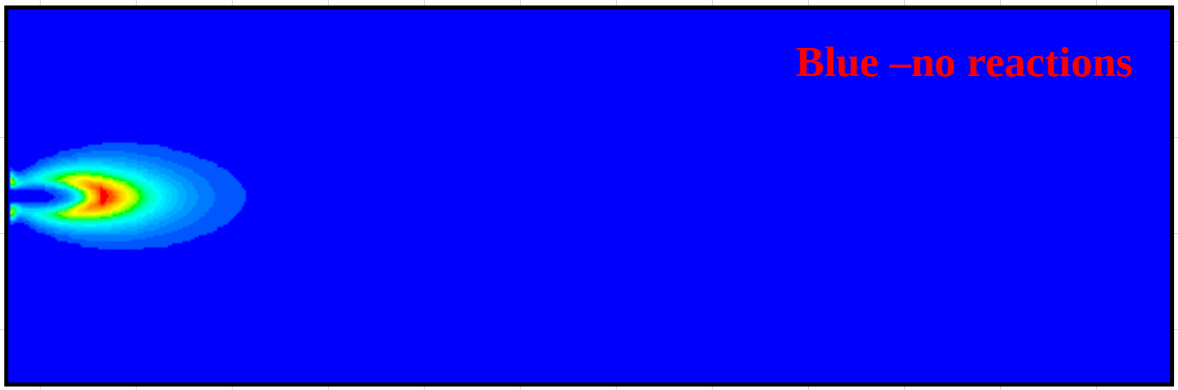
Chemistry Modeling with FLUENT

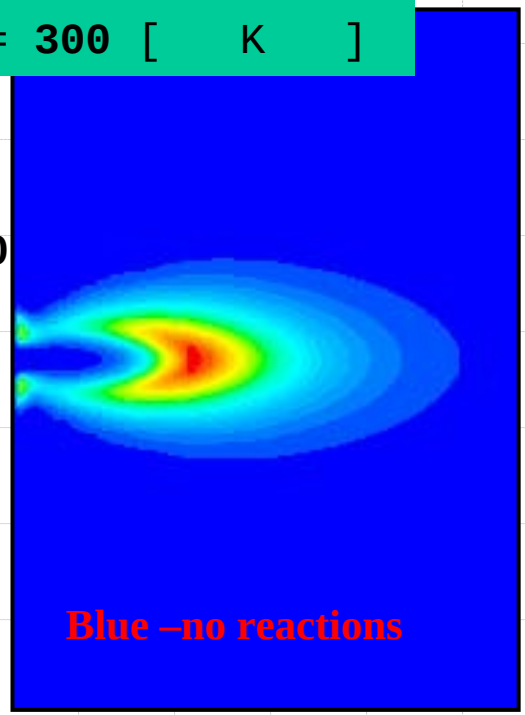
Reaction Rate CH3CHO+O2=CH3CO+HO2 **-1.44E3 .. 0.0** [KG/M3/S]



U = **0.6** [m/sec]
Tw = **600** [K]
Tg = **300** [K]

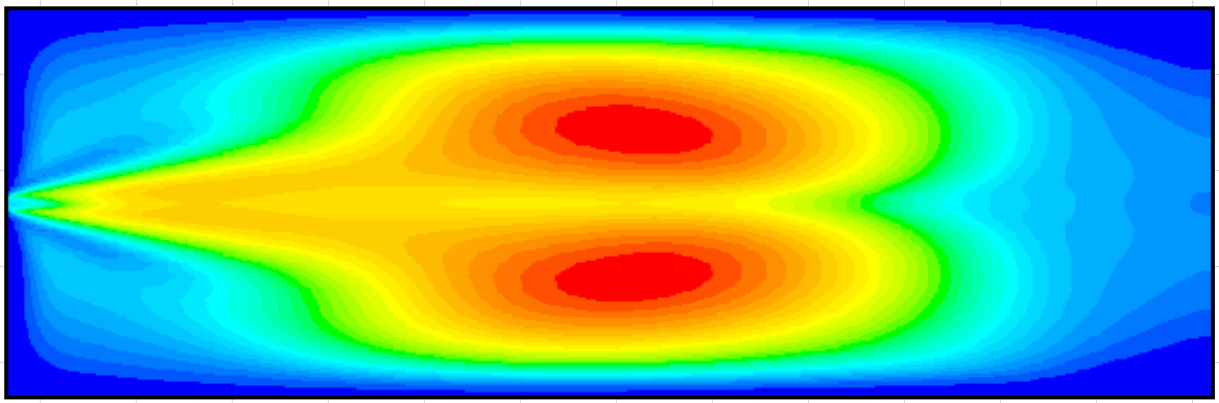
Reaction Rate OH+CH3CHO=CH3CO+H2O **2288.179 .. 0.0**





Gas Dynamics Modeling

Effective Viscosity of Gas Mixture **1.6E-05 .. 0.5E-3** [KG/M-S]

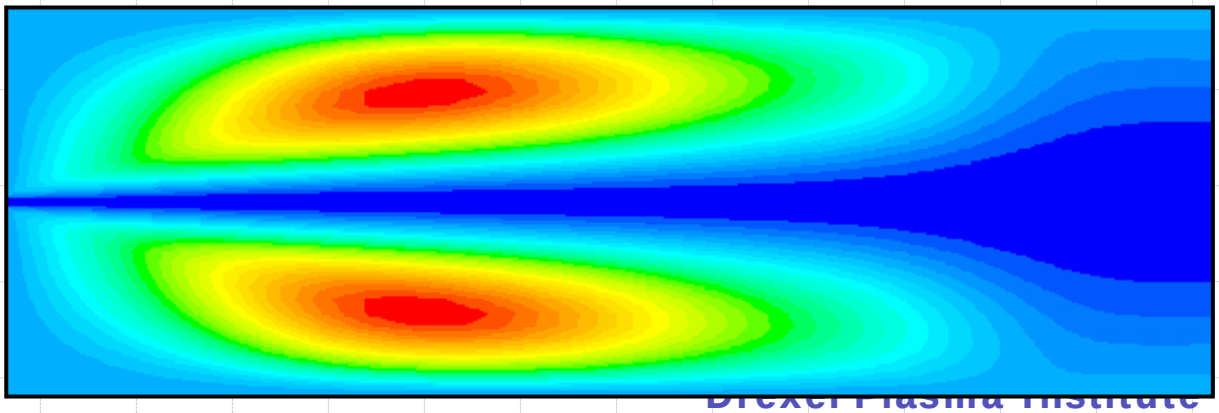


U = **5** [m/sec]

Tw = **adiabatic**

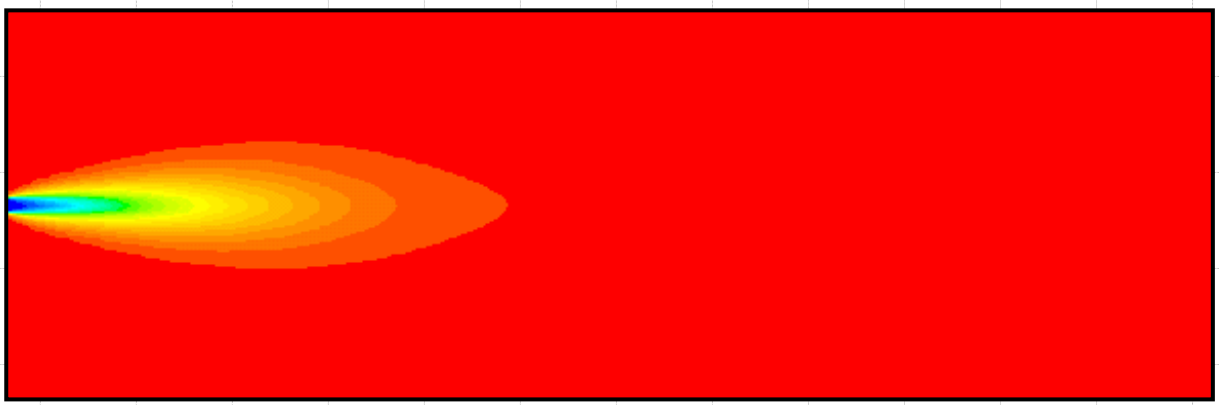
Tg = **300** [K]

Stream Function of Gas Mixture **0 .. 2.65E-04** [M3/S]



Temperature Distribution

Temperature distribution **300 .. 635** [K]

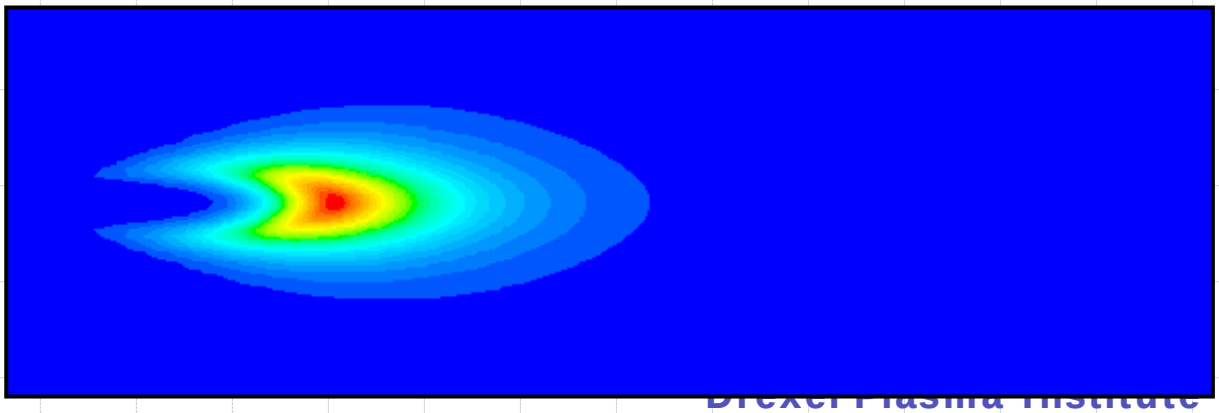


U = **5** [m/sec]

Tw = **adiabatic**

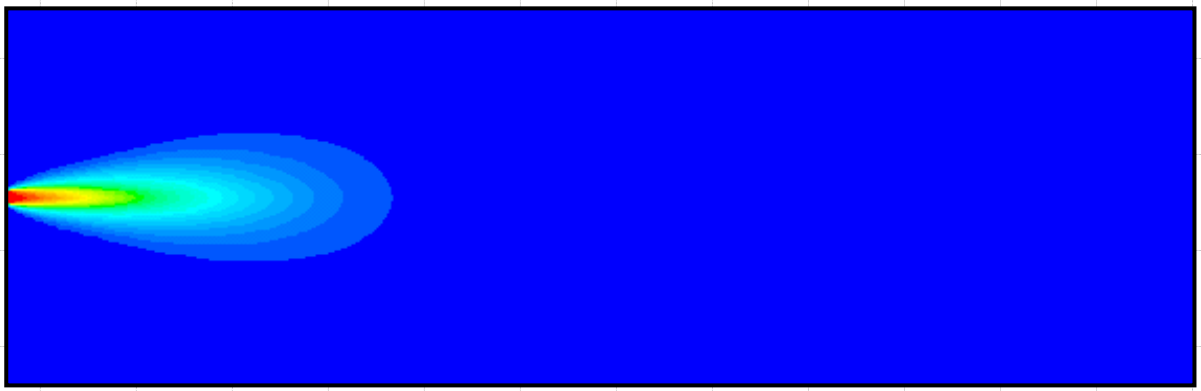
Tg = **300** [K]

Mole fraction of OH **0 .. 1.66E-3**



Mole Fractions of Species

Mole fraction of O2 **0.04 .. 0.1**

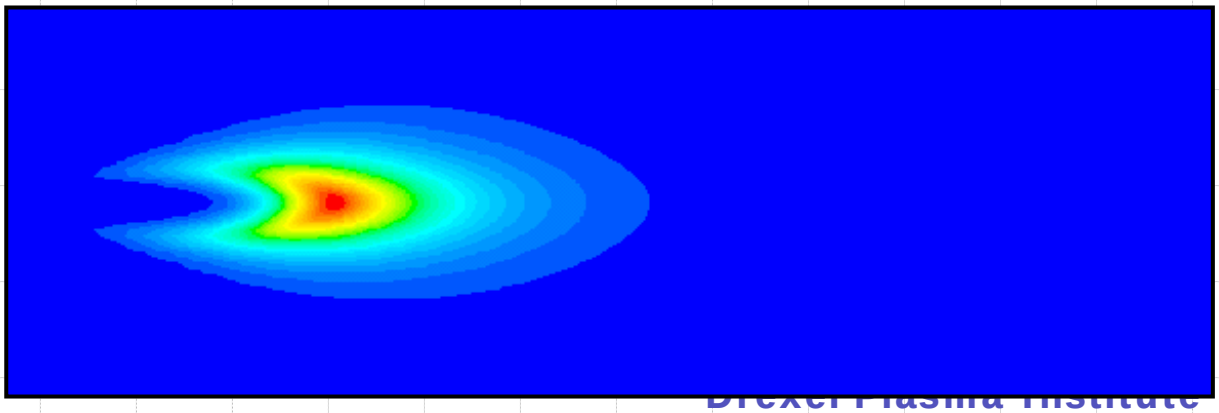


U = **5** [m/sec]

Tw = **adiabatic**

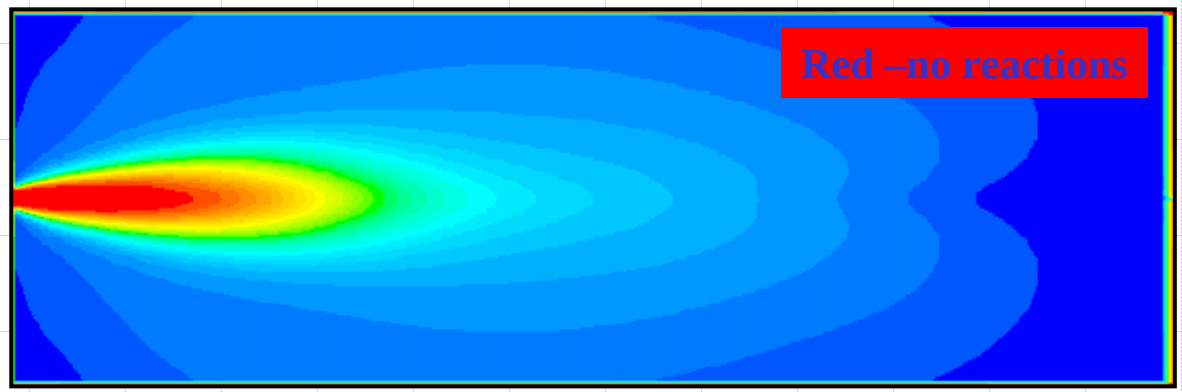
Tg = **300** [K]

Mole fraction of OH **0 .. 1.66E-3**



Chemistry modeling with FLUENT

CH3CHO+O2=CH3CO+HO2 0 .. 0.003342973[KG/M3/S]

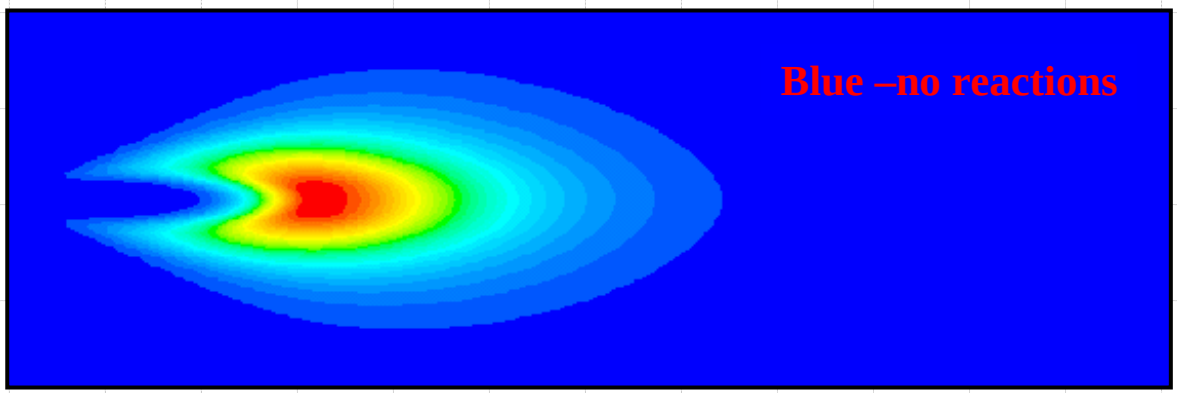


U = **5** [m/sec]

Tw = **adiabatic**

Tg = **300** [K]

CH3CO3H+O2=CH3+OH+CO2 0 .. 0.149 [KG/M3/S]



CHEMKIN Framework

Gas-Phase Reactions
[chem.inp]

Thermodynamic Database
[therm.dat]

COOL Flame Input file
[cool flame.inp]

CHEMKIN Interpreter

ODE Solver

CHEMKIN link file
[chem.bin]

CHEMKIN Gas-Phase Subroutine Library

COOL Flame FORTRAN Program

Debug information output
Used for control precision of solution
[debug.out]

Digitally formatted output
Contain the same data as [cool flame.out] but in EXEL format
[cool flame.ex]

Text Formatted Output file
[cool flame.out]

Post Processing Framework

CHEMKIN link file
[chem.bin]

SENKIN input file
[senkin.inp]

SENKIN

Sensitivity analysis of Gas-Phase Reactions Mechanism

SENKIN Binary file
[senkin.bin]

MECHMOD

XSenkPlot

KINALC

Processing sensitivity analysis results
Extracting information from reaction rates and stoichiometry
Redundant species and QSSA species

Modification and transformation of mechanism files

Reactions Paths
Net Rate and Reaction Flux integration

Post Processing of results of Chemistry kinetics modeling.
Used for
- ***Proving and Enhancement***
- ***Visualization***
- ***Understanding***
- ***Reducing***
- ***Validation***

of **Gas-Phase Reactions Mechanism**

Version info of used Software

1.	CHEMKIN Gas-Phase Subroutine Library CHEMKIN-II	Version 4.5
2.	CHEMKIN Gas-Phase Subroutine Library CHEMKIN-II	Version 4.9
3.	CHEMKIN Interpreter	Version 3.6
4.	CHEMKIN Interpreter	Version 3.9
5.	KINALC	Version 1.3
6.	MECHMOD	Version 1.2
7.	SENKIN	Version 3.1
8.	LSODE Livermore solver for ODE march 30, 1987	Version
9.	XSenkPlot	Version 1.2

Gas-Phase Reactions Mechanism

REACTIONS CONSIDERED	(k = A T**b exp(-E/RT)) A	b	E
1. CH3CHO+O2=>CH3CO+HO2	3.00E+12	0.0	25237.1
2. CH3CO+O2=>CH3CO3	2.00E+11	0.0	0.0
3. CH3CO3+CH3CHO=>CH3CO3H+CH3CO	1.00E+13	0.0	10139.0
4. CH3CO3H=>CH3+OH+CO2	2.00E+14	0.0	40170.3
5. CH3CO+M=>CH3+CO+M	3.00E+12	0.0	16722.0
6. CH3+O2=>CH3O2	1.00E+12	0.0	15065.4
7. CH3O2=>CH3+O2	1.00E+14	0.0	27641.7
8. 2CH3=>C2H6	2.50E+13	0.0	0.0
9. CH3O2+CH3O2=>CH3O+CH3O+O2	1.00E+12	0.0	0.0
10. CH3O+CH3O=>CH2O+CH3OH	1.00E+12	0.0	0.0
11. CH3O2+CH3CHO=>CH3O2H+CH3CO	1.00E+12	0.0	10329.8
12. CH3O2H=>CH3O+OH	2.00E+15	0.0	40649.4

NOTE: A units mole-cm-sec-K, E units cal/mole

Source: "Measurements on the Oscillatory Cool Flame Oxidation of Acetaldehyde and comparison with Reaction Mechanism Models" J. Phys. Chem. 1995, 99, 12835 – 12845 Lisa L. Skrumeda and John Ross*

Gas-Phase Reactions Mechanism

REACTIONS CONSIDERED	(k = A T**b exp(-E/RT)) A	b	E
13. OH+CH3CHO=>CH3CO+H2O	1.00E+12	0.0	2391.6
14. CH3O+O2=>CH2O+HO2	1.00E+12	0.0	5964.1
15. OH+CH2O=>HCO+H2O	6.00E+11	0.0	0.0
16. HCO+M=>H+CO+M	1.50E+14	0.0	18991.7
17. HCO+O2=>CO+HO2	1.00E+12	0.0	5978.0
18. OH+CO=>H+CO2	3.00E+11	0.0	600.4
19. H+O2=>OH+O	2.00E+14	0.0	16492.8
20. H+O2+M=>HO2+M	5.00E+09	0.0	-1300.2
21. O+CH2O=>HCO+OH	5.00E+13	0.0	4598.3
22. HO2+CH2O=>HCO+H2O2	1.00E+12	0.0	7995.9
23. 2HO2=>H2O2+O2	1.80E+12	0.0	0.0
24. H2O2+M=>2OH+M	3.10E+17	0.0	46977.3
25. OH+H2O2=>HO2+H2O	3.60E+12	0.0	0.0

NOTE: A units mole-cm-sec-K, E units cal/mole

ODE Solver

We Solve:

dYi(x)/dx = Fi(x; y1 .. YN); i= 1 .. N

In *initial value problems* all the **Yi** are given at some starting value **Xs** ,and it is desired to find the **Yi** 's at some final point **Xf** , or at some discrete list of points (for example, at tabulated intervals).

We use:

Predictor-corrector methods store the solution along the way, and use those results to extrapolate the solution one step advanced; they then correct the extrapolation using derivative information at the new point. Ideal for high-precision solution of smooth equations with complicated right-hand sides.

Implementation:

"LSODE" Livermore solver for ordinary differential equations that use Adams-Bashforth-Moulton method.

Adams-Bashforth-Moulton method

The Adams-Bashforth part is the predictor. For example, the third-order case is predictor:

$$\text{predictor:} \qquad y_{n+1} = y_n + \frac{h}{12}(23y'_n - 16y'_{n-1} + 5y'_{n-2}) + O(h^4)$$

Here information at the current point **Xn** , together with the two previous points **Xn-1** and **Xn-2** (assumed equally spaced), is used to predict the value **Yn+1** at the next point, **Xn+1** . The Adams-Moulton part is the corrector. The third-order case is corrector:

$$\text{corrector:} \qquad y_{n+1} = y_n + \frac{h}{12}(5y'_{n+1} + 8y'_n - y'_{n-1}) + O(h^4)$$

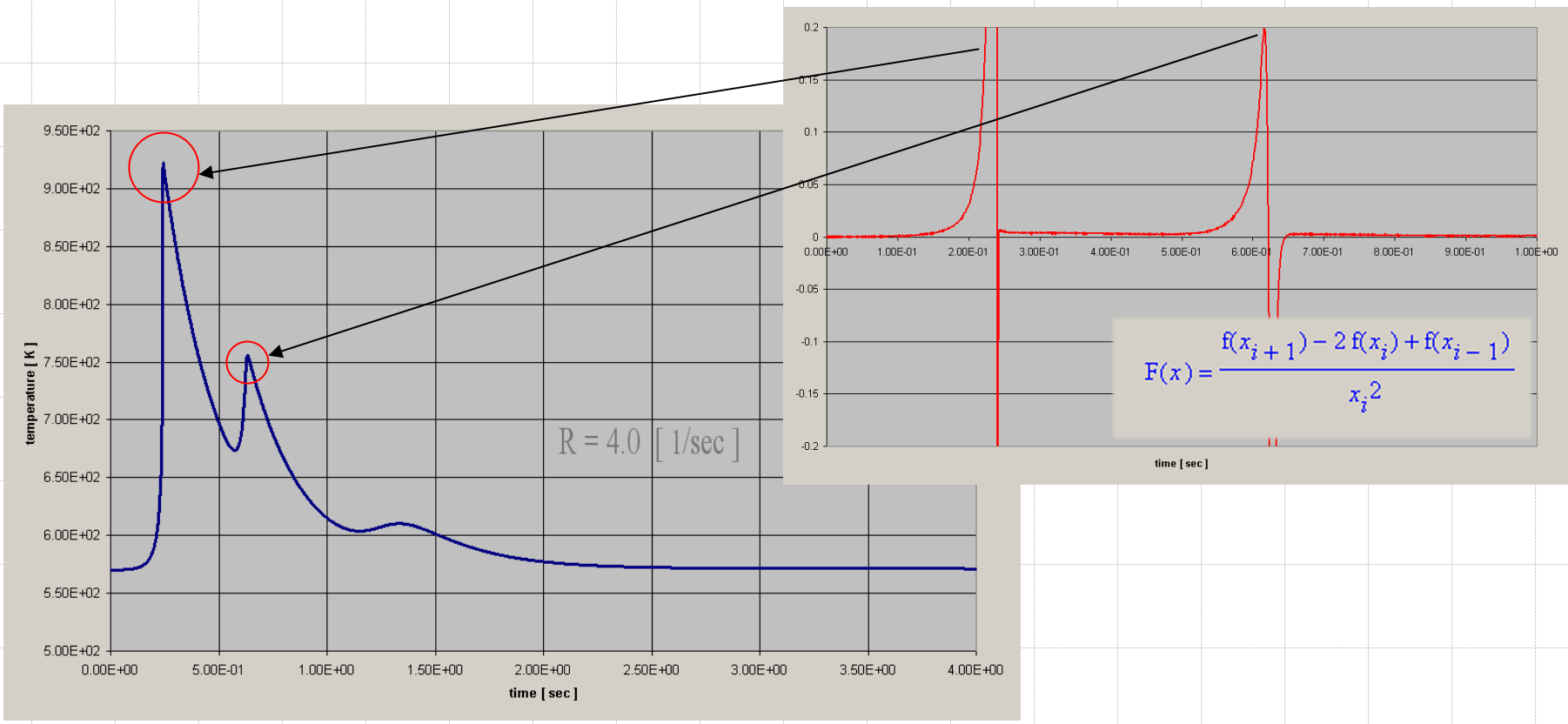
Without the trial value of **Yn+1** from the predictor step to insert on the right-hand side, the corrector would be a nasty implicit equation for **Yn+1** .
The difference between the
predicted and corrected function values supplies information on the local truncation error that can be used to control accuracy and to adjust stepsize.

RMS(e(i)/ewt(i))<1, where ewt(i)=rtol*abs(y(i))+atol;

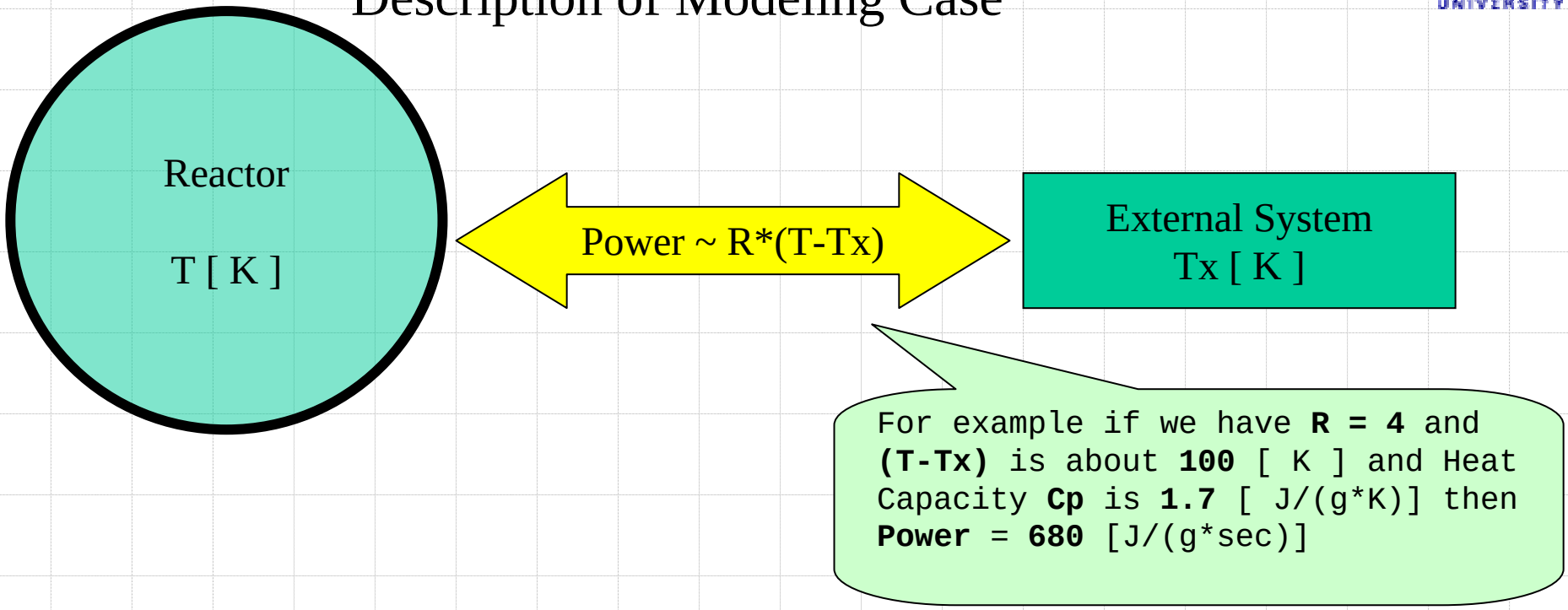
All calculations were made with
rtol=1.0E-8 relative tolerance
atol=1.0E-15 absolute tolerance

Tolerance of *Predictor-Corrector*

The tolerance of *Predictor-corrector* is highly affected by the second derivative of solution. Because *Predictor* step performs extrapolation of solution, and when the second derivative is high this step leads to high local errors.



Description of Modeling Case



n = vector of molar fractions of species
T = Temperature of Gas Mixture in Reactor

Ignition time of gas mixture

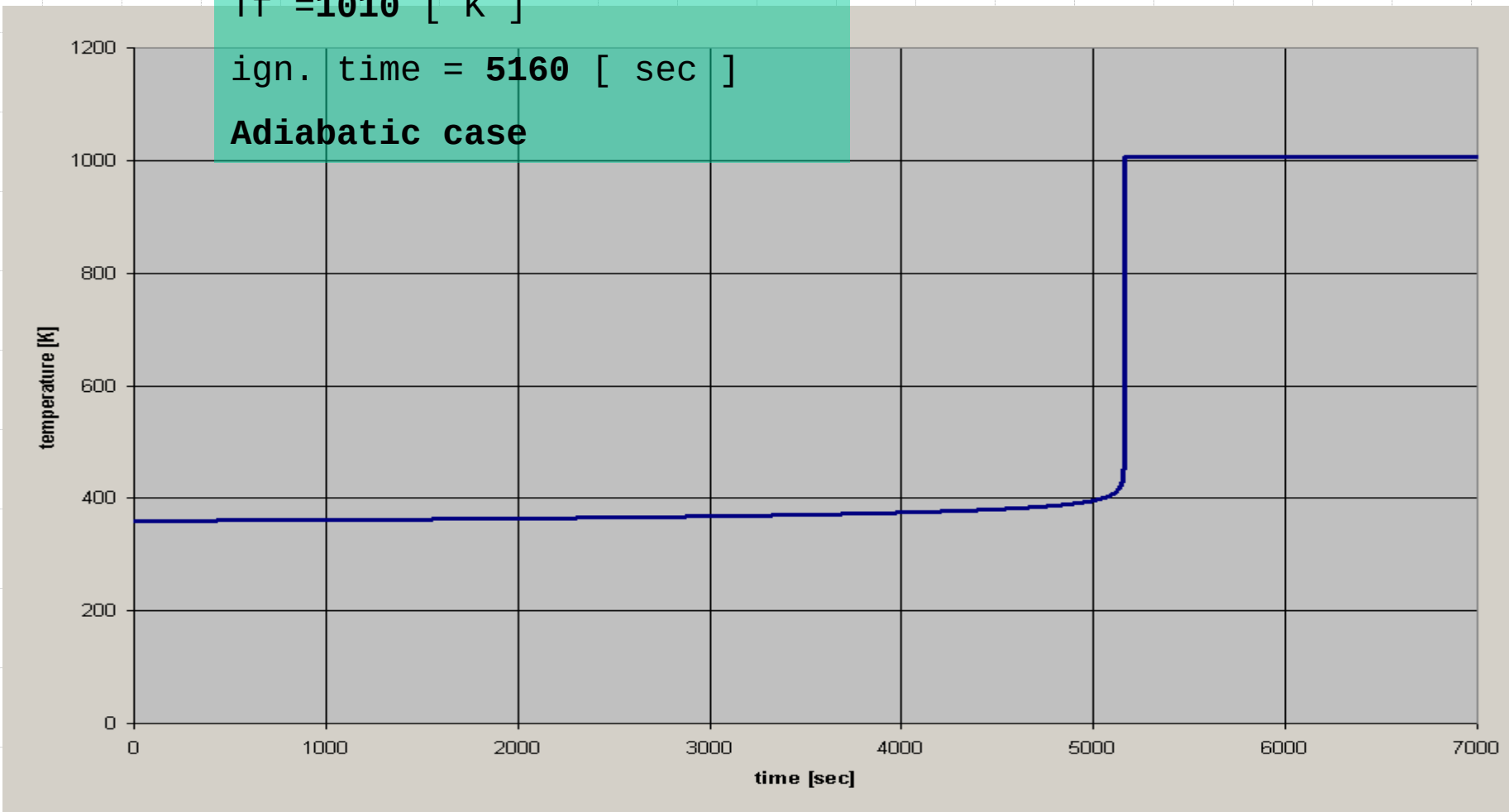
Ti = **360** [K]

Tf =**1010** [K]

ign. time = **5160** [sec]

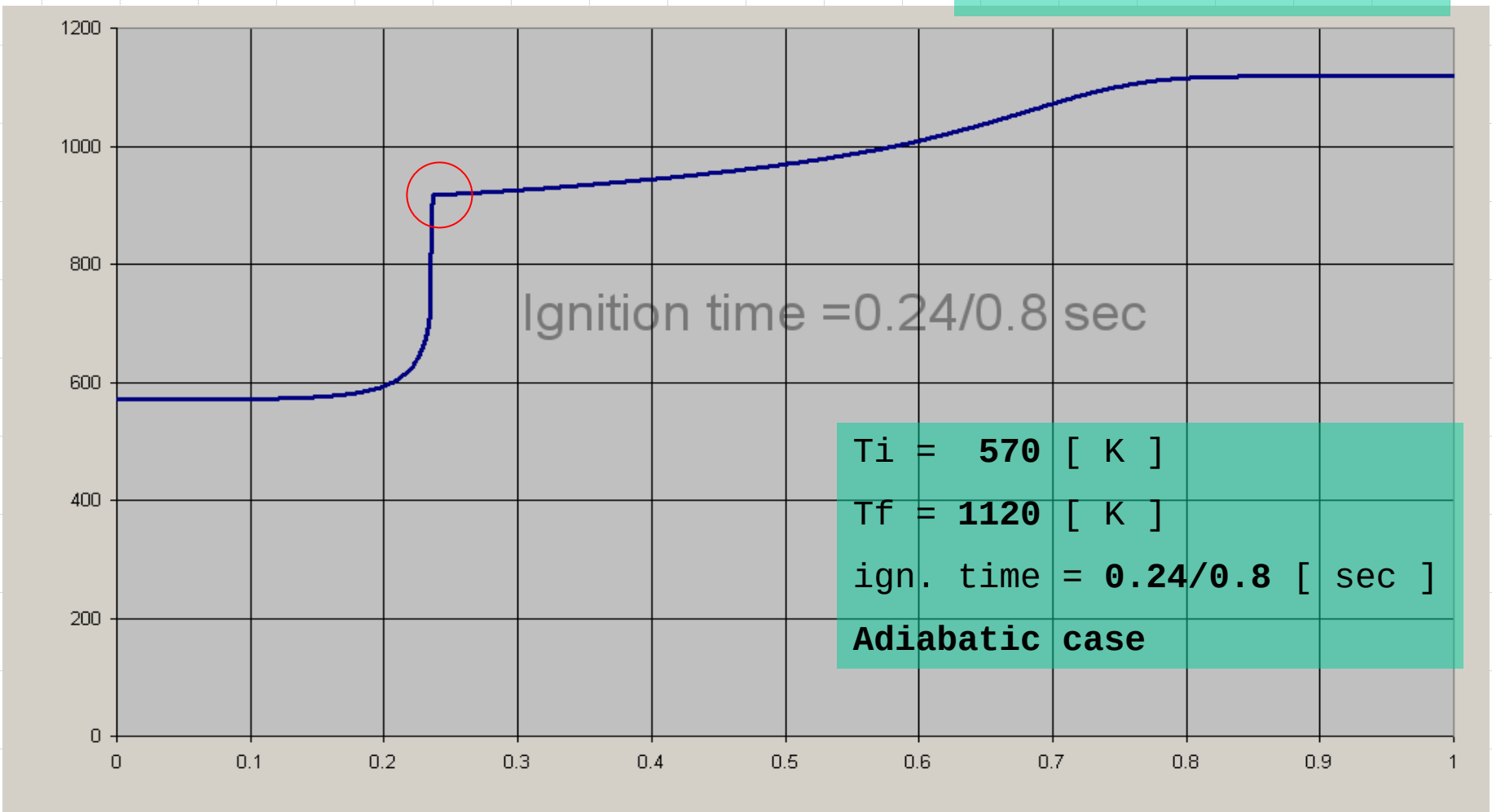
Adiabatic case

O2:CH3CHO=**1:8**



Ignition time of gas mixture

O2:CH3CHO=**1:8**



Ti = **570** [K]

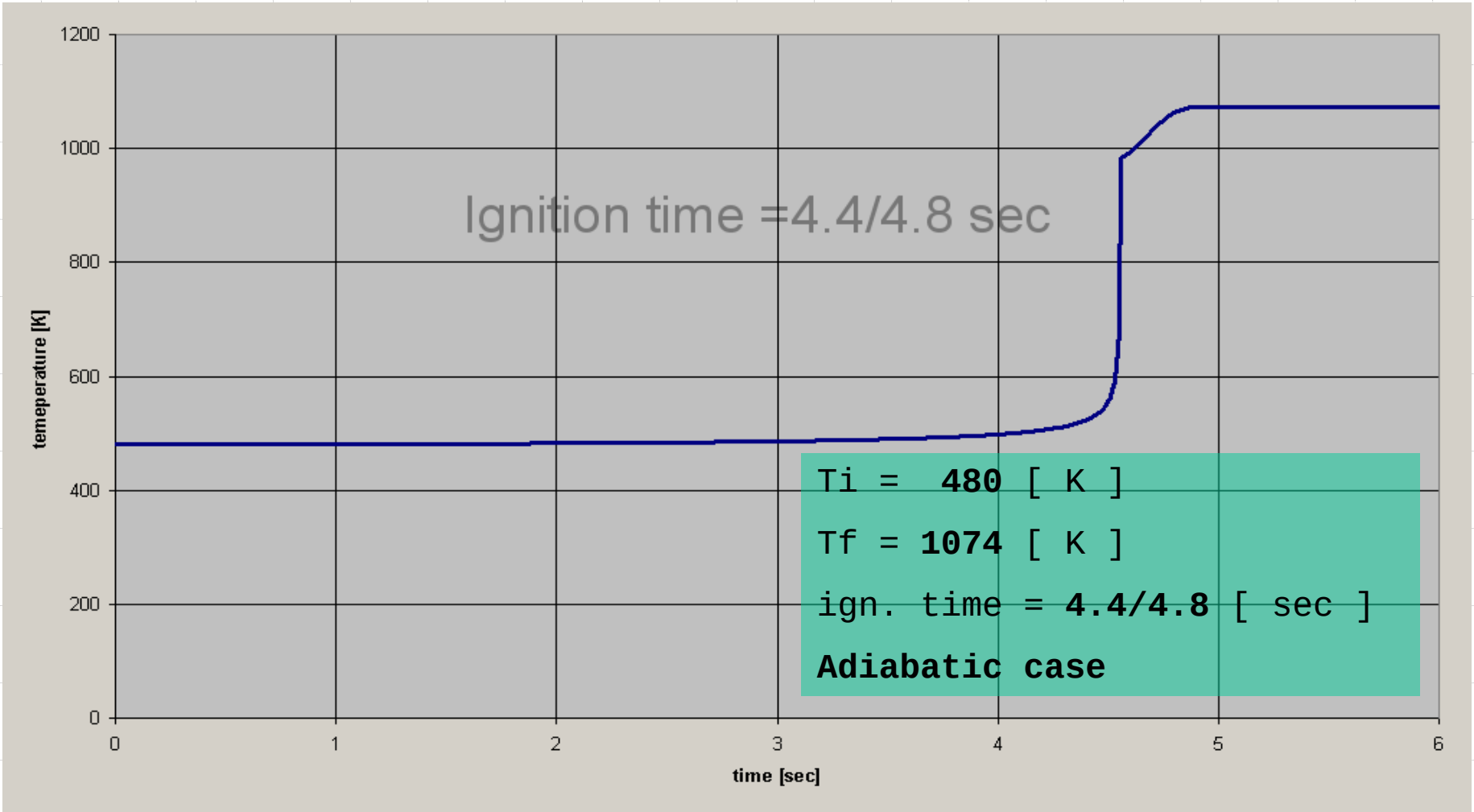
Tf = **1120** [K]

ign. time = **0.24/0.8** [sec]

Adiabatic case

Ignition time of gas mixture

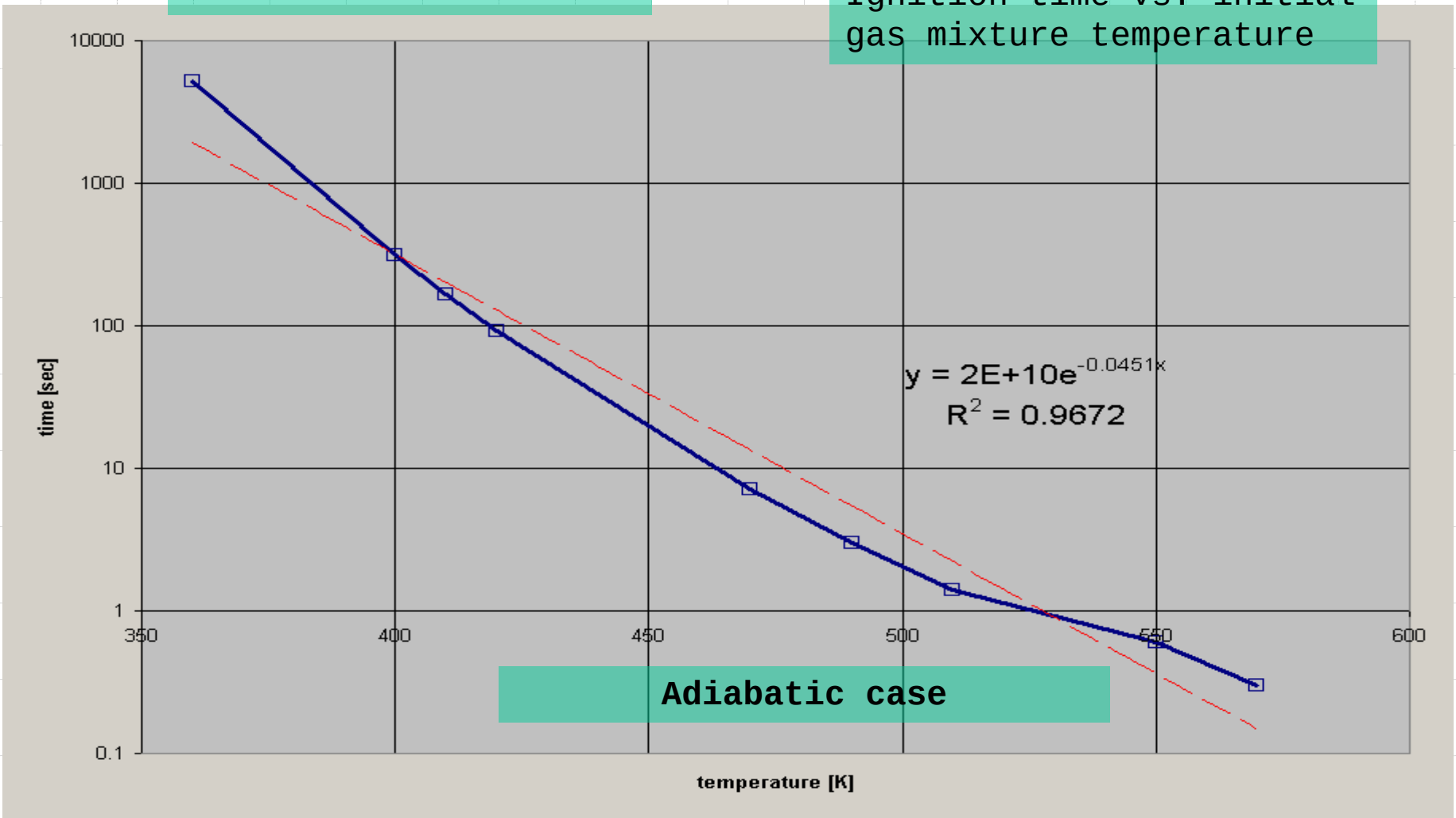
O2:CH3CHO=**1:8**



Ignition time of gas mixture

O2:CH3CHO=**1:8**

Ignition time vs. initial gas mixture temperature

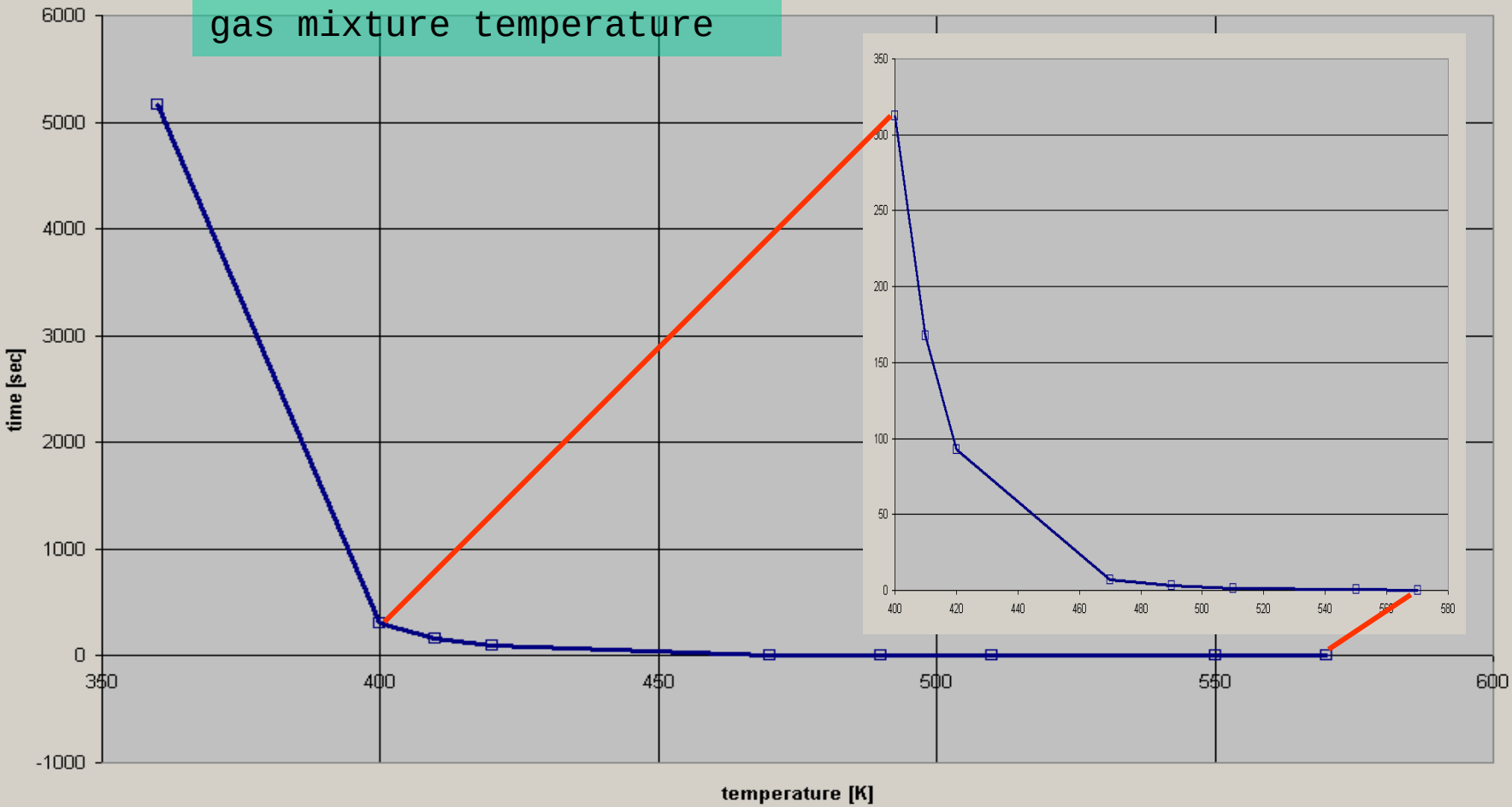


Adiabatic case

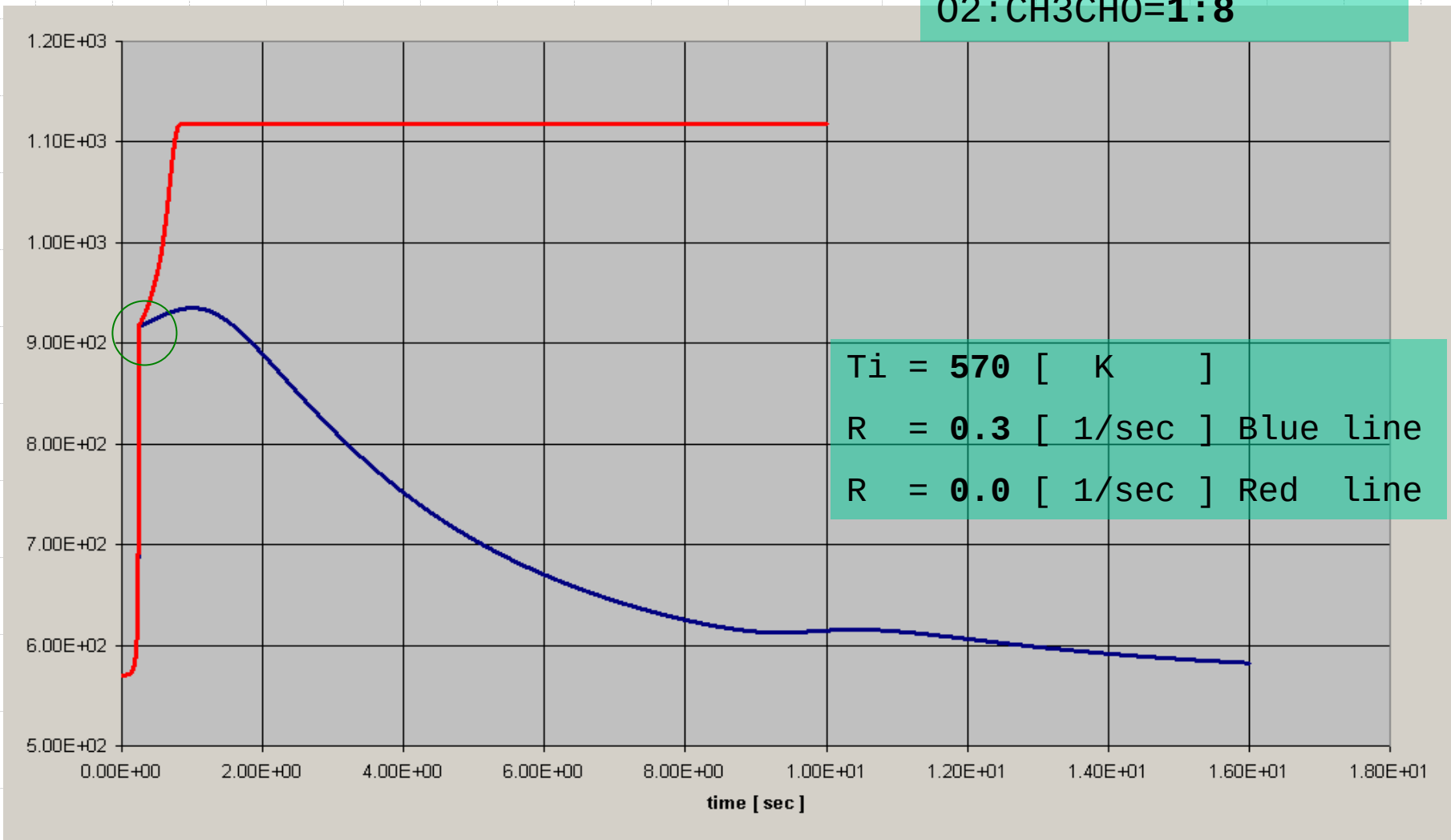
Ignition time of gas mixture

Ignition time vs. initial gas mixture temperature

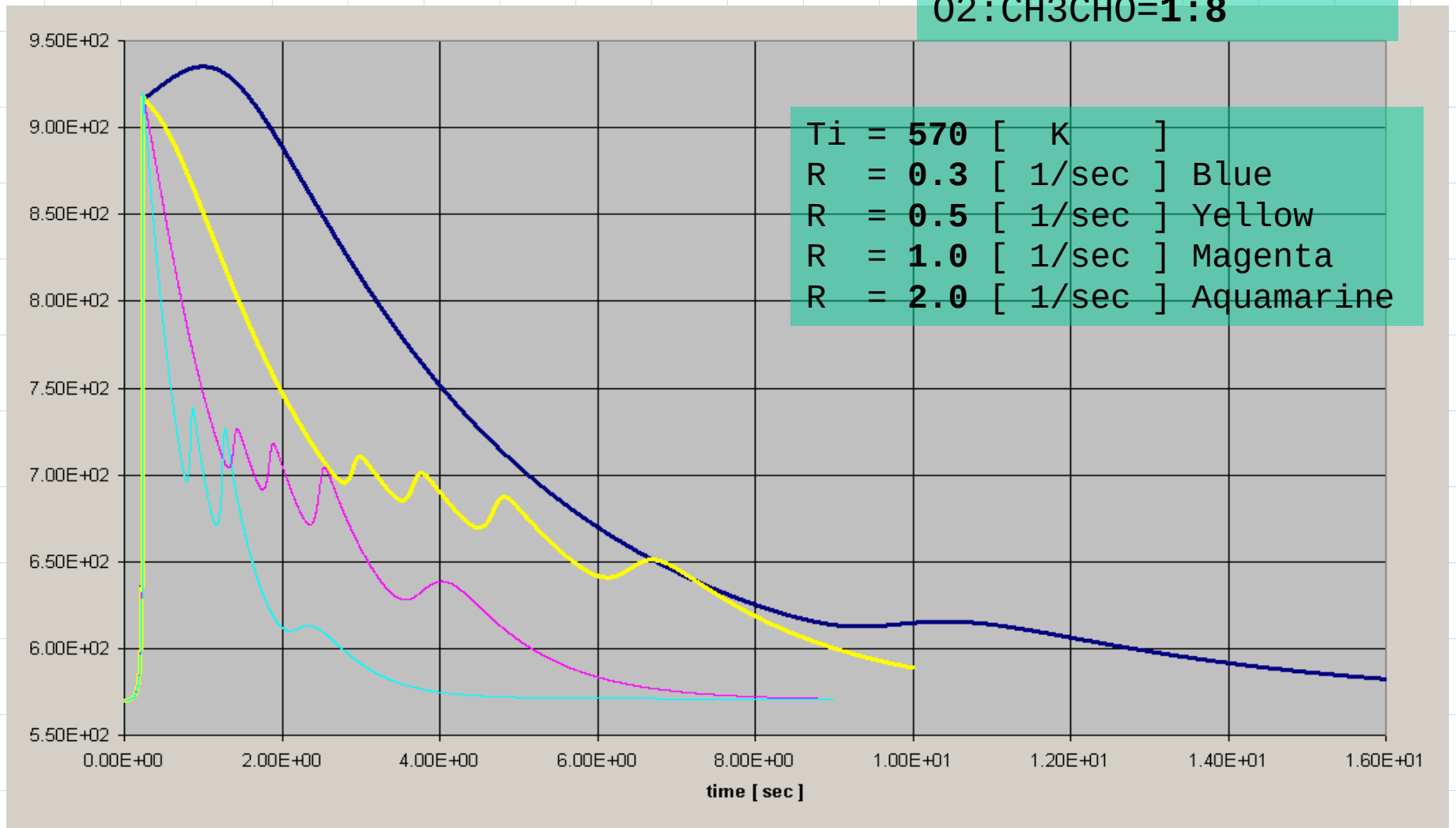
O2:CH3CHO=**1:8**



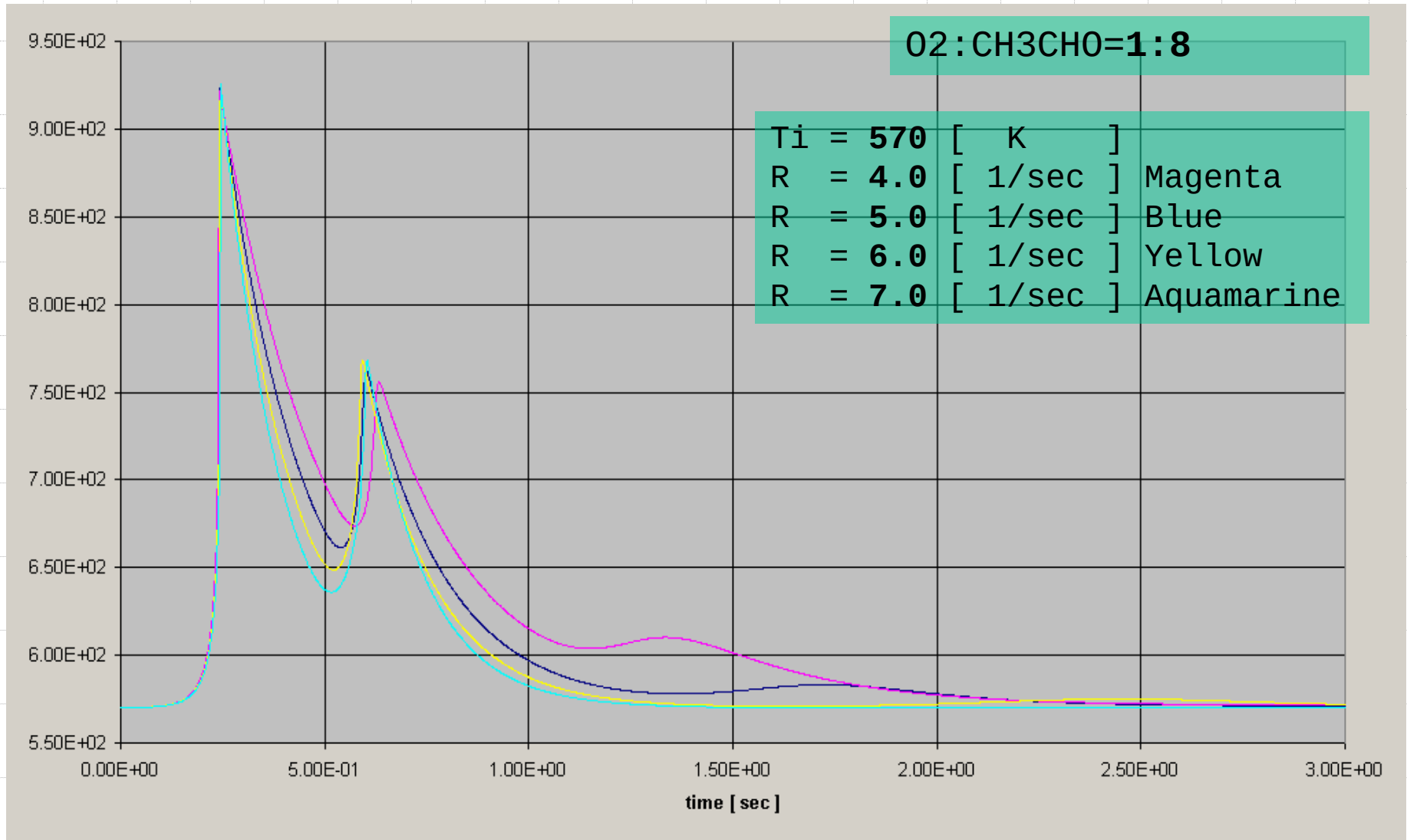
Temperature vs. time



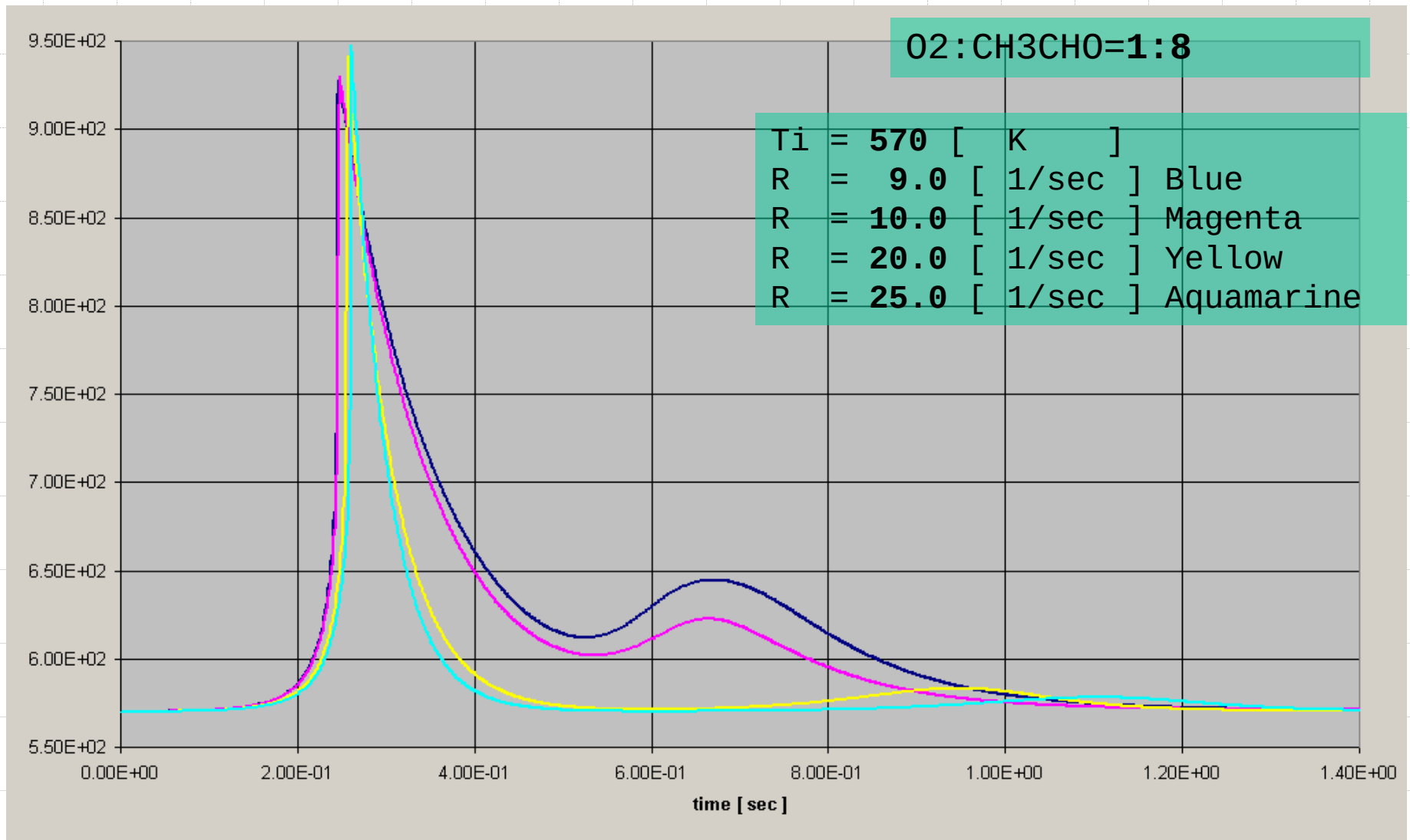
Temperature vs. time



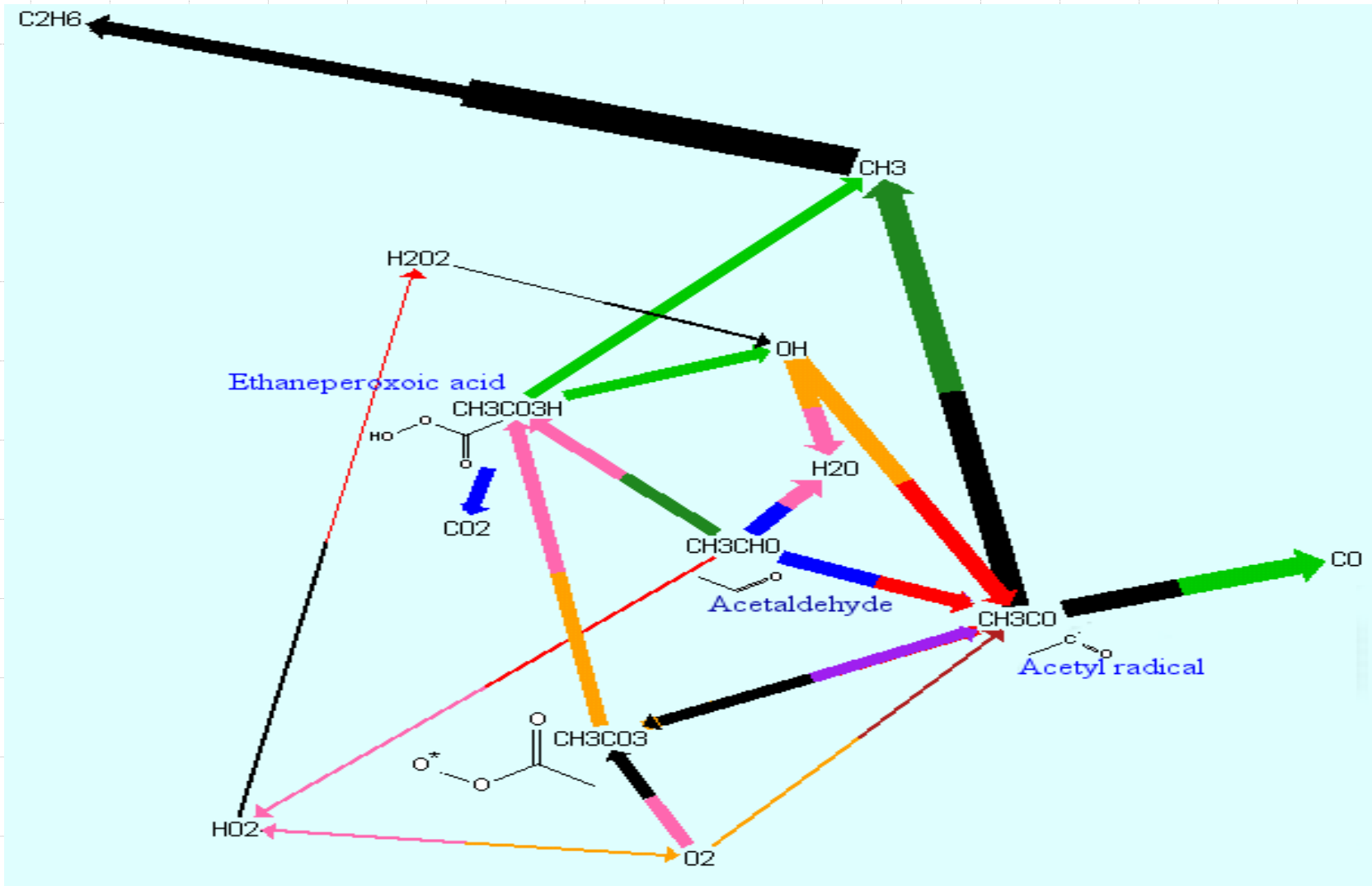
Temperature vs. time



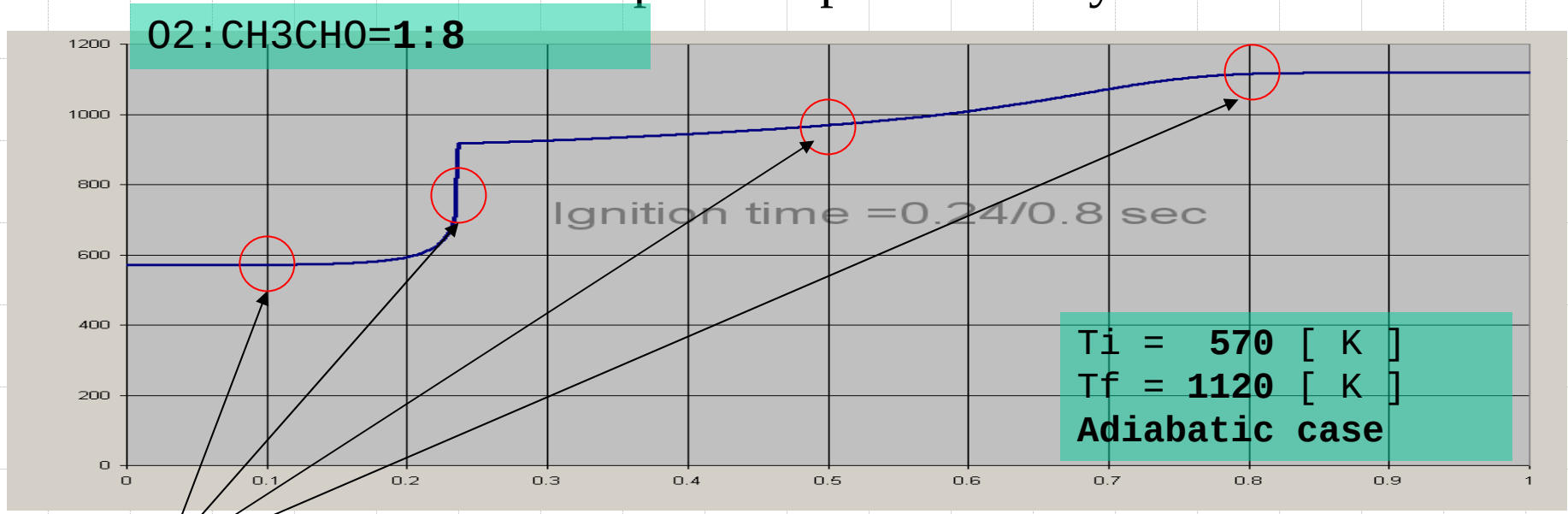
Temperature vs. time



Reaction Pathway



Principal Component Analysis

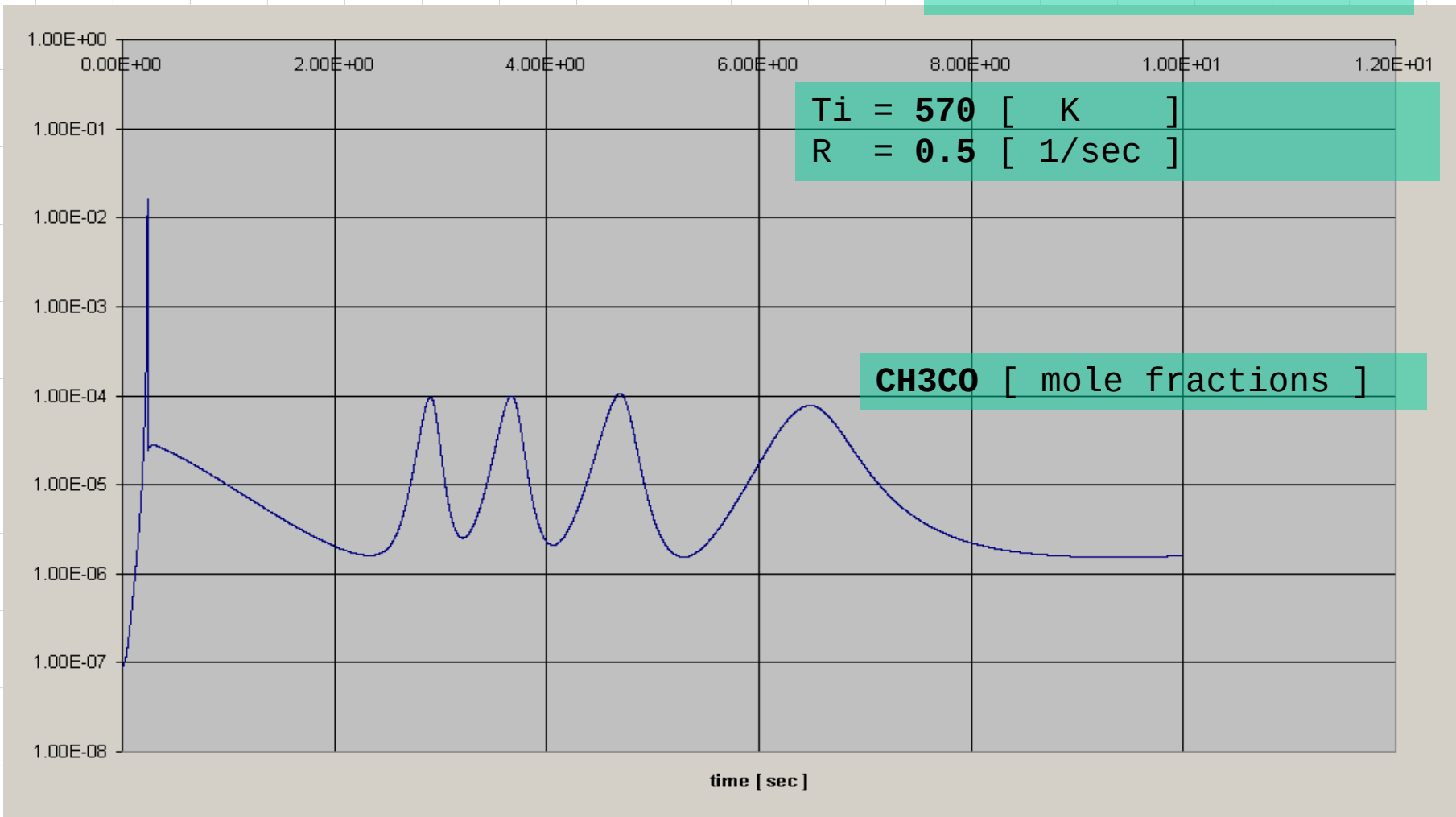


TIME 0.1 0.24 0.5 0.8 [sec]	S	1234
1 CH3CHO+O2=>CH3CO+HO2	*	****
2 CH3CO+O2=>CH3CO3	*	****
3 CH3CO3+CH3CHO=>CH3CO3H+CH3CO	*	****
4 CH3CO3H=>CH3+OH+CO2	*	****
5 CH3CO+M=>CH3+CO+M	*	****
6 2CH3=>C2H6	*	****
7 OH+CH3CHO=>CH3CO+H2O	*	****
8 2HO2=>H2O2+O2	*	****
9 H2O2+M=>2OH+M	*	***

Reactions, denoted by * below a reaction time number are important at this reaction time. Reactions, denoted by * below letter S are important at least at one reaction time.

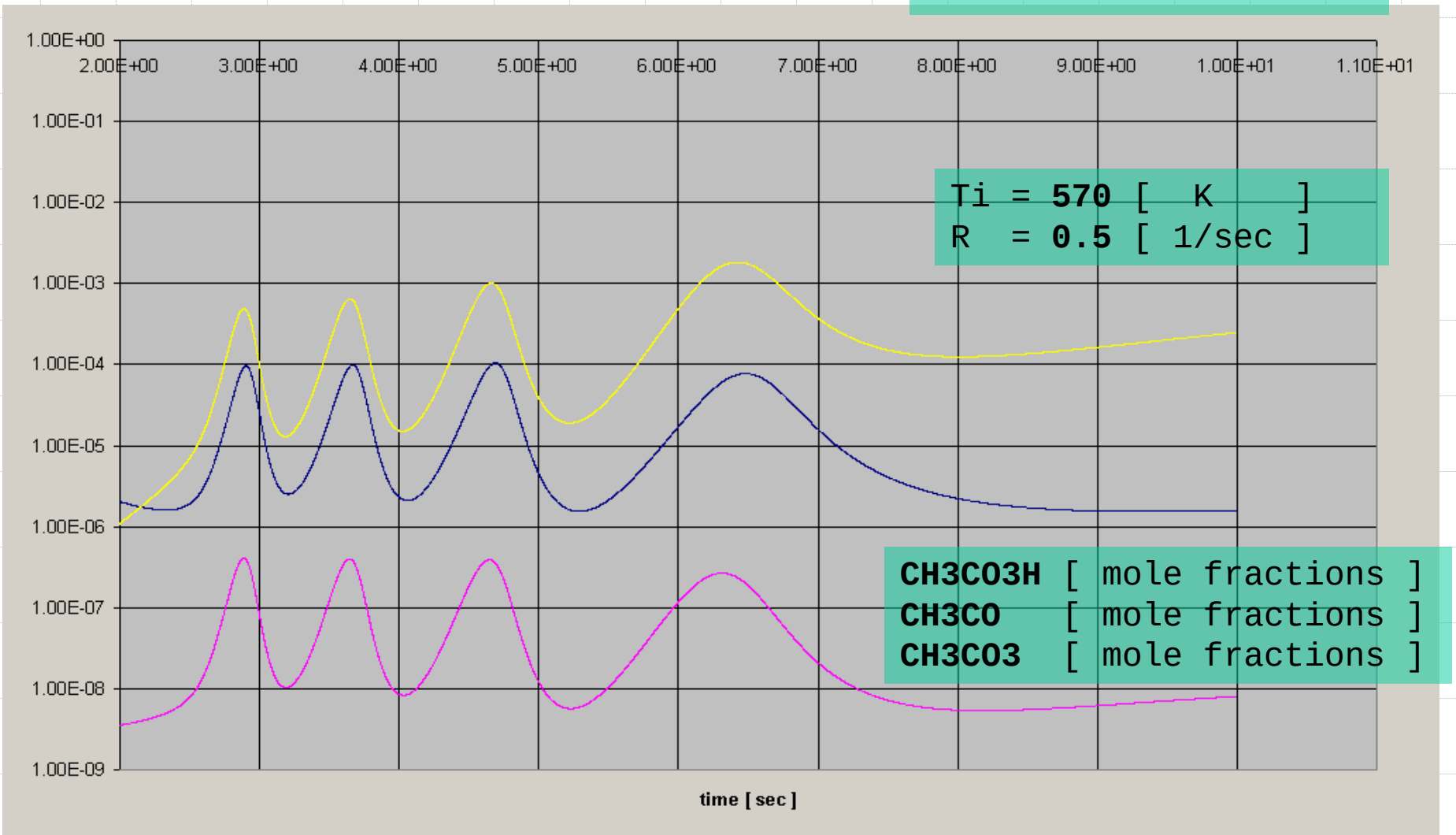
Mole fraction of CH3CO

O2:CH3CHO=**1:8**



Mole fraction

O2:CH3CHO=**1:8**

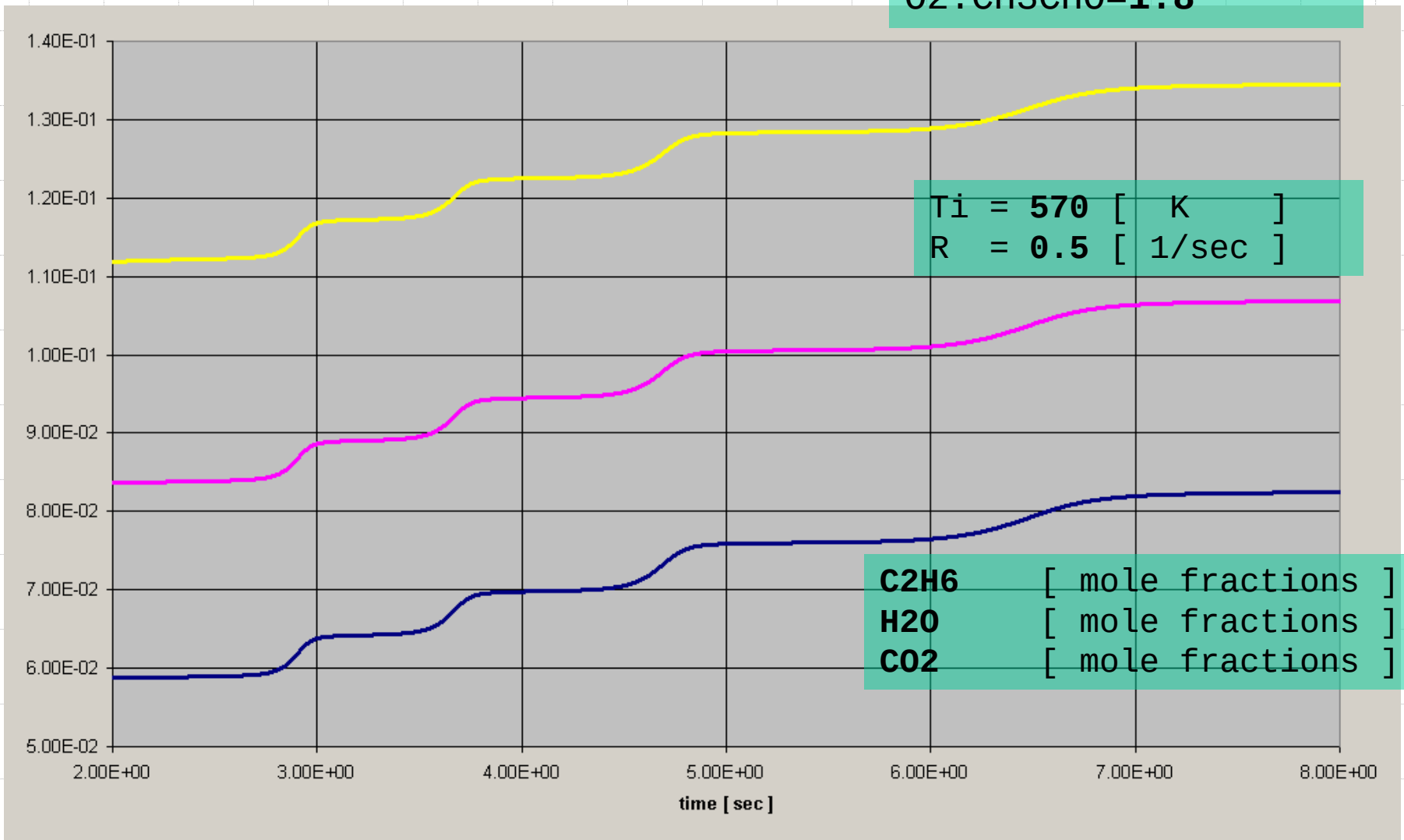


Ti = **570** [K]
R = **0.5** [1/sec]

CH3CO3H [mole fractions]
CH3CO [mole fractions]
CH3CO3 [mole fractions]

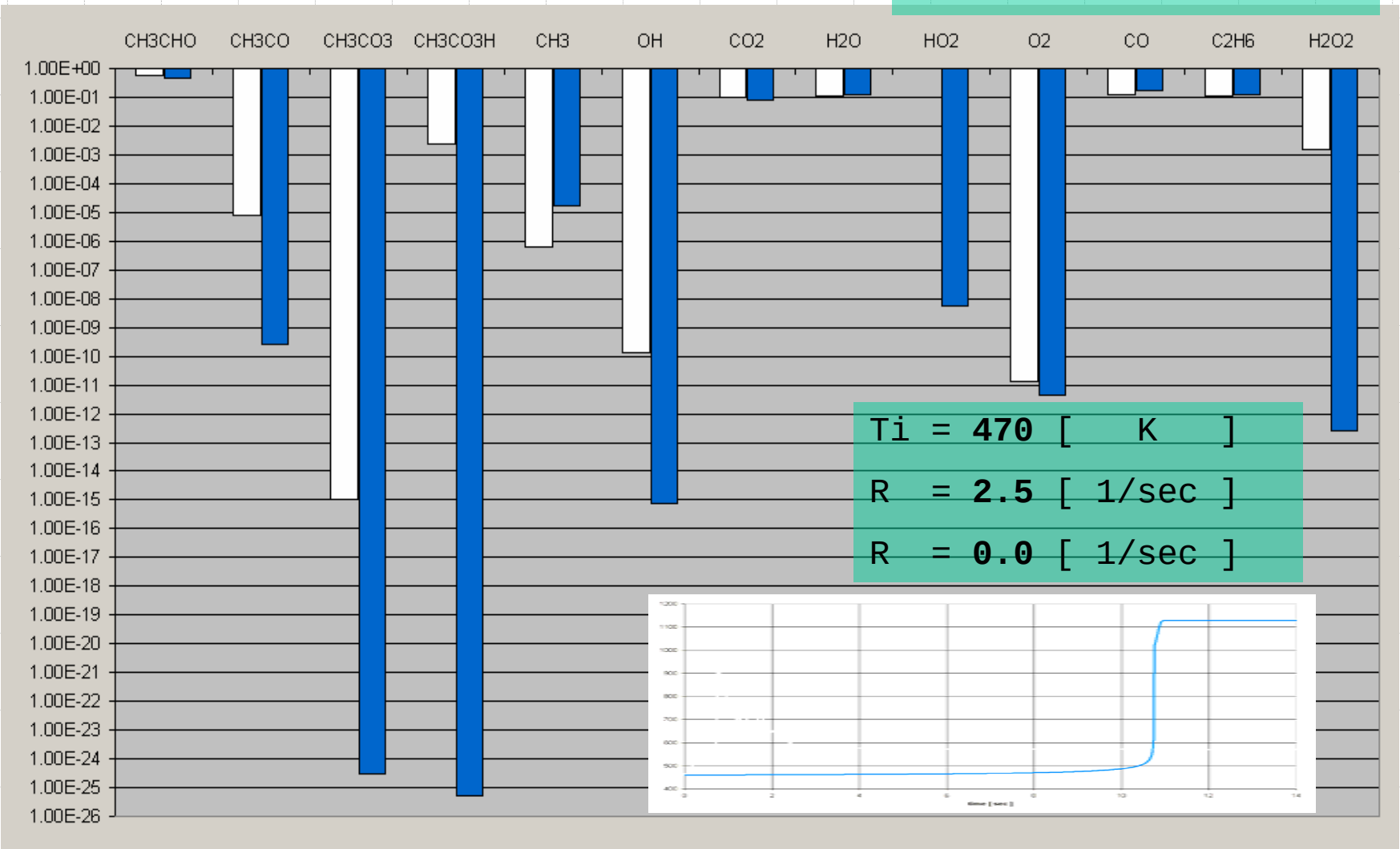
Mole fraction of Products

O2:CH3CHO=**1:8**



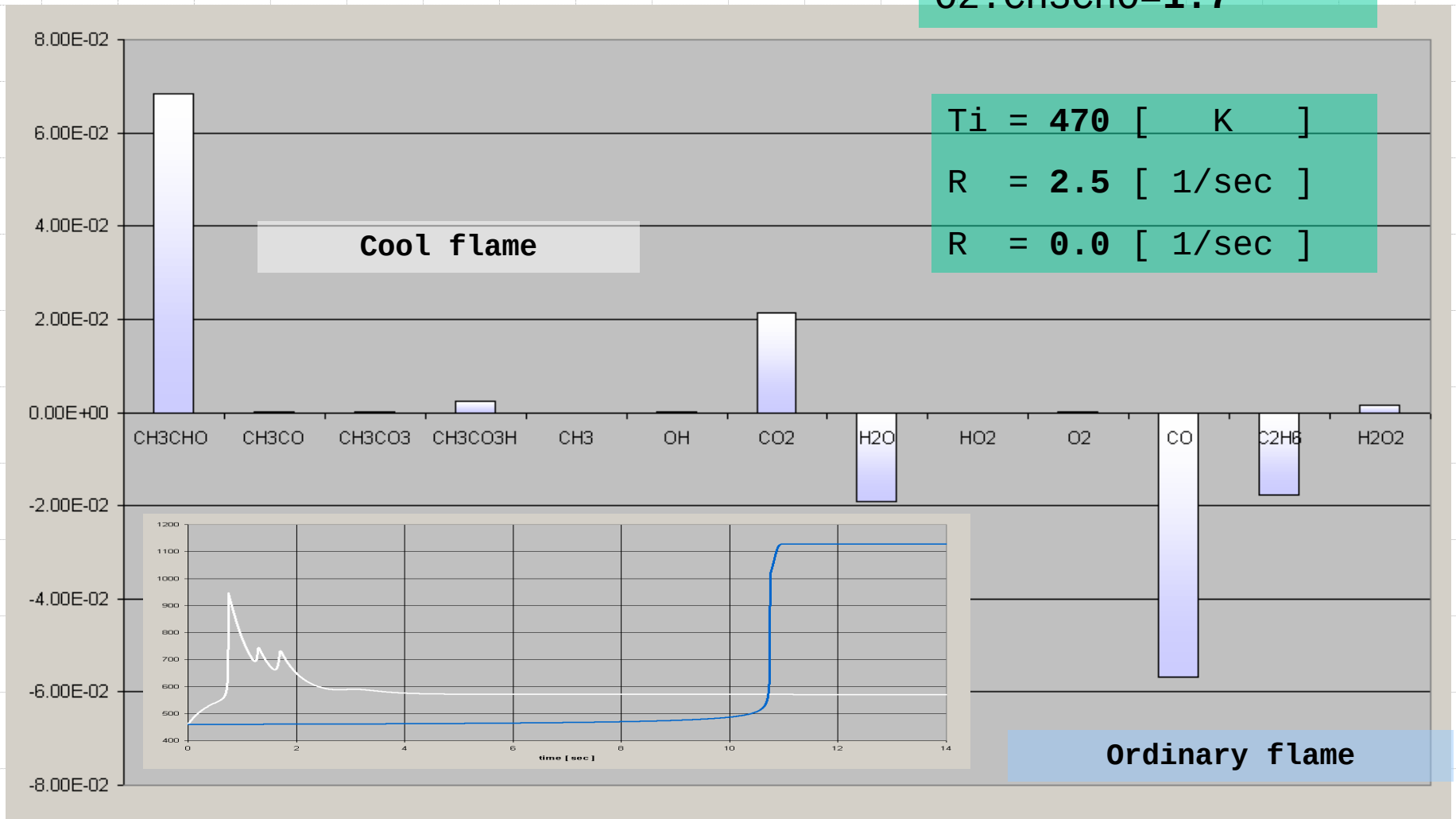
Comparison of Products

O2:CH3CHO=**1:7**



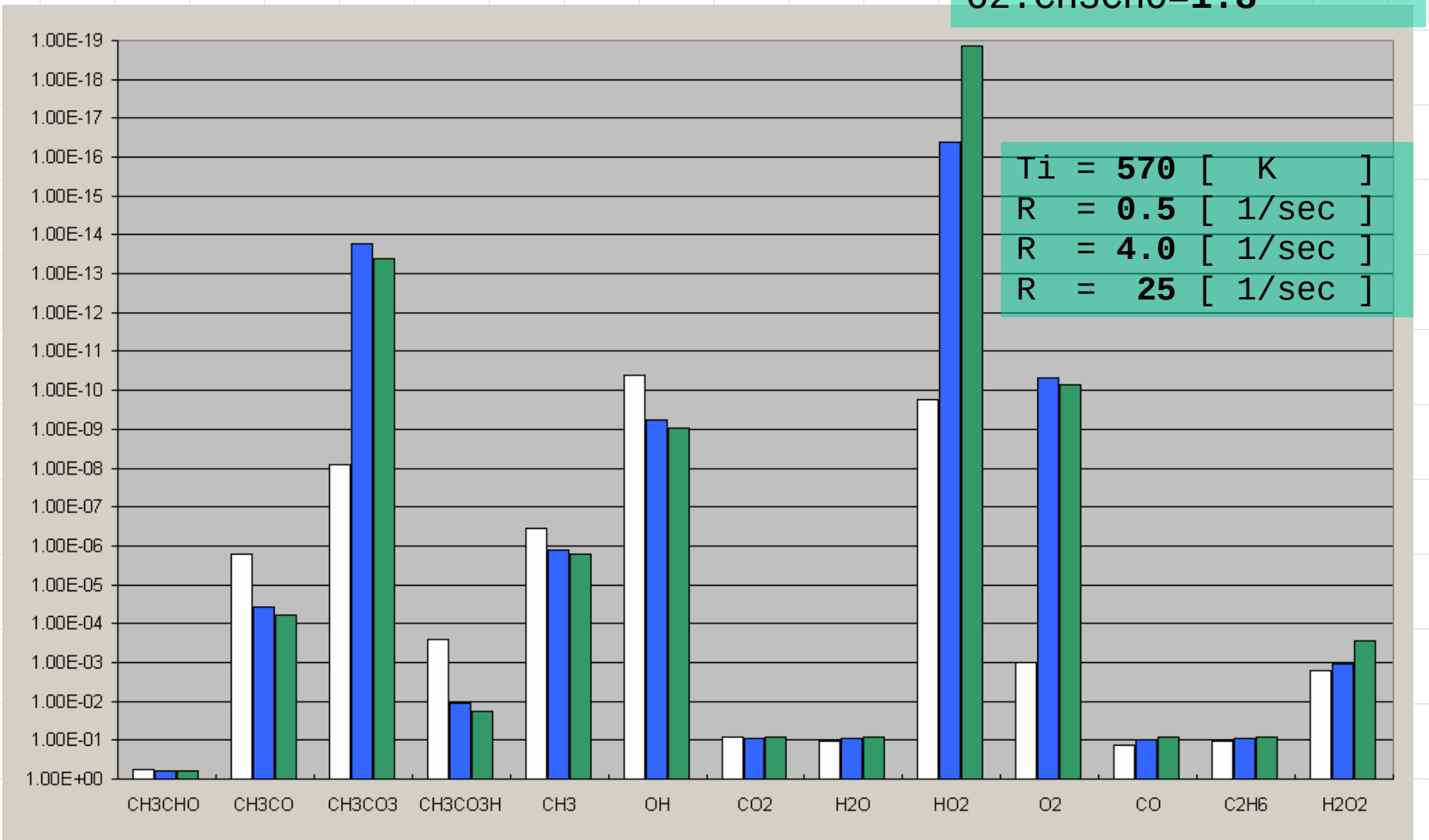
Comparison of Products

O2:CH3CHO=**1:7**

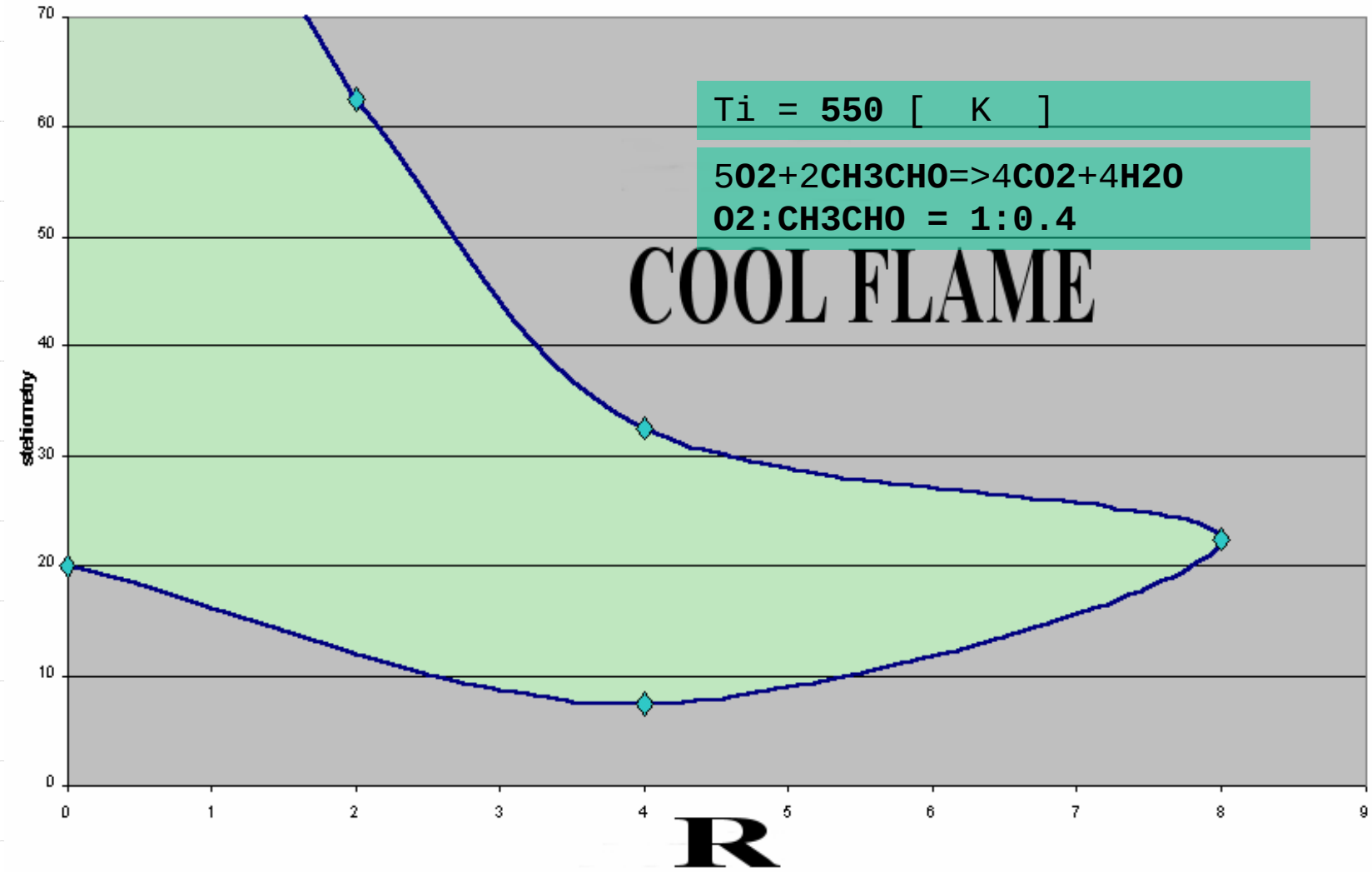


Comparison of Products

O2:CH3CHO=**1:8**



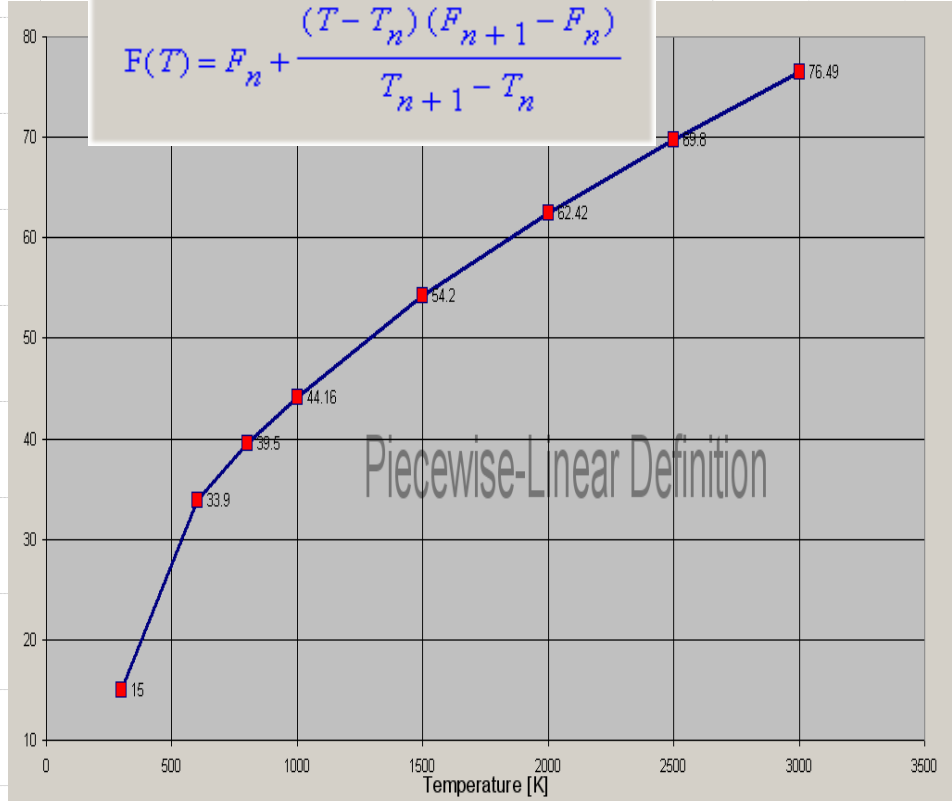
Region of Cool Flame



Physical Properties for Reacting flow

- Density
- Viscosity
- Formation Enthalpies
- Heat Capacity
- Thermal Conductivity
- Mass Diffusion Coefficient

$$F(T) = F_n + \frac{(T - T_n)(F_{n+1} - F_n)}{T_{n+1} - T_n}$$

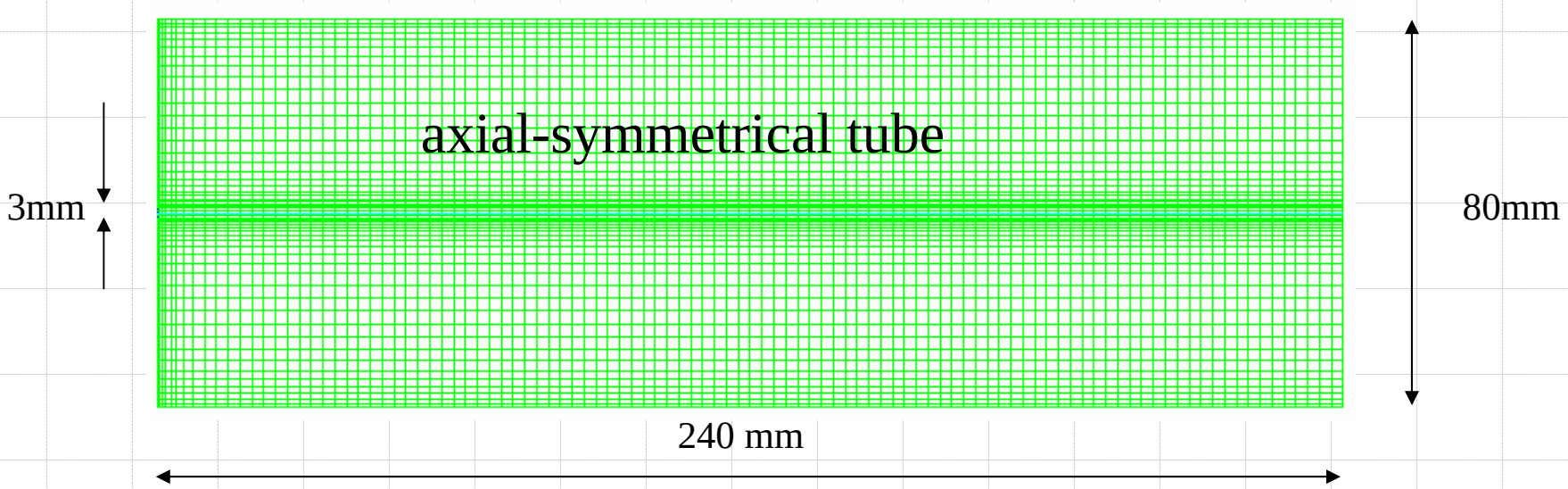


300	600	800	1000	1500	2000	2500	3000	K

13 Species → 5 Physical Properties → at 8 Temperature points

Piecewise-Linear Variation with Temperature

Gas Dynamics Modeling



We solve Gas Dynamics equations on 2D axial-symmetrical non-uniform Grid.
We vary the following parameters:

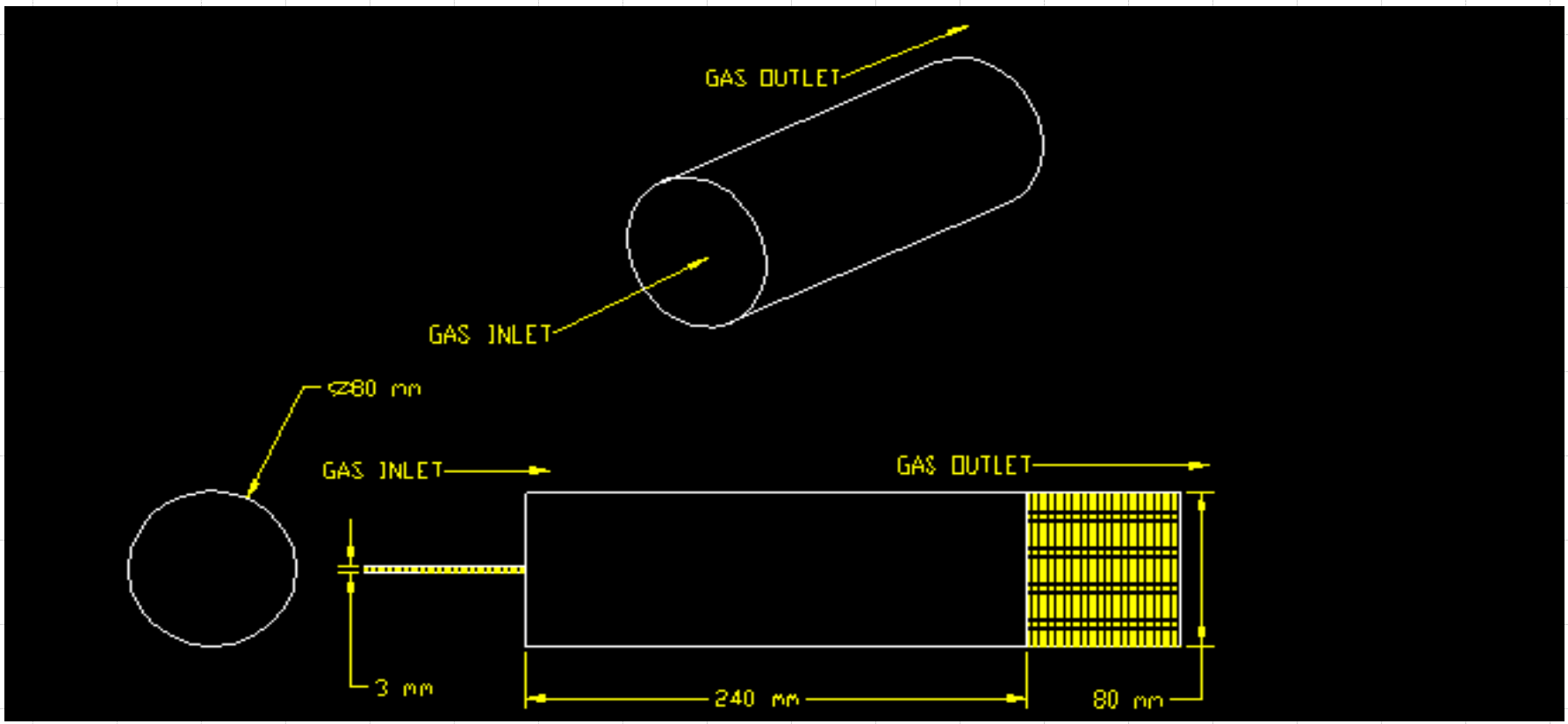
- Gas Mixture inlet velocity **0.2 .. 50** [m/sec]
- Temperature boundary conditions on Tube walls **600 .. 1200**[K]

and we try **adiabatic walls**.

We kept constant the following parameters:

- Gas Mixture composition **1:8** [O2:CH3CHO] molar fractions
- Gas Mixture inlet temperature **300** [K]

Tube

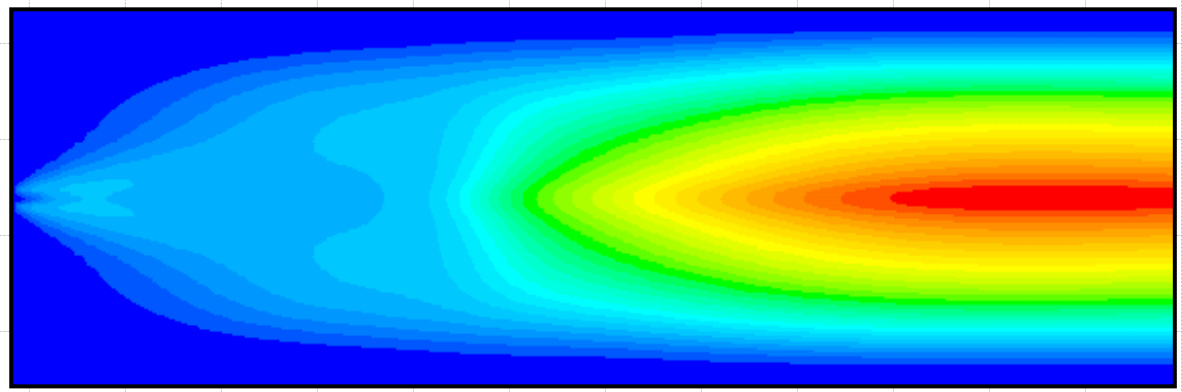


Tube Parameters

Length	=	**240**	[mm]
Inner diameter	=	**80**	[mm]
Outlet diameter	=	**80**	[mm]
Inlet diameter	=	**3**	[mm]

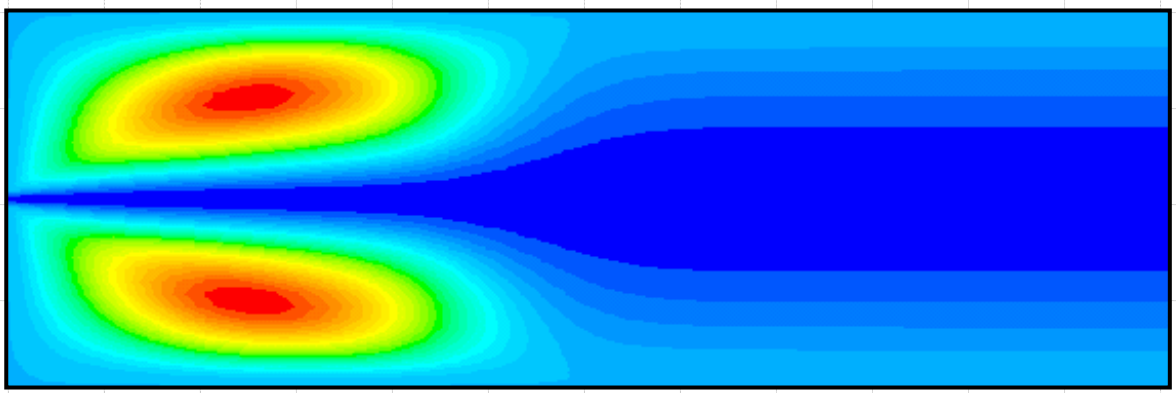
Gas Dynamics Modeling

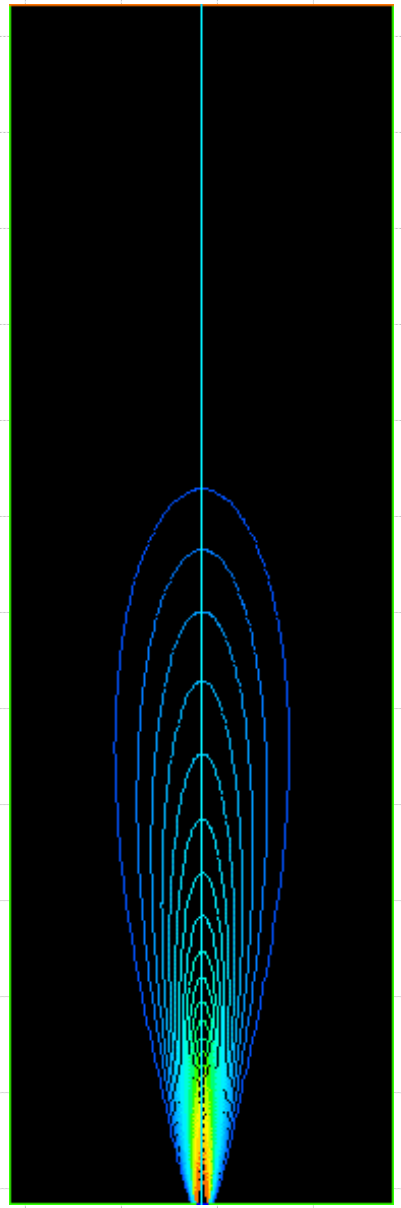
Effective Viscosity of Gas Mixture **1.8E-05 .. 0.35E-3** [KG/M-S]



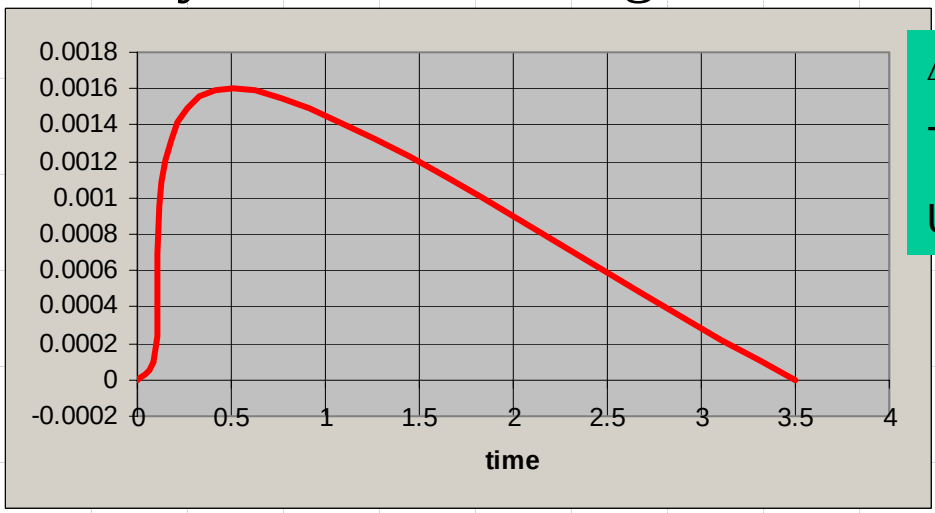
U =**0.6** [m/sec]
Tw=**600** [K]
Tg=**300** [K]

Stream Function of Gas Mixture **0.0 .. 2.65E-05** [M3/S]





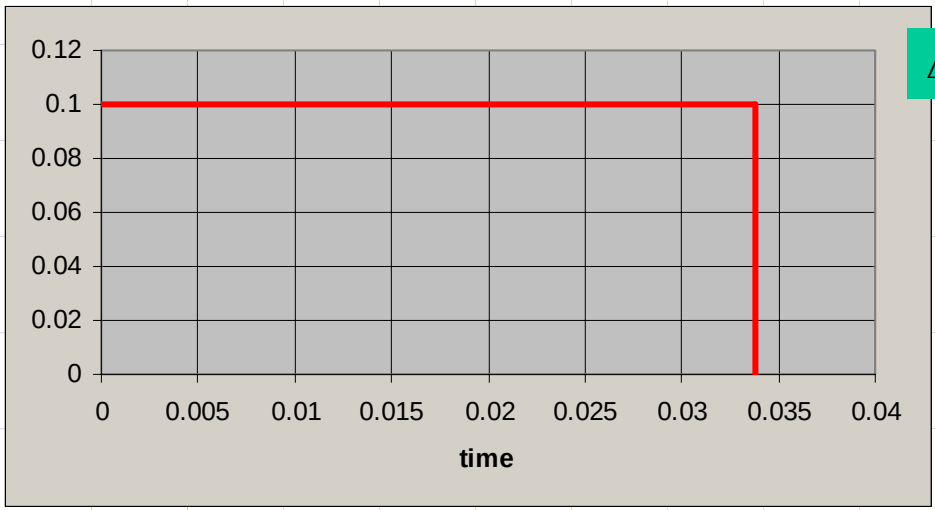
Gas Dynamics Modeling



ΔT = **3.5** sec

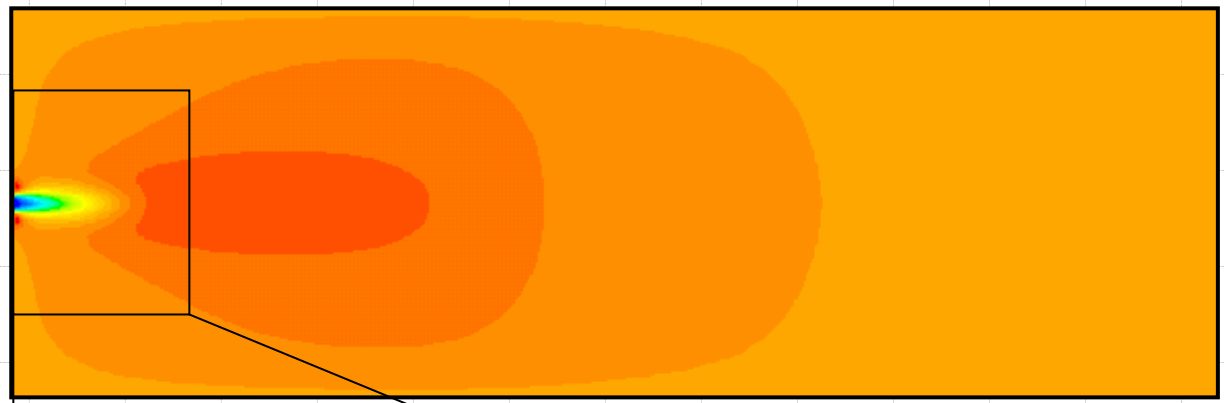
Tm = **0.5** sec

U = **50** m/sec



ΔT =**0.0338** sec

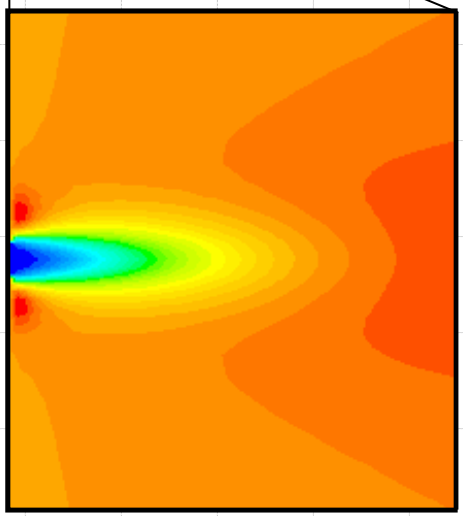
Temperature Distribution



U = **0.6** [m/sec]

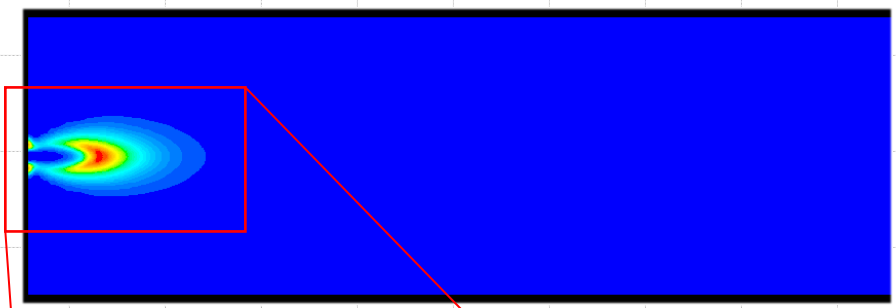
Tw = **600** [K]

Tg = **300** [K]

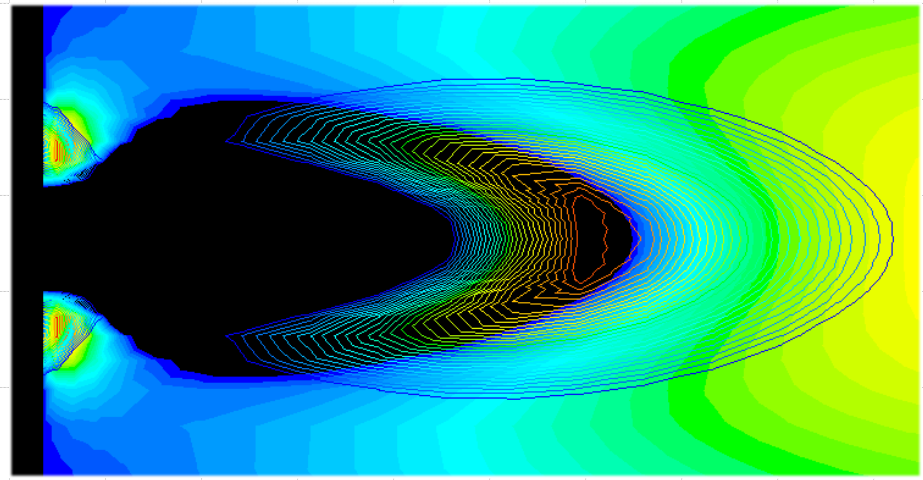


Zoom region

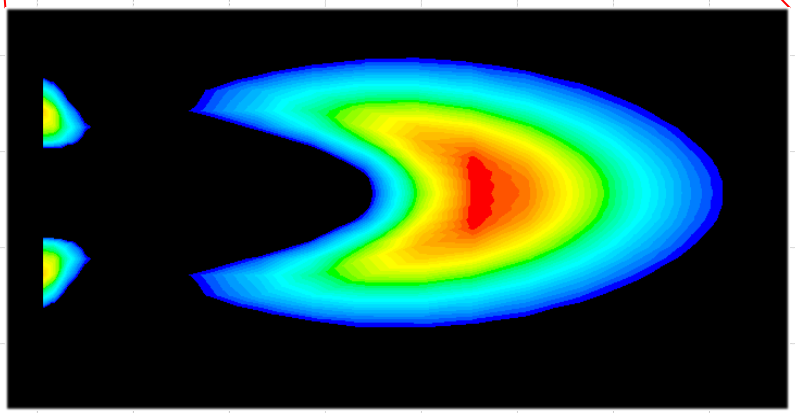
Temperature distribution **300 .. 650** [K]



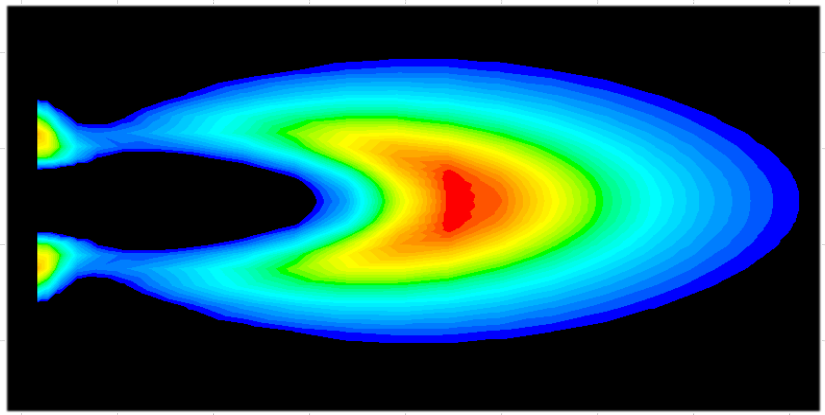
Temperature + OH [600K.. 650K]



0.001 … 0.0031

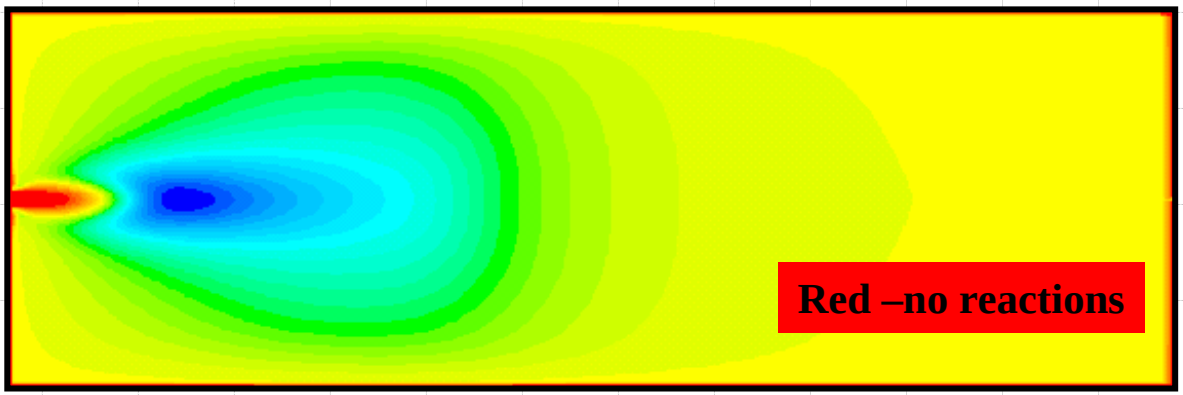


0.0005 … 0.0031



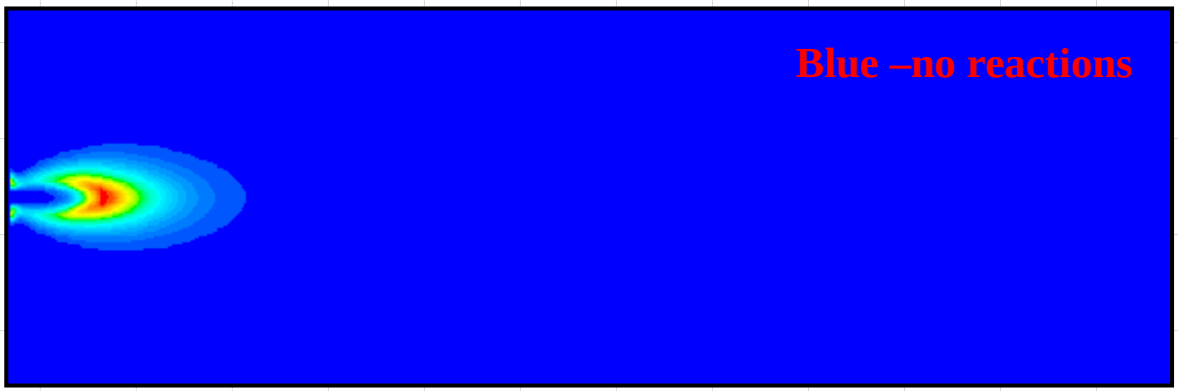
Chemistry Modeling with FLUENT

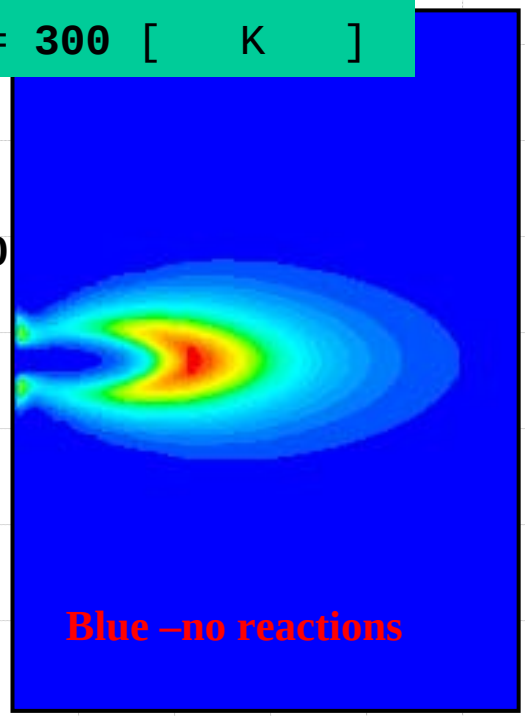
Reaction Rate CH3CHO+O2=CH3CO+HO2 **-1.44E3 .. 0.0** [KG/M3/S]



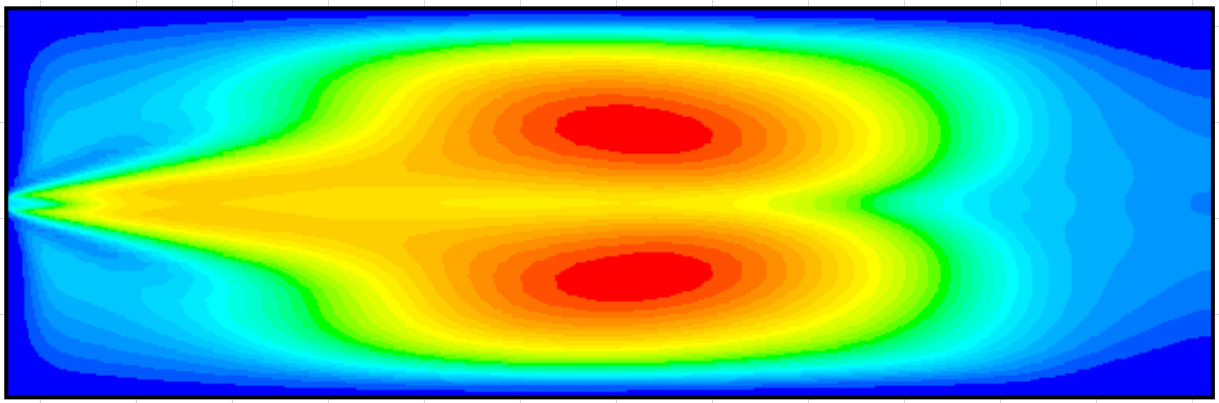
U = **0.6** [m/sec]
Tw = **600** [K]
Tg = **300** [K]

Reaction Rate OH+CH3CHO=CH3CO+H2O **2288.179 .. 0.0**





Effective Viscosity of Gas Mixture **1.6E-05 .. 0.5E-3** [KG/M-S]

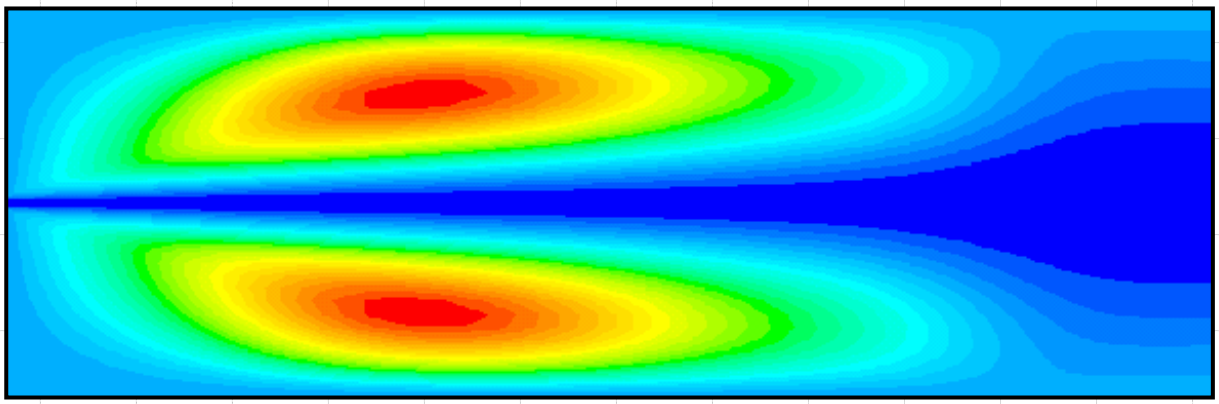


U = **5** [m/sec]

Tw = **adiabatic**

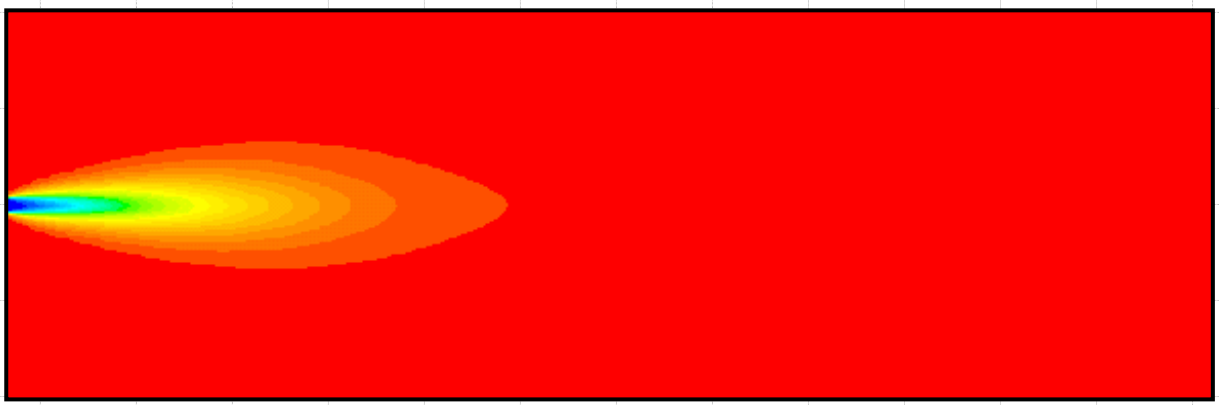
Tg = **300** [K]

Stream Function of Gas Mixture **0 .. 2.65E-04** [M3/S]



Temperature Distribution

Temperature distribution **300 .. 635** [K]

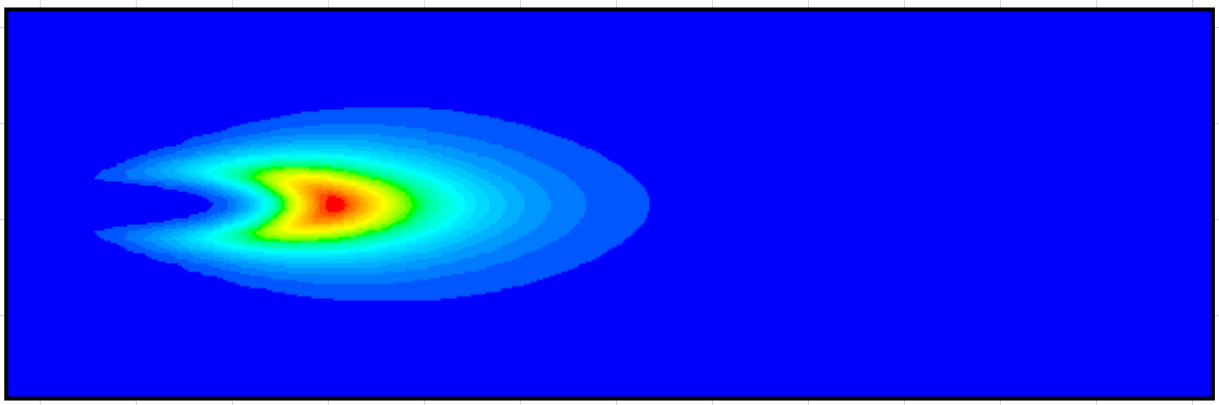


U = **5** [m/sec]

Tw = **adiabatic**

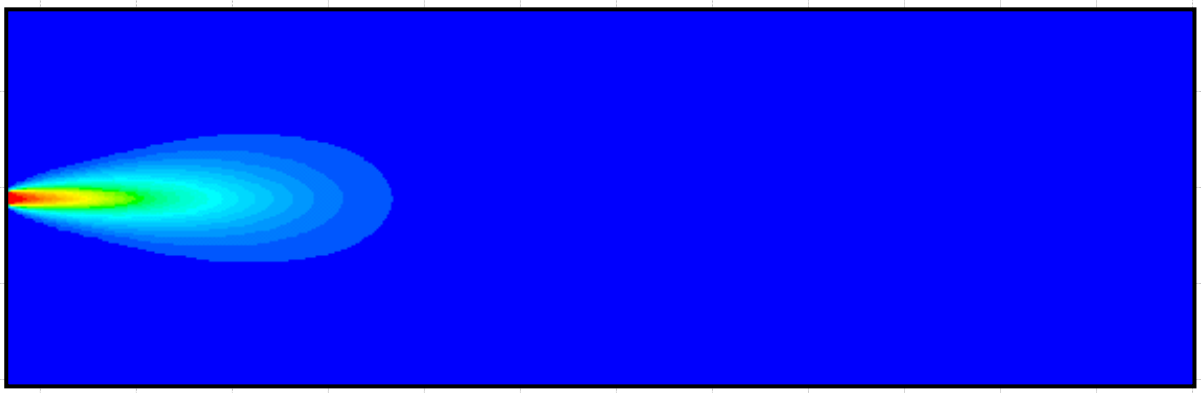
Tg = **300** [K]

Mole fraction of OH **0 .. 1.66E-3**



Mole Fractions of Species

Mole fraction of O2 **0.04 .. 0.1**

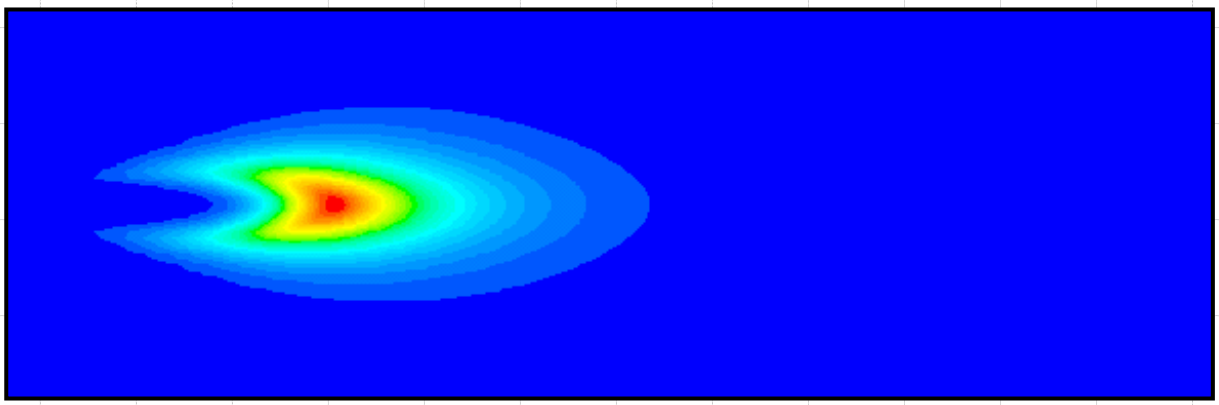


U = **5** [m/sec]

Tw = **adiabatic**

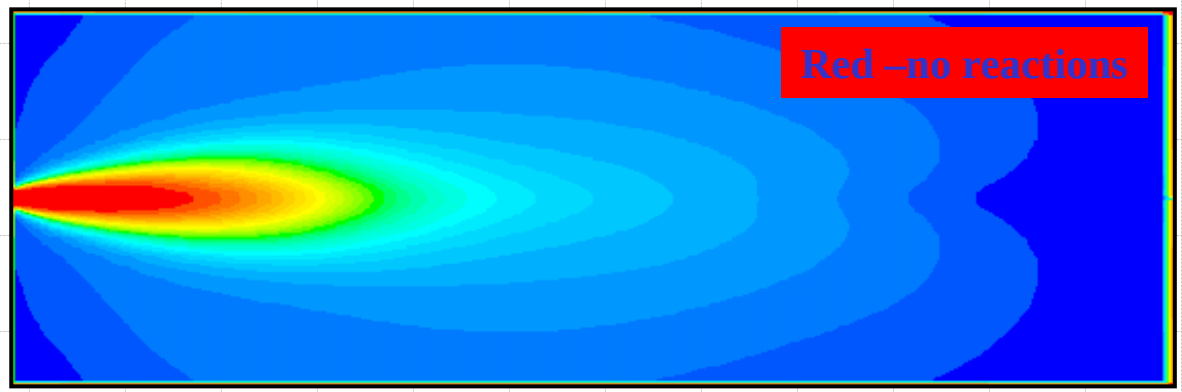
Tg = **300** [K]

Mole fraction of OH **0 .. 1.66E-3**



Chemistry modeling with FLUENT

CH3CHO+O2=CH3CO+HO2 0 .. 0.003342973[KG/M3/S]



U = **5** [m/sec]

Tw = **adiabatic**

Tg = **300** [K]

CH3CO3H+O2=CH3+OH+CO2 0 .. 0.149 [KG/M3/S]