Reaction Kinetics Simulation

Chemked – A Program for Chemical Kinetics of Gas-Phase Reactions

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Chemked is a program designed for creating and editing thermodynamic and chemical kinetics databases, for formation of reaction mechanisms and simulation of problems of complex gas-phase chemistry. The program will be useful for you, if you work in the field of the chemical kinetics and study the atmospheric chemistry, air pollution, combustion chemistry and waste gas treatment.

A number of samples have been prepared to test Chemked and to illustrate its capabilities; a part of the samples is presented here.

Sample Problems

Problem 1. Collisional De-Excitation of Excited State

```
CH2(S) + AR <=> CH2 + AR     9.00E+12      0       600          !CGIMech3.0
```

Input values.
Pressure P=1 atm
Constant temperature T=2000K
$[CH2(S)]_0$: $[CH2]_0$: $[AR]_0$ = 0.02 : 0.01 :1
Start step size 1.0E-10 sec
Relative tolerance 1E-06
Absolute tolerance 1E-10

Forward rate constant and equilibrium constant are K_{for} = 7.739E+12 cm^3/mol s, K_{eq} = 20.650. Exact solution is

$$[CH2(S)] = C_0 [\, a_{oo} - (a_{oo} - a_0) \exp(-bt)]$$
$$C_0 = [CH2(S)]_0 + [CH2]_0$$
$$a_0 = [CH2(S)]_0 / C_0,\ a_{oo} = 1/(1 + K_{eq}),$$
$$b = K_{for} [AR] (1 + K_{eq}) / K_{eq}$$
$$[CH2] = C_0 - [CH2(S)]$$

where t is time.

Analytical and numerical results are presented in Table 1; the three significant digits of the solutions coincide.

Table 1. Molar concentrations [CH2(S)] and [CH2] vs. time, units are (mol/cm^3).

Time, sec	0	1.E-09	1.e-08	1.E-07	1.E-06
[CH2(S)]	1.18E-07	1.13E-07	7.63e-08	9.11E-09	8.20E-09
[CH2]	5.92E-08	6.43E-08	1.01E-07	1.68E-07	1.69E-07

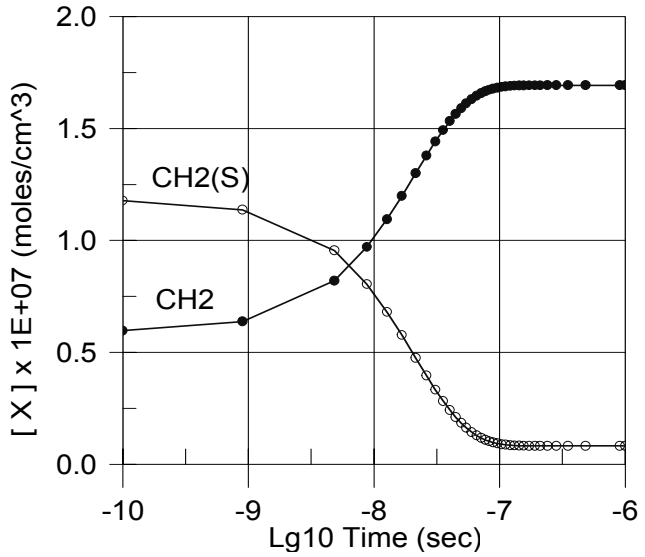

Fig 1. Molar concentrations of [CH2(S)] and [CH2]

Problem 2. Recombination Fall-off Reaction

```
OH + OH (+M) <=> H2O2 (+M)     7.40E+13      -0.37          0       !CGIMech3.0
  LOW /  2.30E+18       -0.9     -1700 /
  TROE / 0.7346         94       1756       5182 /
  H2/2./ H2O/6./ CH4/2./ CO/1.5/ CO2/2./ C2H6/3./ AR/0.7/
```

Input values:
Pressure P=3 atm
Constant temperature T=700K.
$[OH]_0$: $[CH4]_0$: $[AR]_0$ = 3.E-05 : 2 :1
Start step size 1.0E-10 sec
Relative tolerance 1E-06
Absolute tolerance 1E-17

Rate constants and equilibrium constant are
high-pressure limit K_{for} = 6.555E+12 cm^3/mol s,
low-pressure limit K_{low} = 2.147E+16 cm^6/mol^2 s,
K_{eq} = 4.461E+13 cm^3/mol.

Forward rate constant at specified temperature and pressure is K_T = 8.304E+11 cm^3/mol s.
An approximate solution can be obtained taking into account that OH is a small additive to CH4 and AR.

The solution is

$$[\mathrm{OH}] = \frac{C_0}{2b}\left(d\,\frac{\mathrm{th}\, z + c}{1 + c \cdot \mathrm{th}\, z} - 1 \right)$$

$$C_0 = [\mathrm{OH}]_0 + 2[\mathrm{H2O2}]_0,\ a_0 = [\mathrm{OH}]_0 / C_0,$$

$$d^2 = 1 + 4b,\ c = (1 + 2a_0 b) / d,\ b = 2C_0 K_{eq},$$

$$z = t \cdot d \frac{K_T}{K_{eq}}$$

$$[\mathrm{H2O2}] = (C_0 - [\mathrm{OH}]) / 2$$

where t is time, th denotes hyperbolic tangent.

Analytical and numerical results are presented in Table 2; the three significant digits of the solutions coincide.

Table 2. Molar concentrations [OH] and [H2O2] vs. time, units are (mol/cm^3).

Time, sec	0.	1.0E-05	1.0E-03	0.1	10
[OH]	5.22E-10	5.18E-10	2.80E-10	6.28E-12	2.43E-12
[H2O2]	0.E+00	2.25E-12	1.21E-10	2.58E-10	2.60E-10

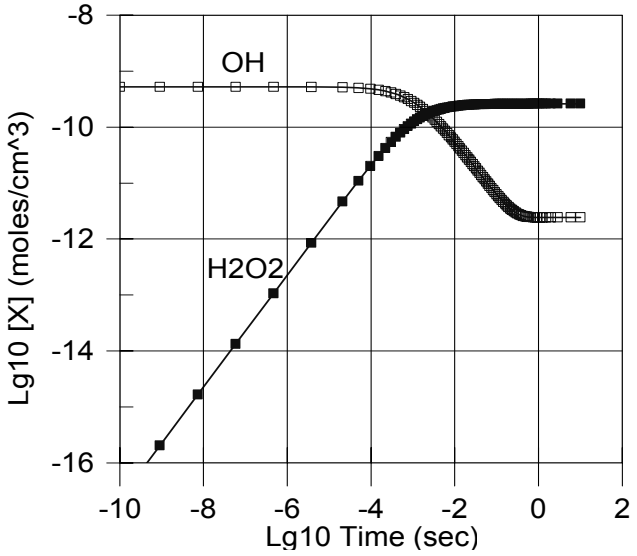

Fig 2. Molar concentrations [OH] and [H2O2]

Problem 3. Hydrogen-Air Reaction Mechanism (CHEMKIN II/III)

For this sample the reaction mechanism from the CHEMKIN II/III manual example [1] is used. The mechanism includes 23 reactions with 11 species. A fixed pressure problem is solved

Input values:
Pressure P=1 atm
Temperature T_0=1000K
Gas mixture: $[H2]_0 : [O2]_0 : [N2]_0 = 1 : 3 : 0.1$
Start step size 1.0E-10 sec
Relative tolerance 1E-06
Absolute tolerance 1E-17

The CHEMKIN results [1] and data of this solution are presented in Table 3; three significant digits of the values coincide.

Table 3. Mole fractions and temperature vs. time

Time	H2	O2	OH	H2O	H	O
3.E-05 sec	2.44E-01	7.32E-01	1.44E-06	2.59R-05	8.17E-06	4.25E-06
3.E-04 sec	1.79E-03	6.72E-01	3.07E-02	2.56E-01	1.03E-03	1.15E-02
1 sec	1.72E-03	6.69E-01	2.98E-02	2.57E-01	9.61E-03	1.08E-02
Time	HO2	H2O2	N2	NO	N	T(K)
3.E-05 sec	1.29E-05	1.03E-08	2.44E-02	3.75E-20	1.81E-21	1.00E+03
3.E-04 sec	6.00E-05	1.52E-06	2.73E-02	2.17E-05	2.41E-09	2.49E+03
1 sec	5.84E-05	1.48E-06	2.37E-02	7.26E-03	3.82E-08	2.48 E+03

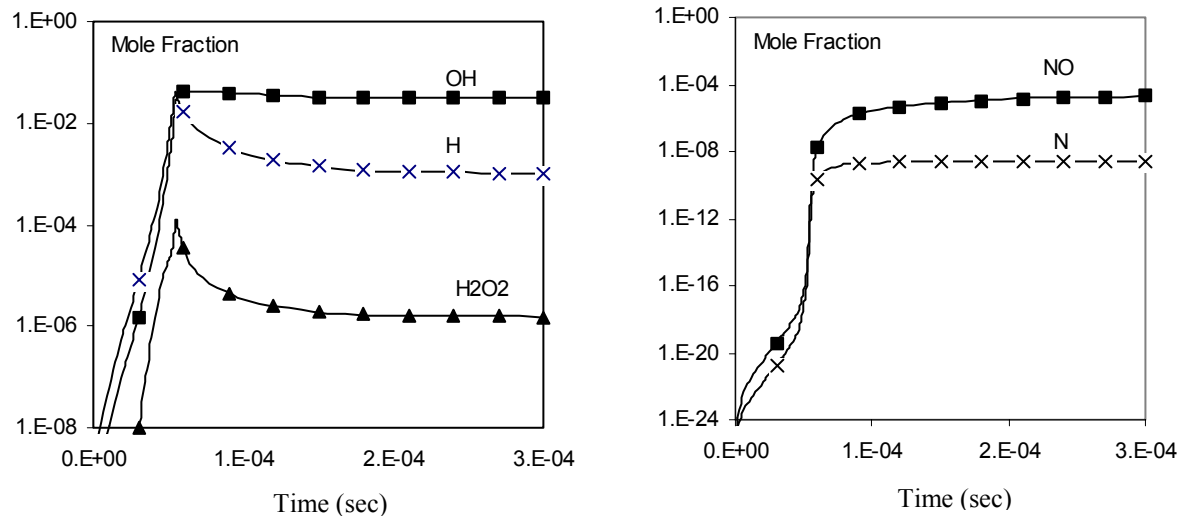

Fig 3. Comparison of calculated profiles: points – CHEMKIN data [1], lines – this calculation.

The same reaction set and initial conditions are used for checking calculation of gas parameters in equilibrium region. In this case the problem must be solved for a long time (for example, the final time is 1 sec) to make sure that the equilibrium is established. The species mole fractions of the equilibrium region are presented in Table 3. These data are excellently agreed with equilibrium gas composition obtained independently with CHEMKIN Equil [1].

Problem 4. Methane-Air Reaction Mechanism (GRI-Mech 3.0)

In this section, the methane-air reaction mechanism from GRI-Mech 3.0 [3] are considered. The mechanism consists of 325 reactions that involve 53 species. The following problems were solved to make comparison our results with independent calculations of other authors.

4.*a* Parameters of the this problem are similar to that studied in [4]. We don't concern the main subject of the work [4] (creating a reduced mechanism for NO emission) and take only the numerical data for NO reburning. A fixed pressure problem is solved.

Input values:
Pressure P=1 atm,
Start step size 1.0E-10 sec
Relative tolerance 1E-06, absolute tolerance 1E-17

Table 4. Initial mole fractions and temperature

CH4	C2H6	O2	NO	H2O	N2	T, K
2.864E-03	2.98E-04	5.09E-03	9.47E-04	2.16E-02	0.9692	1600

Some results obtained with Chemked are shown in table 5. Comparison of this calculation with data from [4] is given in Figure 4.

Table 5. Mole fractions of species and temperature for different time points

Time	O2	OH	N	HCN	NO	T. K
0 sec	5.09E-03	0	0	0	9.47E-04	1.60E+03
0.001 sec	4.72E-03	6.92E-06	4.69e-10	1.71E-05	9.07E-04	1.60E+03
0.003 sec	1.81E-03	1.54E-04	1.02E-06	7.61E-05	6.19E-04	1.63E+03
0.010 sec	8.56E-05	1.49E-04	3.66E-09	1.77E-07	6.16E-04	1.65E+03

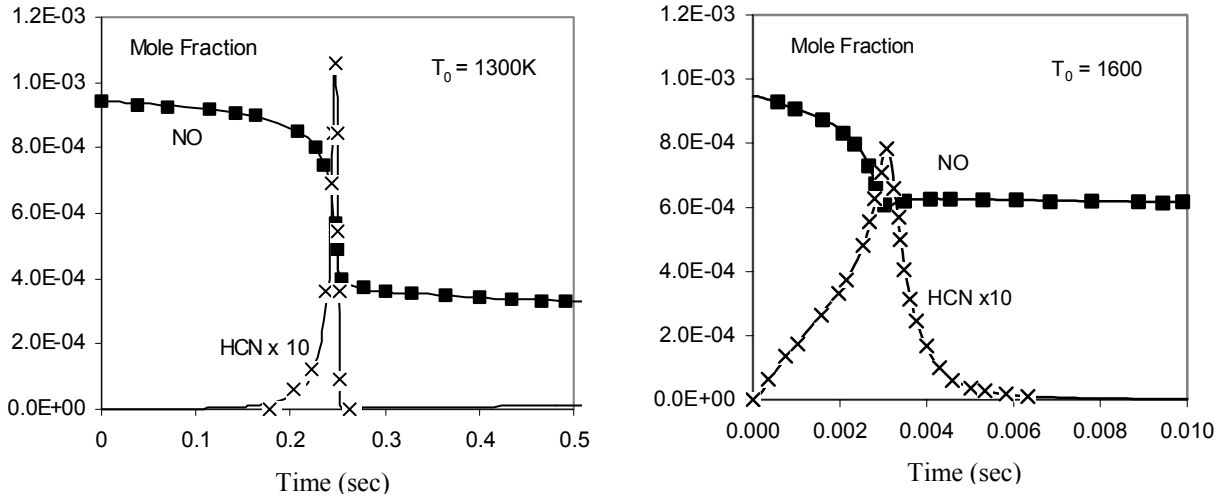

Fig 4. Comparison of calculated profiles: points –data from [4], lines – this calculation.

The following two problems are taken from the GRI-Mech collection of experimental targets [3].

4.*b* Thermal decomposition of CH2O at fixed pressure and fixed temperature

Conditions of this calculation correspond to the experiments [5].

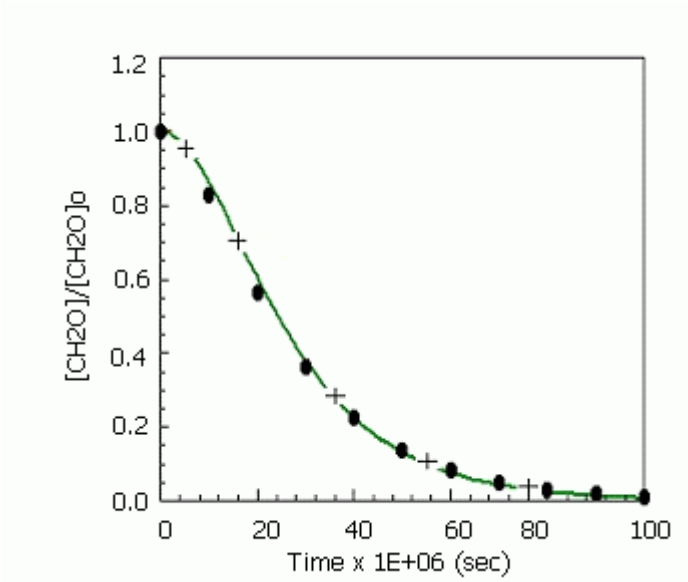

Fig 5. Normalized CH2O profile; circles – experimental data [5], line – calculation [3], crosses – this calculation

Input values:
Temperature *T*=1805K.
Gas mixture: [CH2O]0 : [AR]0 = 4 : 96, AR concentration is 1.9E-05 mol/cm3
Start step size 1.0E-10 sec
Relative tolerance 1E-06
Absolute tolerance 1E-16

4.*c* Oxidation of methane at fixed pressure and fixed temperature

Conditions of this calculation correspond to the experiments [6].

Input values:
Pressure P=1 atm
Temperature T= 2454K
Gas mixture: $[CH4]_0 : [O2]_0 : [AR]_0 = 0.1 : 0.4 : 99.5$
Start step size 1.0E-10 sec
Relative tolerance 1E-06
Absolute tolerance 1E-16

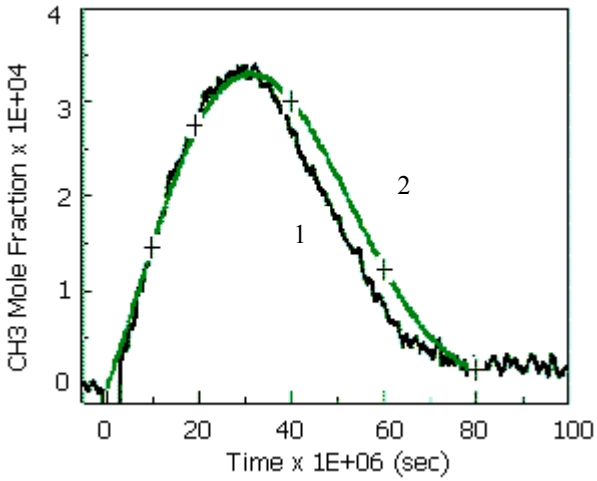

Fig 6. Mole fraction of CH3; *1* – experiments [6], *2* – calculation [3], crosses – this calculation

The above samples demonstrate a good agreement between Chemked calculations and results of other authors. The GRI-Mech reaction database contains all types of reactions and we believe that all program units of the chemical kinetics were tested and properly operate.

Problem 5. Thermodynamic Propertied of Heated Air

In this sample, the program units for calculation of of mean gas parameters are tested. The change of properties of abruptly heated air at fixed pressure and fixed temperature is considered.

Input values:
Pressure P=1 atm
Interval of initial temperatures T_0=298 - 4000K
Normal air composition: $[N2]_0 : [O2]_0 : [Ar]_0 : [CO2]_0 = 78.084 : 20.9476 : 0.9365 : 0.0319$
Start step size 1.0E-10 sec
Relative tolerance 1E-06
Absolute tolerance depends on T_0.

All the calculations have been made to equilibrium states. A few profiles for T_0 = 3000K are shown in Figure 7.

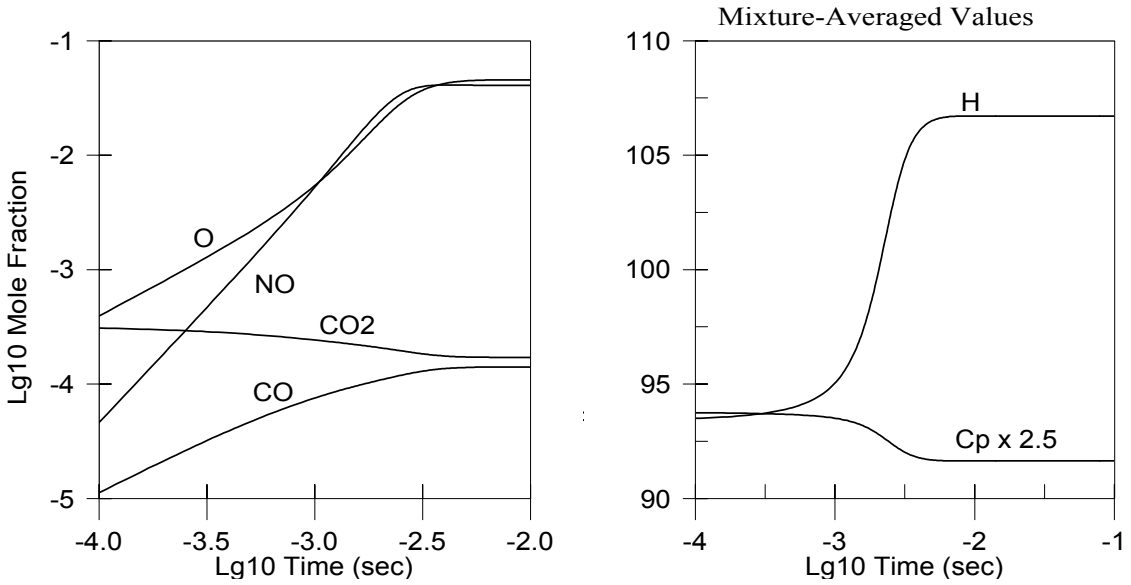

Fig 7. Temporal variations of species mole fractions and mean values of enthalpy H (kJ/mol) and heat capacity C_p (J/K mol); T_0 = 3000k, P = 1atm

Here we are interested in mixture-averaged gas parameters for initial and equilibrium gas mixture. These values for the enthalpy, the heat capacity and the molecular weight are grouped in table 6; the corresponding profiles are shown in Figure 8.

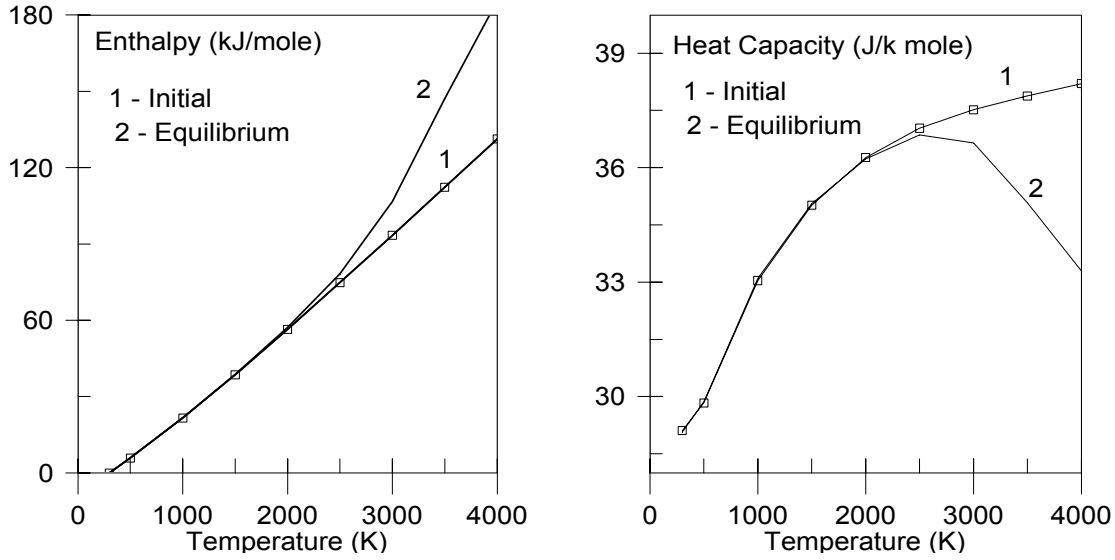

Fig 8. The enthalpy and the heat capacity vs. temperature, lines – this calculation, points – calculation from the polynomials [2]

Table 6. Mixture-averaged parameters of heated air at 1arm

Temperature, K		298	1000	2000	3000	4000
Enthalpy (kJ/mol)	Initial	-0.129	21.4	56.5	93.4	131
	Equilibrium	-0.129	21.5	57.2	107	186
Heat Capacity (J7K mol)	Initial	29.1	33.1	36.2	37.5	38.2
	Equilibrium	29.1	33.1	36.2	36.7	33.3
Molecular Weight (g/mol)	Initial	28.97	28.97	28.97	28.97	28.97
	Equilibrium	28.97	28.97	28..96	28.30	25.16

The thermodynamic properties of air at initial conditions (non-dissociated air) are compared with the independent calculations from the polynomials [2]. The polynomials are presented below; the calculations were made using the standard NASA formulas. The polynomials calculations coincide with the Chemked data (Table 6); the comparison for the enthalpy and the heat capacity is shown in Figure 8.

```
AIR calculated from ingredients %N2=78.084 %O2=20.9476 %Ar=0.9365 %CO2=0.0319
AIR               L 9/95                  0.G   200.000  6000.000  B  28.96518 1
 3.08792717E+00 1.24597184E-03-4.23718945E-07 6.74774789E-11-3.97076972E-15    2
-9.95262755E+02 5.95960930E+00 3.56839620E+00-6.78729429E-04 1.55371476E-06    3
-3.29937060E-12-4.66395387E-13-1.06234659E+03 3.71582965E+00-1.50965000E+01    4
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References

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http://garfield.chem.elte.hu/Burcat/burcat.html

[3] GRI-Mech 3.0. The Gas Research Institute.
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[4] C.J.Sung, C:K:Law and J.-Y.Chen. Augmented Reduced Mechanisms for NO Emission in Methane Oxidation. Combustion and Flame, 125, p.906(2001)

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