Arrhenius kinetic parameters for a reversed equilibrium reaction

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1 Introduction

The use of Arrhenius law requires some times to know the kinetic parameters of a reversible reaction written in the reverse direction. Concretely, the scope of this report is to derive the pre-exponential factor A' and the activation energy Ea' of the reaction $C+D \Leftrightarrow A+B$ knowing those (A and Ea) of the reaction $A+B \Leftrightarrow C+D$.

2 Method to reverse the equilibrium reaction

This study is based on the following set of reactions (CM2 mechanism see apendix A) :
$CH4 + 1.5O2 \Rightarrow CO + 2H2O$
$CO + 0.5O2 \Leftrightarrow CO2$

The aim of this report is to find out the kinetic parameters of the reaction 1.

$$CO + 0.5O2 \Leftrightarrow CO2 \tag{1}$$

A_1[cgs]	β	E_{a1}[cal/mol]
2.0e9	0.0	12000

TAB. 1 – kinetic parameters

Forward Order		Reverse Order	
CO	1.0	CO2	1.0
O2	0.5		

TAB. 2 – kinetic orders

In order to find out the kinetic parameters of the reaction 1 written in the reverse direction :

$$CO2 \Leftrightarrow CO + 0.5O2 \tag{2}$$

It is necessary to know the variation of the equilibrium constant K1 of the reaction 1 with the temperature :

T [K]	log(K1)
298	45.043
400	32.41
600	20.07
800	13.9
1000	10.199
1200	7.742
1400	5.992
1600	4.684
1800	3.672
2000	2.863
2200	2.206
2400	1.662
2600	1.203
2800	0.807
3000	0.469
3200	0.175
3500	-0.201
4000	-0.699
4500	-1.081
5000	-1.387

Tab. 3 – Logarithms to the base 10 of the equilibrium constant K1 for the reaction 1 (based on information provided by the National Bureau of Standards)

The variation of equilibrium constant against the temperature can be determined thanks to a 1D-flame using the equation (3).

$$K = \frac{\prod_j (X_j)^{\nu_j}}{\prod_i (X_i)^{\nu_i}} \tag{3}$$

Where X_i and X_j are respectively the molar fractions of the reactant i and product j. ν_i and ν_j are respectively the stoichiometric coefficients of the reactant i and product j.

For the reaction 1 the equilibrium constant K is defined as (4) :

$$K1 = \frac{(X_{CO2})^{\nu_{CO2}}}{(X_{O2})^{\nu_{O2}}(X_{CO})^{\nu_{CO}}} = \frac{X_{CO2}^1}{X_{O2}^{0.5} X_{CO}^1} \tag{4}$$

A way to find out the Arrhenius parameters of the reverse reaction is to start from the assumption : "reaction 1 is equivalent to reaction 2 if (for example) the production rate of the species CO2 in reaction 1 is equal to that of reaction 2".

This can be mathematically translated by (5) :

$$\left(\frac{d[CO2]}{dt}\right)_{reaction1} = \left(\frac{d[CO2]}{dt}\right)_{reaction2} \tag{5}$$

Which is equivalent to (6) :

$$kf1[O2]^{\nu_{O2}}[CO]^{\nu_{CO}} - kb1[CO2]^{\nu_{CO2}} = kb2[O2]^{\nu_{O2}}[CO]^{\nu_{CO}} - kf2[CO2]^{\nu_{CO2}} \tag{6}$$

Where kfi and kbi are respectively the forward and reverse rates of the reaction i, Y_k and W_k the mass fraction and the molar mass of the species k.

The backward rates are derived from equilibrium constants of reaction and the forward rates as shown in (7) :

$$kbi = \frac{kfi}{Ki} \tag{7}$$

In addition, the equilibrium constant of the reaction 2 can be written with that of reaction 1, see (8).

$$K2 = \frac{X_{O2}^{0.5} X_{CO}^1}{X_{CO2}^1} = \frac{1}{K1} \tag{8}$$

Using equations (6, 7 and 8), it is now possible to derive a simple relation between kf1 and kf2 through (9).

$$kf1\left([O2]^{1/2}[CO]^1 - \frac{1}{K1}[CO2]^1\right) = kf2.K1\left([O2]^{1/2}[CO]^1 - \frac{1}{K1}[CO2]^1\right) \tag{9}$$

In this case, the reaction rates are modeled using an Arrhenius law :

$$kfi = A_i T^{\beta} exp(\frac{-E_{ai}}{RT}) \tag{10}$$

Where A_i is the pre-exponential factor defined previously, E_{ai} the activation energy, R the universal gas constant and T the temperature.

Thanks to relation (11) it is possible to extract Arrhenius parameters of reaction 2, plotting $Tln(kf2)$ against T.

$$kf2 = \frac{kf1}{K1} = \frac{A_1 exp(\frac{-T_{a1}}{T})}{K1} = A_2 exp(\frac{-T_{a2}}{T}) \tag{11}$$

Note : before plotting it is necessary to convert the unit of kf1 (cgs) into SI-unit.

$$kf1(SI) = kf1(cgs).10^{6.(1-(\nu_{O2}+\nu_{CO}))} = kf1(cgs).10^{-3} \tag{12}$$

Where ν_{O2} and ν_{CO} are the stoichiometric coefficients of O2 and CO in the reaction 1.

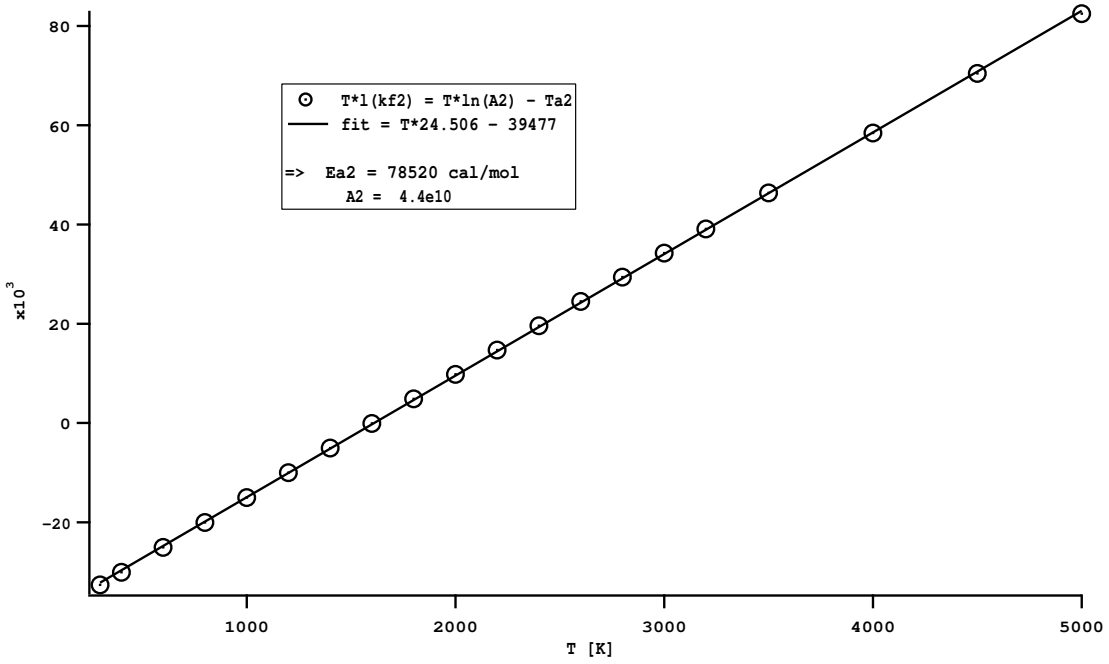

FIG. 1 – T ln(kf2) against T

Finally, the next tables sum up the new kinetic parameters of the reaction 2 :

A [cgs]	β	Ea[cal/mol]
4.4e10	0.0	78520

TAB. 4 – kinetic parameters of the reversed reaction

Forward Order		Reverse Order	
CO2	1.0	CO	1.0
		O2	0.5

TAB. 5 – kinetic orders of the reversed reaction

3 Test of the reversed reaction with COSILAB

This section presents the results of the test of the CM2 mechanism with its second reaction reversed (see appendix A and B to obtain all the kinetic parameters of CM2 and "reversed" CM2 schemes).

The resulting profiles have been compared with those of the usual CM2 scheme.

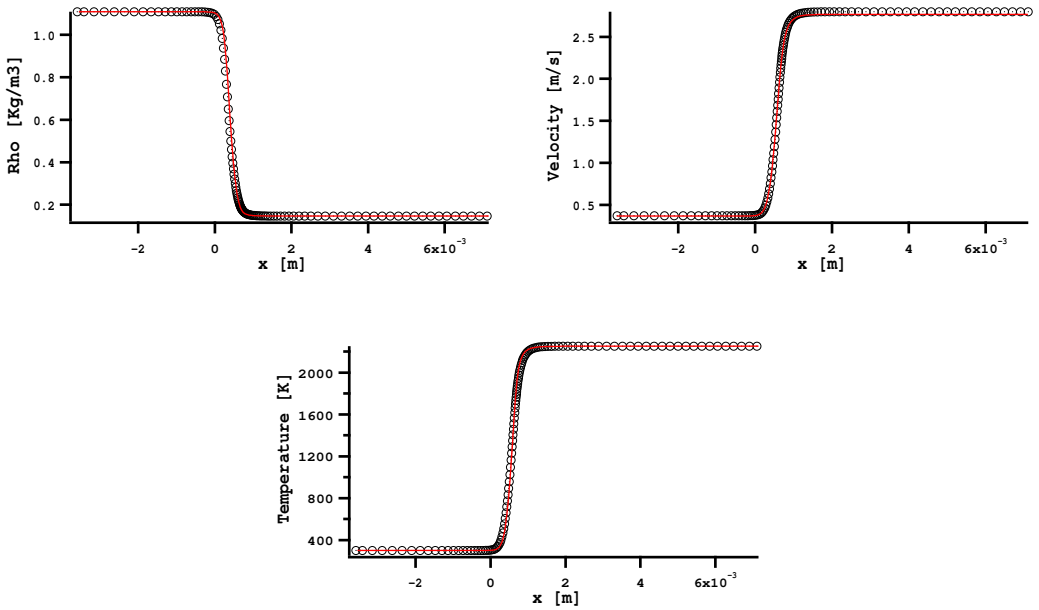

FIG. 2 – NS variables spatial profiles for phi=1.0, T0=300K and P=1bar. Cercles : usual CM2 and line : CM2 with reverse equilibrium reaction

	left conditions		right conditions	
	CM2 reversed	CM2	CM2 reversed	CM2
P[Pa]	100000	100000	100000	100000
T[K]	300	300	2253	2252
velocity[m/s]	0.367	0.371	2,767 0	2.798
ρ[kg/m3]	1.108	1.108	0.1467	0.1468

TAB. 6 – NS Far field conditions.

	Sl[m/s]
CM2	0.371
CM2 reversed	0.367

TAB. 7 – Laminar flame speed

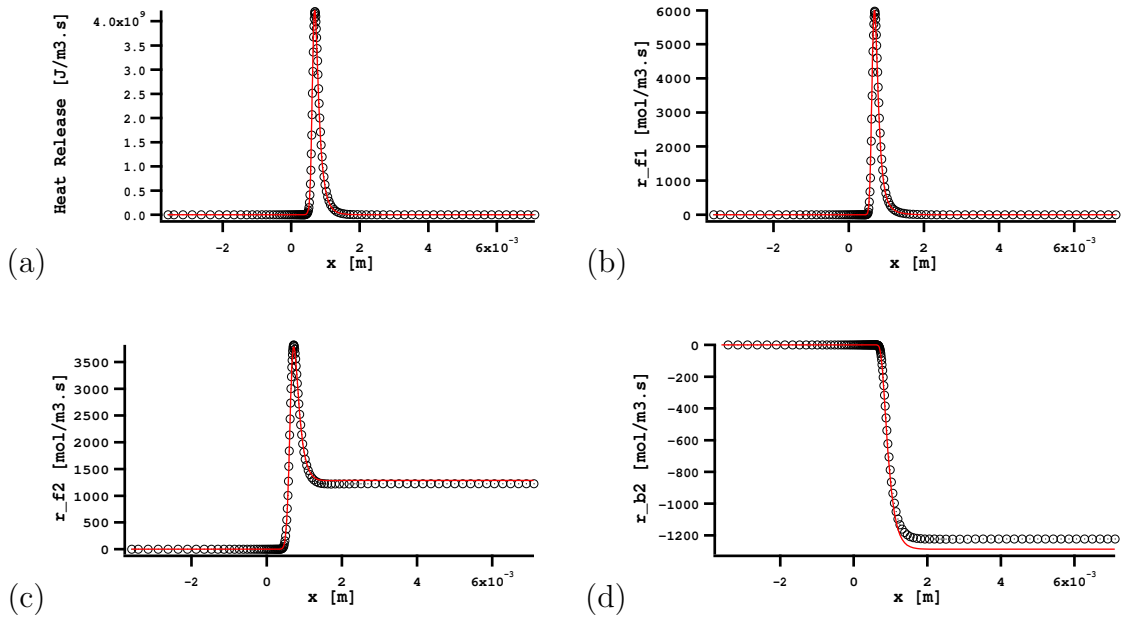

FIG. 3 – Spatial profiles of the reaction variables for phi=1.0, T0=300K and P=1bar. Cercles : usual CM2 and line : CM2 with reversed equilibrium reaction. (c) represents the comparison between $rf2_{CM2}$ (cercles) and $-rb2_{CM2reversed}$ (line) ; (d) represents the comparison between $rb2_{CM2}$ (cercles) and $-rf2_{CM2reversed}$ (line).

The discrepancies observed on plots (c) and (d) come from slight errors in the interpolation process of the previous section.

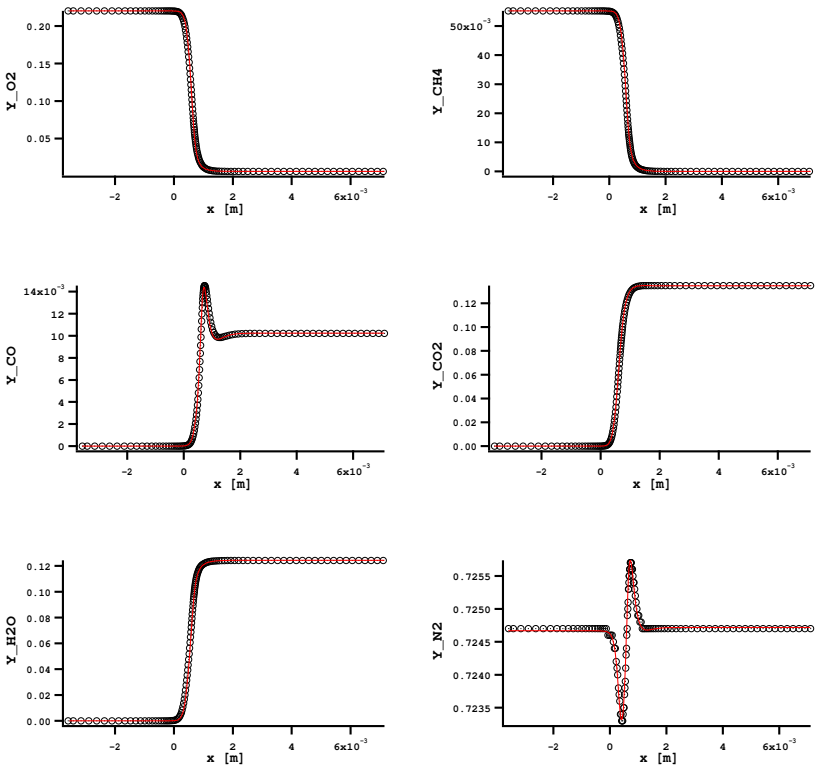

FIG. 4 – Mass fraction spatial profiles for phi=1.0, T0=300K and P=1bar. Cercles : usual CM2 and line : CM2 with reverse equilibrium reaction

	left conditions		right conditions	
	CM2 reversed	CM2	CM2 reversed	CM2
YO2	2.201e-1	2.201e-1	6.105e-3	6.096e-3
YCH4	5.520e-2	5.520e-2	8.288e-11	8.280e-11
YCO	0.000	0.000	1.024e-2	1.021e-2
YCO2	0.000	0.000	1.347e-1	1.348e-1
YH2O	0.000	0.000	1.242e-1	1.242e-1
YN2	7.247e-1	7.247e-1	7.246e-1	7.247e-1

TAB. 8 – Mass fraction far field conditions.

4 Test of the reversed reaction with AVBP

The comparison between the CM2 and the "reversed" CM2 schemes has been carried out with AVBP_V5.5. The following results show that the new kinetic parameters are well supported by AVBP.

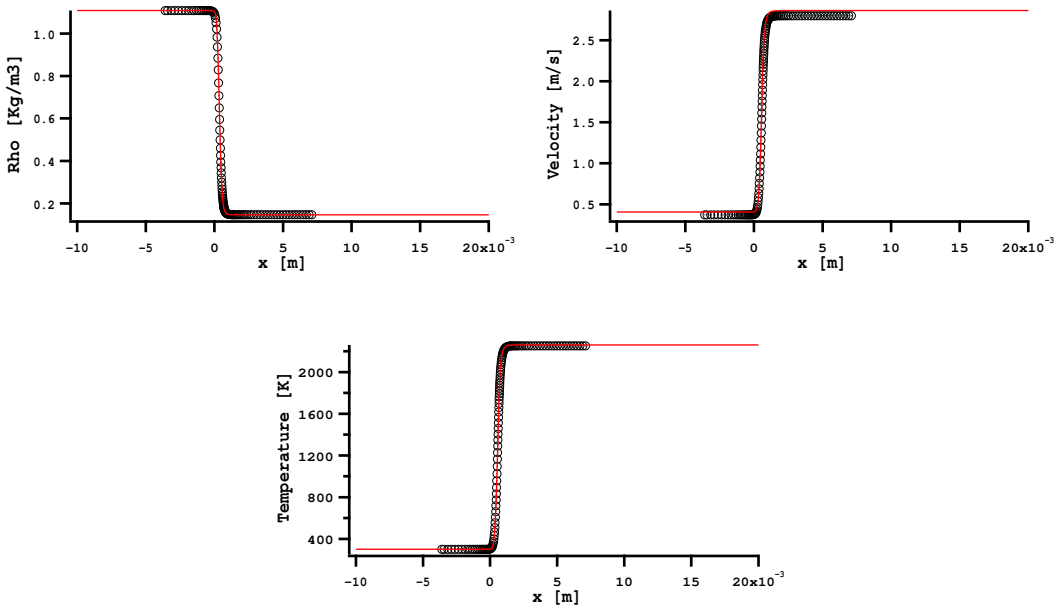

FIG. 5 – NS variables spatial profiles for phi=1.0, T0=300K and P=1bar. Cercles : usual CM2 computed with COSILAB and line : CM2 with reverse equilibrium reaction computed with AVBP

	left conditions		right conditions	
	AVBP with reversed CM2	COSILAB	AVBP with reversed CM2	COSILAB
P[Pa]	100000	100000	99999	100000
T[K]	300	300	2259	2252
velocity[m/s]	0.405	0.371	2.861	2.798
ρ[kg/m3]	1.108	1.108	0.1464	0.1468

TAB. 9 – NS Far field conditions.

	Sl[m/s]
AVBP :CM2 reversed	0.369
COSILAB : usual CM2	0.371

TAB. 10 – Laminar flame speed

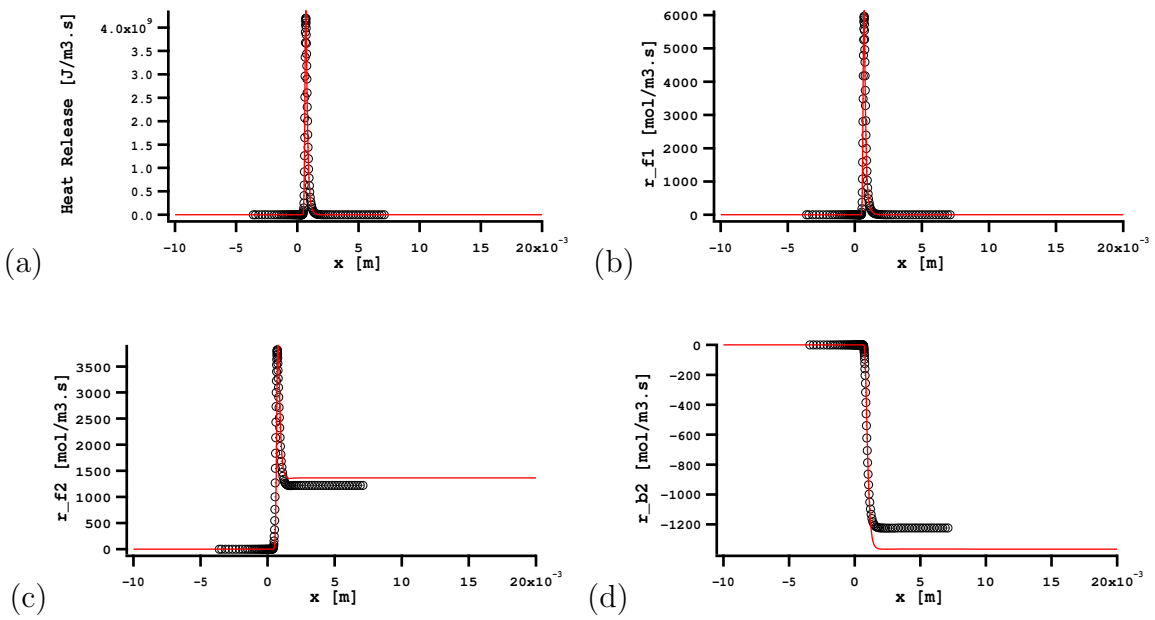

FIG. 6 – reaction variables spatial profiles for phi=1.0, T0=300K and P=1bar. Cercles : usual CM2 computed with COSILAB and line : CM2 with reversed equilibrium reaction computed with AVBP. (c) represents the comparison between $rf2_{CM2}$ (cercles) and $-rb2_{CM2reversed}$ (line) ; (d) represents the comparison between $rb2_{CM2}$ (cercles) and $-rf2_{CM2reversed}$ (line).

The discrepancies observed on plots (c) and (d) come from slight errors in the interpolation process of the section : "Method to reverse the equilibrium reaction".

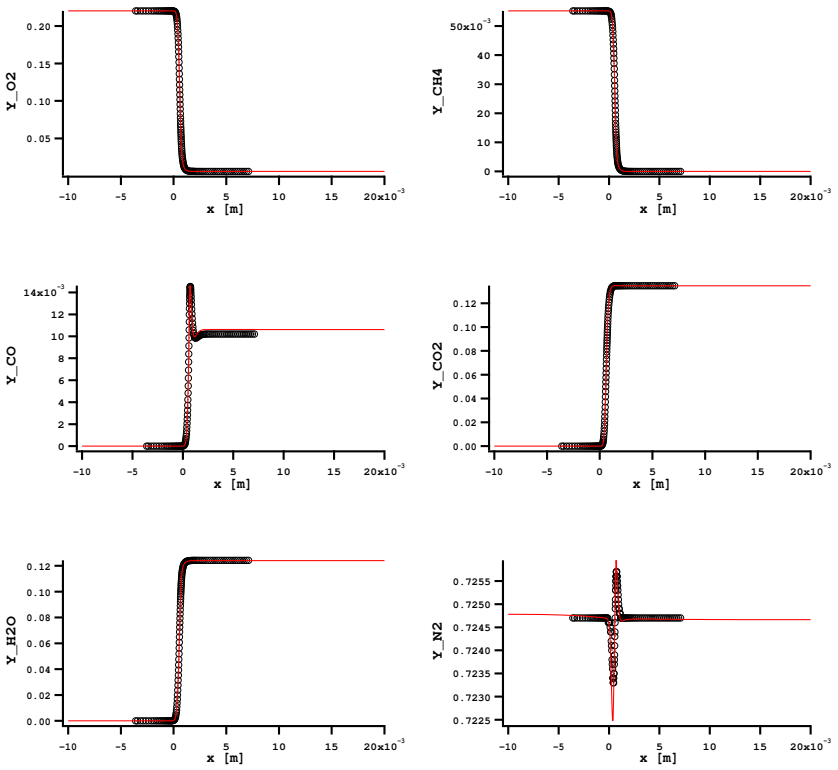

FIG. 7 – Mass fraction spatial profiles for phi=1.0, T0=300K and P=1bar. Cercles : usual CM2 computed with COSILAB and line : CM2 with reverse equilibrium reaction computed with AVBP

	left conditions		right conditions	
	AVBP with reversed CM2	COSILAB	AVBP with reversed CM2	COSILAB
YO2	2.201e-1	2.201e-1	6.050e-3	6.096e-3
YCH4	5.520e-2	5.520e-2	0.000	8.280e-11
YCO	0.000	0.000	1.062e-2	1.021e-2
YCO2	0.000	0.000	1.347e-1	1.348e-1
YH2O	0.000	0.000	1.239e-1	1.242e-1
YN2	7.248e-1	7.247e-1	7.246e-1	7.247e-1

TAB. 11 – Mass fraction far field conditions.

5 Conclusion

This document explains how to find out the Arrhenius parameters of a reversed equilibrium reaction. The little differences observed during comparison are highly susceptible to come from curb fitting errors. However, test results of the new scheme with the reversed reaction have shown good agreements with the initial scheme and the new parameters are well supported by AVBP_V5.5.

A Input_premix.dat file of the CM2 scheme

```
-------------------------------------------------------------------------
  6                   ! neqs (number of chemical species)

'CH4'  0.677d0
'CO2'  0.945d0
'CO'   0.750d0
'O2'   0.739d0
'H2O'  0.544d0
'N2'   0.726d0

-------------------------------------------------------------------------
  2                   ! nreac (number of chemical reactions)

*** Reaction #  1 : CH4+ 1.5O2=>CO+2H2O
4                     ! nspec (number of species involved in the reaction)
'CH4'    -1.00     +0.90       0.0
'O2'     -1.50     +1.10       0.0
'CO'     +1.00     +0.00       0.0
'H2O'    +2.00     +0.00       0.0
 2.0D15                ! Pre-exponential factor (cgs)
 35000.0D0             ! Activation Energy (cal/mol)

*** Reaction #  2 : CO+ 5.00E-01O2<=>CO2
3                     ! nspec (number of species involved in the reaction)
'CO'    -1.00     +1.00 0.0
'O2'    -0.50     +0.50 0.0
'CO2'   +1.00     +0.00 1.0
-2.0D9                ! Pre-exponential factor (cgs)
 12000.0D0            ! Activation Energy (cal/mol)
```

B Input_premix.dat file of the "reversed" CM2 scheme

```
 ---------------------------------------------------------------------
  6                   ! neqs (number of chemical species)

'CH4'  0.677d0
'CO2'  0.945d0
'CO'   0.750d0
'O2'   0.739d0
'H2O'  0.544d0
'N2'   0.726d0

---------------------------------------------------------------------
  2                   ! nreac (number of chemical reactions)

*** Reaction #  1 : CH4+ 1.5O2=>CO+2H2O
4                     ! nspec (number of species involved in the reaction)
'CH4'    -1.00     +0.90       0.0
'O2'     -1.50     +1.10       0.0
'CO'     +1.00     +0.00       0.0
'H2O'    +2.00     +0.00       0.0
 2.0D15                ! Pre-exponential factor (cgs)
 35000.0D0             ! Activation Energy (cal/mol)

*** Reaction #  2 : CO2<=>CO+ 5.00E-01O2
3                     ! nspec (number of species involved in the reaction)
'CO2'   -1.00     +1.00 0.0
'CO'      1.00      0.00 1.0
'O2'      0.50      0.00 0.5
-4.4D10               ! Pre-exponential factor (cgs)
 78520.0D0            ! Activation Energy (cal/mol)
```