

User Guide - *AtCSolv*1.0

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1 Installation and Test

This section describes the installation process for the software package AtCSol. The code can be compiled on Linux and macOS machines.

1. Open a terminal and change to the AtCSol home directory.
- 5 2. To clean the AtCSol installation, delete the AtCSol object files and the executable type:
 make clean
3. Edit the M_DEF_[OS] file depending on the machine. Mac user have to specify the path to the NetCDF library folder and the path to the local include folder:
 LocNCDF = /usr/local/lib
10 **LocINCL = /usr/local/include**
 If you use a Linux machine you just have to specify the **LocNCDF** path to the NetCDF library.
4. Make sure you have installed gfortran and mpif90. To test this type "**which gfortran**" or "**which mpif90**".
5. Open the Makefile and choose corresponding M_DEF_[OS] file (first line):
 IN1 = M_DEF_Mac or **IN1 = M_DEF_Linux**
- 15 6. Creating the AtCSol executable with:
 make AtCSol (optimized version, -O3, see M_DEF_[OS])
 make AtCSol_dbg (debugging version, -g -O0, see M_DEF_[OS])
7. To run several examples type "**make test**" in the AtCSol home directory. This will execute AtCSol with six different mechanisms successively. The generated output is stored as NetCDF files in the NetCDF/ folder.

2 Description of the chemical reaction mechanism for atmospheric mechanisms (*.sys -File)

2.1 Head of the *.sys file:

- All characters following an hash symbol "#" or the keyword "COMMENT" will be ignored.
- At the beginning of the document, the user has to specify the units for the initial data using the keywords
5 UNIT GAS and UNIT AQUA respectively. Default values are 0 for both phases.

```
# =====  
# ===== CHEMIE =====  
# ===== Output - Chemical Reaction Data =====  
10 # =====  
  
# Created: Wed June 14 12:00:00 2006 (AT)  
# Chemical Mechanism: CAPRAM 3.0 (URBAN CASE)  
  
15 # ===== Unit options =====  
  
UNIT GAS 0 # Gas phase units ( 0 = molec/cm3, 1 = mol/cm3)  
UNIT AQUA 0 # Aqueous phase units ( 0 = mol/l)
```

20 2.2 General directives for the reaction mechanism input structure

Syntax:

```
CLASS: classname # Comment  
Chemical equation  
25 TypeName: List of parameters  
[FACTOR: List of factors ] # optional
```

1. The input structure consists of at least 3 lines.
2. The reaction description can begin anywhere on the line.
- 30 3. All characters following an hash symbol "#" or the keyword "COMMENT" will be ignored.
4. The length of an input line is limited to 400 characters.
5. Character "□+□" separates two reactants from each other. Note: Blank spaces are necessary!

6. Each reaction description must have "□=□" between the last reactant and the first product. All blank spaces, except those and between reaction rate parameters are ignored.
7. Each reaction description must be contained on one line.
8. Blank lines in between the reaction structure will be ignored.
- 5 9. The reaction rate parameter on each reaction line, separated from each other and from the reaction type description by at least one blank space; no blanks are allowed within the numbers themselves. The reaction rate parameter shall be taken from table [3.7], the respective values has to be set either in exponential or floating point notation.
10. Colons are declared as separator for the parameter list.
- 10 11. SMILES notation for chemical species is allowed.
12. Higher order reactions can be declared as either: $\text{OH} + \text{OH} = \text{H}_2\text{O}_2$ or $2\text{OH} = \text{H}_2\text{O}_2$
13. Blank spaces within species names are not allowed!
14. examples: see section [2.6]

2.3 Further syntax rules

15 Species names:

- use arbitrary numbers, upper and lower case letters, exept special conventions as:

Special conventions:

- aXXX - dissolved substance in aqueous phase (e.g. aO3)
- sXXX - solid substance in aqueous phase (e.g. sCACO3)
- XXXp - cation (e.g. $\text{H}^+ = \text{Hp}$, $\text{Fe}^{3+} = \text{Feppp}$)
- XXXm - anion (e.g. $\text{OH}^- = \text{OHm}$)

Other conventions:

- [] - passive species, is used for calculation of the rate constant, concentration will not be calculated dynamicly (e.g. [H2O])
- 20 () - species acts like a dummy, concentration will not be calculated dynamicly (e.g. (dummy))
- \$ - external species for microphysical properties (e.g. \$N2)

CLASS:	Description
GAS	gaseous reaction
HENRY	phase transfer reaction (equilibrium pseudo-reaction)
DISS	chemical dissociation (fast equilibrium reaction)
AQUA	aqueous reaction

2.4 CLASS and TYPE Dependencies

In principal, the rules for the computation of the reaction rate constants can be used for all classes. The following table gives an overview about the useful combinations.

CLASS:	GAS	HENRY	DISS	AQUA
PHOTABC:	X			X
PHOTAB:	X			X
PHOTMCM:	X			X
CONST:	X	X		X
TEMP:	X	X		X
TEMP1:	X	X		X
TEMP2:	X	X		X
TEMP3:	X	X		X
TEMP4:	X			
S4H2O:	X			
T1H2O:	X			
TROE:	X			
TROEF:	X			
TROEQ:	X			
TROEQF:	X			
TROEXP:	X			
TROEMCM:	X			
SPEC1:	X			
SPEC2:	X			
SPEC3:	X			
SPEC4:	X			
SPEC1MCM:	X			
SPEC2MCM:	X			
SPEC3MCM:	X			
SPEC4MCM:	X			
SPEC5MCM:	X			
SPEC6MCM:	X			
SPEC7MCM:	X			
SPEC8MCM:	X			
ASPEC1:				X
ASPEC2:				X
ASPEC3:				X
DTEMP:			X	
DTEMP2:			X	
DTEMP3:			X	
DTEMP4:			X	
DCONST:			X	

Table 1. Tabular overview of possible combinations for reaction types.

2.5 Modification of a Rate Constant by FACTOR:

CLASS: GAS

HO = HO2

TEMP1: K0: $5.5E-12$ E/R: 2000.

FACTOR: [H2] EX: 1.E0 A: 1.E0

FACTOR: \$H2O

The reaction rate constant k^* (here of type TEMP1) is per line modified by factor:

$$k = k^* \cdot (\text{A} \cdot [\text{H2}]^{\text{EX}}) \cdot \$\text{H2O}$$

- 5 Here denoted [H2] the concentration of a reactive or non-reactive species. The term \$H2O stands for a value given external by meteorology or micro-physics. Two or more "factor lines" are possible. In principle, all rate constants can be modified.

2.6 Examples

```
# ===== MCM3.1 + CAPRAM =====
# = Please copy the data into your sys-file for =
5 # ===== chemical input. =====
#
# ===== Unit options =====

UNIT GAS    0   #    Gas phase units    (0 = molec/cm3, 1 = mol/m3)
10 UNIT AQUA  0   #    Aqueous phase units (0 = mol/l)

# ===== Gas Phase =====

CLASS: GAS
15 HO = HO2
TEMP1:  K0: 5.5E-12    E/R:  2000.
FACTOR:  [H2]  EX: 1.E0  A: 1.E0

COMMENT chlorine chemistry — propylene oxidation
20 CLASS: GAS  #G77
CL + CC=C = CC(O[O])CCL
TROE:   KO: 4.0E-28  N:  0.0  KINF:  2.8E-10  M:  0.00

# ===== Phase transfer =====
25
CLASS: HENRY
SO2 = aSO2
TEMP3:  K0: 1.23E0    E/R:  3.12E3

30 # ===== Aqueous phase =====

CLASS: AQUA    #Po00001
aCOO = aC[O] + aHO
35 PHOTMCM:  I: 8.625e-06  M: 1.043  N: 0.271
```

3 Definition of Reaction Rate Constants

Legend for the variables used in the following:

$\chi := \chi(t)$	zenith angle being time dependent
β	number of products - educts
γ	number of educts
$\varepsilon_{\text{dust}}$	loss factor (where $0 \leq \varepsilon_{\text{dust}} \leq 1$, usually: $\varepsilon_{\text{dust}} = 1.0$)
T	current temperature (usually: 288.15[K])
T_{ref}	reference temperature (usually: 298.15[K])
p	current pressure (usually: 850[Pa])
p_0	standard atmospheric pressure: 1013.25[Pa]
$[N_2]$	concentration gaseous ($\approx 1.960 \cdot 10^{19}[\text{cm}^{-3}]$)
$[H_2O]$	concentration gaseous ($\approx 5.100 \cdot 10^{17}[\text{cm}^{-3}]$)
$[X]$	sum of all collision partners ($\approx 2.47 \cdot 10^{19}[\text{cm}^{-3}]$)
$[M]$	molecularity (usually: $M = [X] \cdot T_{\text{ref}}/T \cdot p/p_0$)

Figure 1. List of frequently used parameters for the calculation of reaction rates within atmospheric chemistry simulations. All of the above listed parameters are constant during the simulation time with exception to the zenith angle being a time dependent function.

3.1 Creating custom-built rate constant functions

```
CLASS:      classname      # comment
chemical equation
SPECIAL:    formula      ;      number of variables
```

- 5 – The formula has to be specified in one line and Fortran notation.
- Semicolon separates formula from the number of variables used in the formula.
- **Pro:** High flexibility for new developed reaction rates constants.
- **Con:** Needs way more CPU time to evaluate the formula.

```
10 CLASS: MICROPHYS
RHO + RHOV + RHOL      =      RHO
SPECIAL:  2.2E-13*exp(620./TEMP)+1.9E-33*RHOV*abs(sqrt(RHO*RHO+RHOV*RHOV)); 3
```

3.2 Gas and Aqueous Phase (CLASS: GAS or AQUA)

TYP: PHOTABC photolysis

$$\chi_z = C \cdot \chi$$

$$\chi_y = B \cdot \left(1 - \frac{1}{\cos(\chi_z)}\right)$$

$$\chi_x = \begin{cases} \exp(\chi_y), & \chi_y > -30 \\ 9.357 \cdot 10^{-14}, & \text{otherwise} \end{cases} \quad (1)$$

$$k = \begin{cases} \varepsilon_{\text{dust}} \cdot A \cdot \chi_x, & \chi > \pi/2 \\ 0, & \text{otherwise} \end{cases}$$

$$A = j[\text{s}^{-1}], \quad B = b[-], \quad C = c[-]$$

Parameter: $A \quad B \quad C$

Ref: cp. Roeth, 1992

TYP: PHOTAB photolysis

$$k = \begin{cases} \varepsilon_{\text{dust}} \cdot A \cdot \exp\left(-\frac{B}{\cos(\chi)}\right), & \chi > \pi/2 \\ 0, & \text{otherwise} \end{cases} \quad (2)$$

$$A = a[\text{s}^{-1}], \quad B = b[-]$$

Parameter: $A \quad B$

TYP: PHOTMCM photolysis as used in MCM (M, N dimensionless parameter to describe shape of curve)

$$\chi_z = \exp\left(-\frac{N}{\cos(\chi)}\right)$$

$$\chi_y = \cos(\chi)^M$$

$$k = \begin{cases} \varepsilon_{\text{dust}} \cdot I \cdot \chi_y \cdot \chi_z, & \chi > \pi/2 \\ 0, & \text{otherwise} \end{cases} \quad (3)$$

$$I = i[\text{s}^{-1}], \quad M = m[-], \quad N = n[-]$$

Parameter: $I \quad M \quad N$

TYP: CONST simple constant

$$k = K_0$$

$$K_0 = a[(\text{cm}^{-3})^{\beta-1} s^{-1}],$$

Parameter: K_0

(4)

TYP: TEMP temperature dependent reaction (Arrhenius expression)

$$k = A \cdot T^N \cdot \exp\left(-\frac{B}{T}\right)$$

$$A = a[(\text{cm}^{-3})^{\beta-1} s^{-1}], \quad N = n [-] \quad B = E/R = -\Delta H/R [K]$$

Parameter: $A \quad N \quad E/R$

(5)

TYP: TEMP1 temperature dependent reaction (Arrhenius expression)

$$k = A \cdot \exp\left(-\frac{B}{T}\right)$$

$$A = a[(\text{cm}^{-3})^{\beta-1} s^{-1}], \quad B = E/R = -\Delta H/R [K]$$

Parameter: $A \quad E/R$

(6)

TYP: TEMP2 temperature dependent reaction (Arrhenius expression)

$$k = K_0 \cdot T^2 \cdot \exp\left(-\frac{B}{T}\right)$$

$$K_0 = a[(\text{cm}^{-3})^{\beta-1} s^{-1}], \quad E/R = -\Delta H/R [K]$$

Parameter: $K_0 \quad E/R$

(7)

TYP: TEMP3 temperature dependent reaction Arrhenius expression in the format

$$k = A \cdot \exp\left(B\left(\frac{1}{T} - \frac{1}{T_{\text{ref}}}\right)\right)$$

$$A = a[(\text{cm}^{-3})^{\beta-1} s^{-1}], \quad B = E_a/R = -\Delta H/R [K]$$

Parameter: $A \quad B$

(8)

TYP: TEMP4 temperature dependent reaction (Arrhenius expression)

$$k = A \cdot T \cdot \exp\left(-\frac{B}{T}\right)$$

$$A = a[(\text{cm}^{-3})^{\beta-1} s^{-1}], \quad B = E_a/R = -\Delta H/R [K]$$

Parameter: $A \quad B$

(9)

TYP: S4H2O (cp. the special reactions in RADM/ RACM by Stockwell)

$$k = [H_2O] \cdot C_1 \cdot \exp\left(\frac{C_2}{T}\right) + C_3 \cdot [M] \cdot [H_2O] \cdot \exp\left(\frac{C_4}{T}\right) \quad (10)$$

Parameter: A C_1 C_2 C_3 C_4

Note: $[H_2O]$ is prescribed or taken from meteorology.

TYP: T1H2O

$$k = [H_2O] \cdot A \cdot \exp\left(-\frac{B}{T}\right) \quad (11)$$

$$A = a[(\text{cm}^{-3})^{\beta-1} s^{-1}], \quad B = -\Delta H/R [K]$$

Parameter: A B

Note: $[H_2O]$ is prescribed or taken from meteorology.

3.3 Only Gas Phase (CLASS: GAS)

TYP: TROE temperature and pressure dependent reaction (Troe)

$$k_1 = [X] \cdot K_0 \cdot \left(\frac{T}{300}\right)^{-N}$$

$$k_2 = k_\infty \cdot \left(\frac{T}{300}\right)^{-M} \quad (12)$$

$$k = \frac{k_1}{(1 + k_1/k_2)} \cdot 0.6^{(1 + (\log_{10}(k_1/k_2))^2)^{-1}}$$

Parameter: K_0 N k_∞ M

TYP: TROEF temperature and pressure dependent reaction (Troe)

$$k_1 = [X] \cdot K_0 \cdot \left(\frac{T}{300}\right)^{-N}$$

$$k_2 = k_\infty \cdot \left(\frac{T}{300}\right)^{-M} \quad (13)$$

$$k = \frac{k_1}{(1 + k_1/k_2)} \cdot F^{(1 + (\log_{10}(k_1/k_2))^2)^{-1}}$$

Parameter: K_0 N k_∞ M F

TYP: TROEQ Troe - equilibrium

$$\begin{aligned}
 k_1 &= [N_2] \cdot K_0 \cdot \left(\frac{T}{300}\right)^{-N} \\
 k_2 &= k_\infty \cdot \left(\frac{T}{300}\right)^{-M} \\
 k_3 &= \frac{k_1}{(1 + k_1/k_2)} \cdot 0.6^{(1+(\log_{10}(k_1/k_2))^2)^{-1}} \\
 k &= \frac{k_3}{K_1 \cdot \exp(-B/T)}
 \end{aligned} \tag{14}$$

Parameter: K_0 N k_∞ M K_1 B

TYP: TROEQF Troe - equilibrium

$$\begin{aligned}
 k_1 &= [N_2] \cdot K_0 \cdot \left(\frac{T}{300}\right)^{-N} \\
 k_2 &= k_\infty \cdot \left(\frac{T}{300}\right)^{-M} \\
 k_3 &= \frac{k_1}{(1 + k_1/k_2)} \cdot F^{(1+(\log_{10}(k_1/k_2))^2)^{-1}} \\
 k &= \frac{k_3}{K_1 \cdot \exp(-B/T)}
 \end{aligned} \tag{15}$$

Parameter: K_0 N k_∞ M 1 B F

TYP: TROEXP temperature and pressure dependent reaction (Troe)

$$\begin{aligned}
 k_1 &= [X] \cdot K_0 \cdot \exp\left(\frac{B_1}{T}\right) \\
 k_2 &= k_\infty \cdot \exp\left(\frac{B_2}{T}\right) \\
 k &= \frac{k_1}{(1 + k_1/k_2)} \cdot F^{(1+(\log_{10}(k_1/k_2))^2)^{-1}}
 \end{aligned} \tag{16}$$

Parameter: K_0 B_1 k_∞ B_2 F

TYP: TROEMCM MCM version of temperature and pressure dependent reaction (Troe)

$$\begin{aligned}
 k_1 &= [M] \cdot K_1 \cdot \left(\frac{T}{298}\right)^{-K_2} \exp\left(\frac{K_3}{T}\right) \\
 k_2 &= K_4 \cdot \left(\frac{T}{298}\right)^{-K_5} \exp\left(\frac{K_6}{T}\right) \\
 F_c &= K_7 \cdot \exp\left(\frac{K_8}{T}\right) + K_9 \cdot \exp\left(\frac{K_{10}}{T}\right) \\
 k &= \frac{k_1}{(1 + k_1/k_2)} \cdot F_c^{(1+(\log_{10}(k_1/k_2))^2)^{-1}}
 \end{aligned} \tag{17}$$

Parameter: K_1 K_2 K_3 K_4 K_5 K_6 K_7 K_8 K_9 K_{10}

TYP: SPEC1 (cp. the special reactions in RADM/ RACM by Stockwell)

$$k = C_1 \cdot (1 + [M] \cdot C_2) \quad (18)$$

Parameter: C_1 C_2

TYP: SPEC2 (cp. the special reactions in RADM/ RACM by Stockwell)

$$k = [M] \cdot C_1 \cdot \left(\frac{T}{300}\right)^{C_2} \quad (19)$$

Parameter: C_1 C_2

TYP: SPEC3 (cp. the special reactions in RADM/ RACM by Stockwell)

$$\begin{aligned} k_1 &= K_1 \cdot \exp\left(\frac{K_2}{T}\right) \\ k_2 &= K_3 \cdot \exp\left(\frac{K_4}{T}\right) \\ k_3 &= [M] \cdot K_5 \cdot \exp\left(\frac{K_6}{T}\right) \\ k &= k_1 + \frac{k_3}{1 + k_3/k_2} \end{aligned} \quad (20)$$

Parameter: K_1 K_2 K_3 K_4 K_5 K_6

TYP: SPEC4

$$k = C_1 \cdot \exp\left(\frac{C_2}{T}\right) + [M] \cdot C_3 \cdot \exp\left(\frac{C_4}{T}\right) \quad (21)$$

Parameter: C_1 C_2 C_3 C_4

TYP: SPEC1MCM (modified SPEC1 for MCM)

$$5 \quad k = K_1 \cdot \left(1 + \frac{[M]K_2}{K_3 \cdot 300/T}\right) \quad (22)$$

Parameter: K_1 K_2 K_3

TYP: SPEC2MCM (modified SPEC2 for MCM)

$$k = K_1 \cdot \left(\frac{T}{300}\right)^{-K_2} \cdot \exp\left(\frac{K_3}{T}\right) \quad (23)$$

Parameter: K_1 K_2 K_3

TYP: SPEC3MCM (modified SPEC3 for MCM)

$$k = K_1 \cdot \left(1 + \frac{[M]}{K_2}\right) \quad (24)$$

Parameter: K_1 K_2

TYP: SPEC4MCM (modified SPEC4 for MCM)

$$k = K_1 \cdot \left(1 + K_2 \cdot \exp\left(\frac{K_3}{T}\right) \cdot [H_2O]\right) \cdot \exp\left(\frac{K_4}{T}\right) \quad (25)$$

Parameter: K_1 K_2 K_3 K_4

TYP: SPEC5MCM

$$\begin{aligned} k_1 &= [M] \cdot K_1 \cdot 0.21 \cdot \exp\left(\frac{K_2}{T}\right) \\ k_2 &= [M] \cdot K_2 \cdot 0.21 \cdot \exp\left(\frac{K_4}{T}\right) \\ k &= k_1 \cdot (1 - k_2) \end{aligned} \quad (26)$$

Parameter: K_1 K_2 K_3 K_4

TYP: SPEC6MCM

$$\begin{aligned} k_1 &= K_1 \cdot \exp\left(\frac{K_2}{T}\right) \\ k_2 &= K_2 \cdot \exp\left(\frac{K_4}{T}\right) \\ k &= k_1 \cdot (1 - k_2) \end{aligned} \quad (27)$$

Parameter: K_1 K_2 K_3 K_4

TYP: SPEC7MCM

$$\begin{aligned} k_1 &= K_1 \cdot \exp\left(\frac{K_2}{T}\right) \\ k_2 &= K_2 \cdot \exp\left(\frac{K_4}{T}\right) \\ k &= k_1 \cdot \left(K_5 - \frac{K_6}{1+k_2}\right) \end{aligned} \quad (28)$$

Parameter: K_1 K_2 K_3 K_4 K_5 K_6

TYP: SPEC8MCM

$$\begin{aligned} k_1 &= [M] \cdot K_1 \cdot 0.21 \cdot \exp\left(\frac{K_2}{T}\right) \\ k_2 &= [M] \cdot K_2 \cdot 0.21 \cdot \exp\left(\frac{K_4}{T}\right) \\ k &= \frac{k_1}{(1 + k_2) \cdot T} \end{aligned} \quad (29)$$

Parameter: K_1 K_2 K_3 K_4

3.4 Only Aqua Phase (CLASS: AQUA)

TYP: ASPEC1 H^+ times Arrhenius expression in the format

$$k = [H^+] \cdot A \cdot \exp\left(B \cdot \left(\frac{1}{T} - \frac{1}{T_{\text{ref}}}\right)\right) \cdot (1 + 13 \cdot [H^+])^{-1}$$

$$A = a[(\text{cm}^{-3})^{\beta-1} s^{-1}], \quad B = -\Delta H/R [K]$$
(30)

Parameter: A B

Note: $[H^+]$ is the current concentration

TYP: ASPEC2 $(H^+)^B$ times Arrhenius expression in the format

$$k = [H^+]^B \cdot A \cdot \exp\left(C \cdot \left(\frac{1}{T} - \frac{1}{T_{\text{ref}}}\right)\right) \cdot (1 + 13 \cdot [H^+])^{-1}$$

$$A = a[(\text{cm}^{-3})^{\beta-1} s^{-1}], \quad B = b[-], \quad C = -\Delta H/R [K]$$
(31)

Parameter: A B C

Note: $[H^+]$ is the current concentration

TYP: ASPEC3 Arrhenius expression in the format

$$k = A \cdot \exp(-B \cdot \log_{10}([H^+]))$$
(32)

Parameter: A B

Note: $[H^+]$ is the current concentration

5

3.5 Phase Transfer (CLASS: HENRY)

by the resistance model by Schwartz. In the *.sys file only the Henry's Law constant is read, all other values (mass accommodation, gas phase diffusion coefficients and molar mass being necessary for the mass transfer coefficient are defined in the *.dat file).

Parameter: $K_0 = K_H [\text{M atm}^{-1}] \quad E/R = -\Delta H_{\text{sol}}/R [K]$

3.6 Dissociation (CLASS: DISS)

TYP: DTEMP (K_e temperature-dependent, $K_- = \text{constant}$)

$$K_e = K_+/K_- = A \cdot \exp\left(-\frac{B}{T}\right)$$

$$K_- = C$$
(33)

Parameter: A B C

TYP: DTEMP2 (K_e temperature-dependent, $K_- = \text{constant}$)

$$K_e = K_+/K_- = A \cdot \exp\left(-\frac{B}{T}\right)$$

$$K_- = C \cdot \exp\left(-\frac{D}{T}\right)$$
(34)

Parameter: A B C D

TYP: DTEMP3 (K_e temperature-dependent, $K_- = \text{constant}$)

$$K_e = K_+/K_- = A \cdot \exp\left[B \cdot (T_{\text{ref}}/T - 1) + C \cdot \left(1 - T_{\text{ref}}/T + \log_{10}(T_{\text{ref}}/T)\right)\right]$$

$$K_- = D$$
(35)

Parameter: A B C D

TYP: DTEMP4 (K_e temperature-dependent, $K_- = \text{constant}$)

$$K_e = K_+/K_- = A \cdot \exp\left[B \cdot (T/T_{\text{ref}} - 1) + C \cdot \left(1 - T/T_{\text{ref}} + \log_{10}(T/T_{\text{ref}})\right)\right]$$

$$K_- = 1.0$$
(36)

Parameter: A B C D

TYP: DCONST (K_e and $K_- = \text{constant}$)

$$K_e = A$$

$$K_- = B$$
(37)

Parameter: A B

Reaction Type											EqRef.
PHOTABC:	A:	B:	C:								(1)
PHOTAB:	A:	B:									(2)
PHOTMCM:	I:	M:	N:								(3)
CONST:	KO:										(4)
TEMP:	A:	N	E/R:								(5)
TEMP1:	A:	E/R:									(6)
TEMP2:	KO:	E/R:									(7)
TEMP3:	A:	B:									(8)
TEMP4:	A:	B:									(9)
S4H2O:	A:	C1:	C2:	C3:	C4:						(10)
T1H2O:	A:	B:									(11)
TROE:	KO:	N:	KINF:	M:							(12)
TROEF:	KO:	N:	KINF:	M:	F:						(13)
TROEQ:	KO:	N:	KINF:	M:	K1:	B:					(14)
TROEQF:	KO:	N:	KINF:	M:	K1:	B:	F:				(15)
TROEXP:	KO:	B1:	KINF:	B2:							(16)
TROEMCM:	K1:	K2:	K3:	K4:	K5:	K6:	K7:	K8:	K9:	K10:	(17)
SPEC1:	C1:	C2:									(18)
SPEC2:	C1:	C2:									(19)
SPEC3:	K1:	K2:	K3:	K4:	K5:	K6:					(20)
SPEC4:	C1:	C2:	C3:	C:4							(21)
SPEC1MCM:	K1:	K2:	K3:								(22)
SPEC2MCM:	K1:	K2:	K3:								(23)
SPEC3MCM:	K1:	K2:									(24)
SPEC4MCM:	K1:	K2:	K3:	K4:							(25)
SPEC5MCM:	K1:	K2:	K3:	K4:							(26)
SPEC6MCM:	K1:	K2:	K3:	K4:							(27)
SPEC7MCM:	K1:	K2:	K3:	K4:	K5:	K6:					(28)
SPEC8MCM:	K1:	K2:	K3:	K4:							(29)
ASPEC1:	A:	B:									(30)
ASPEC2:	A:	B:	C:								(31)
ASPEC3:	A:	B:									(32)
DTEMP:	A:	B:	C:								(33)
DTEMP2:	A:	B:	C:	D:							(34)
DTEMP3:	A:	B:	C:	D:							(35)
DTEMP4:	A:	B:	C:	D:							(36)
DCONST:	A:	B:									(37)

Table 2. Tabular overview of the parameters notation used for all reaction types.

3.7 Parameter Notation

4 Description of the chemical reaction mechanism for combustion mechanisms (*.sys -File)

The syntax format for combustion mechanisms is the widely used ChemKin format and can be viewed in the ChemKin documentation (Kee et al., 1996, p.40-63). The information about thermodynamic properties are listed in
5 (Kee et al., 1996, p.20-37) and (Kee et al., 1990).

5 Initial Data Input (*.ini-File)

The *.ini file contains all initial data including emissions.

5.1 Head of the *.ini file:

- All characters following an hash symbol "#" or the keyword "COMMENT" will be ignored.
- 10 – At the beginning of the document, the user has to specify the units for the initial data using the keywords UNIT GAS and UNIT AQUA respectively. Default values are 0 for both phases.

```
# =====  
# ===== CHEMIE =====  
15 # ===== Output - Chemical Reaction Data =====  
# =====  
  
# Created: Wed June 14 12:00:00 2006 (AT)  
# Chemical Mechanism: CAPRAM 3.0 (URBAN CASE)  
20  
# ===== Unit options =====  
  
UNIT GAS 0 # Gas phase units ( 0 = molec/cm3, 1 = mol/cm3, 2 = mol/mol_total)  
25 UNIT AQUA 0 # Aqueous phase units ( 0 = mol/l)
```

5.2 Initial and Emission values of gaseous species

1. After the header lines a line follows that specifies the gaseous input: BEGIN_GAS.
END_GAS specifies the end of the gaseous input.
2. Initial values will be set between the keywords: BEGIN_INITIAL and END_INITIAL.

3. – **Atmospheric mechanisms:** Initial values of gaseous species should be given in [molec/cm³] or [mol/cm³] depending on the chosen UNIT. In general for the gas phase part: Be sure that you use here the same units as noted in the upper part (Unit options) and in the reaction system.
 - **Combustion mechanisms:** The simulation of combustion mechanisms only uses gaseous phase species.
- 5 For this case the user should provide mole fractions, such that the sum of all initial values equals one. Also make sure to select the correct UNIT!

4. The syntax rule is: *[name_of_the_species]* blank-space *[value_in_exponential_notation]*

5. Emission values will be set between the keywords: BEGIN_EMISS and END_EMISS.

6. The syntax rule is: *[name_of_the_species]* blank-space *[value_in_exponential_notation]*

```

10 BEGIN_GAS
    BEGIN_INITIAL      #   Initial Concentrations  [ molec/cm^3 ]
        NO2            1.150 e+11
        O3              2.290 e+12
15        HNO3          2.550 e+10
        H2O2            2.550 e+10
        [N2]            1.960 e+19
    END_INITIAL

    BEGIN_EMISS         #   Emissions  [ molec/cm^3/sec ]
        CH2OHCH2OH      2.01 e+5
        HCHO             2.58 e+5
        NH3              3.03 e+6
        NO               1.01 e+7
25        SO2            3.27 e+6
    END_EMISS
END_GAS

```

5.3 Initial values of aqueous species (atmospheric mechanisms only)

1. Initial values of aqueous species are calculated using the liquid water content at time t_0 .
2. The input begins with BEGIN_AQUA and ends with END_AQUA.
3. The user has to specify the mole mass, charge, soluble index and the mass fraction of the corresponding species. The values has to be set between the keywords: BEGIN_AFRAC and END_AFRAC.

4. The declaration of dry particles can be set between the keywords: BEGIN_SPEK and END_SPEK.

5. The first line after BEGIN_SPEK defines the number of aquatic fractions.

Note: The current version of AtCSol does only support one fraction/mode!

6. The following lines contains the dry radius of a particle in [m], the number of particles and the density in [kg/m³] of the i -th fraction. The numbers are separated by blankspace.

```

BEGIN_AQUA
    BEGIN_AFRAC
        #-----
        #  Name      MolMass   Charge   SolubInd      Model
        #              [g/mol]              [g/g]
        #-----
        SO4mm      96.0e+0    -2        1.e0    0.2607873880
        NO3m       62.0e+0    -1        1.e0    0.0248588000
        CLm        35.5e+0    -1        1.e0    0.0192420160
        BRm        79.9e+0    -1        1.e0    0.0006530930
    END_AFRAC

    BEGIN_SPEK
        1          # nModes   ...   number of input modes
        #-----
        #  Dichten:   NaCl = 2160 kg/m3, AmmSulfate = 1770 kg/m3
        #  Radius [m]      Number [# /cm3]      Density [kg/m3]
        #-----
        0.1E-6          1000.0          2160.0E0
    END_SPEK
END_AQUA

```

The calculation of the actual concentration c^A in [molec/cm³] is done by the following equation:

$$c^A = \frac{N \cdot F \cdot \left(\frac{4}{3}\pi r^3\right) \cdot \rho}{m_{mol}} \cdot N_A$$

where m_{mol} is the mole mass, $N_A = 6.02214 \cdot 10^{22}$ [mol⁻¹] is Avogadros-Constant, N the number of particles, F the mass fraction, r the radius and ρ the density.

5.4 Select diagnose species

Next to the initial data, a list of diagnose species has to be specified in the *.ini file. The notation follows the same convention as above:

1. The input begins with BEGIN_DIAG and ends with END_DIAG.
2. The user has to specify one species per line.
3. The output routine generates a new NetCDF file for every run. Older files with the same file name will be overwritten. The user has to set the name of the NetCDF output file in the *.run file, see section 8.

```
10 BEGIN_DIAG
    SO2
    SO4mm
    Hp
    OHm
    CC(C(=O)O)=C
15    aCC(C(=O)O)=C
END_DIAG
```

6 Information about the phase transfer for atmospheric chemistry (*.dat-File)

The *.dat file contains information necessary for the computation of the phase transfer.

20 Information about gas phase species:

1. The input begins with BEGIN_DATAGAS and ends with END_DATAGAS..
2. The user has to specify the mole mass m_{mol} , the mass accommodation coefficient α and the specific gas phase diffusion coefficient D_g .

```
25 BEGIN_DATAGAS
    #-----
    # Name          MolMass  Alpha      Dg
    #              [ g/mol ]
    #-----
30    #
    SO2              64.0     0.11         0.0000128
```

	[O2]	32.0	0.1	0.0000112
	[N2]	28.0	0.0	0.0
	[H2O]	18.0	0.0	0.0
5	END_DATAGAS			

Information about aqua phase species:

1. The input begins with BEGIN_DATAQUA and ends with END_DATAQUA.
2. The user has to specify the mole mass m_{mol} , charge, soluble index, organic index and the activation index.

10	BEGIN_DATAQUA					
	#					
	# Name	MolMass	Charge	SolubInd	OrgIndex	ActIndex
	#	[g/mol]				
	#					
15	aSO2	64.00	0.00	1.00	0.00	0.00
	OHm	17.00	-1.00	1.00	0.00	1.00
	Hp	1.00	1.00	1.00	0.00	1.00
	[H2O]	18.00	0.00	1.00	0.00	0.00
	[aH2O]	18.00	0.00	1.00	0.00	0.00
20	END_DATAQUA					

7 Information about the thermodynamic properties for combustion chemistry (*.dat-File)

The syntax rules for the thermodynamic data base using the ChemKin format is given in (Kee et al., 1996, p.43-45).

8 Specification of simulation parameter (*.run-File)

25 To specify the model run parameters copy one of the example .run files and change the necessary information. The *.run file is organised via Fortran name lists. The first block contains some general information about the run.

- BSP - (character(80)) name of the simulation run
 - WaitBar - (logical) plot a progress bar onto the screen if true
 - ChemKin - (logical) simulate combustion mechanism using ChemKin syntax (only true for combustion mechanisms)
- 30

- **Simulation** - (logical) numerical simulation of a mechanism
- **Reduction** - (logical) experimental reduction procedure (only atmospheric chemistry mechanisms)

```

5  &SCENARIO
    BSP      = 'MCM32+CAPRAM40'
    WaitBar  = .T.
    ChemKin  = .F.
    Simulation = .T.
10 /END

```

The second block contains all the essential information about the paths of the mechanism, initial data and other import.

- **SysFile** - (character(80)) specifies the path to the chemical mechanism
- **DataFile** - (character(80)) contains the path to
 - further information necessary for phase transfer calculations (troposphere)
 - thermodynamic database for computing the polynomial fits to thermodynamic data (combustion)
- **MWFile** - (character(80)) contains molecular weights of species (combustion ONLY)
- **InitFile** - (character(80)) contains the initial values for species concentrations and emission values
- **TargetFile** - (character(80)) is a list of species and species families which is not needed for the simulation
 - itself but necessary for the experimental reduction algorithm

```

25 &FILES
    SysFile  = 'CHEM/MCM32_CAPRAM40_full.sys '
    DataFile = 'DAT/MCM32_CAPRAM40_full.dat '
    InitFile = 'INI/Urban2.ini '
    TargetFile = 'TAR/MCM+CAPRAM_3.ctrl '
    /END

```

The third block contains the simulation time in seconds. **tBegin** = 0.0d0 means that the simulation starts at midnight (crucial for mechanisms with photolytic reactions)

```

&TIMES
    tBegin = 0.0d0
    tEnd   = 172800.0d0

```

/END

The fourth part of the .run file consists of meteorological information.

- pHSet - (logical) concentration for H^+ is calculated based on the initial data of other aquatic species
- 5 – LWCLevelmax and LWCLevelmin - (real) in $[L\ m^{-3}]$ specifies the maximal and minimal liquid water content in the simulation (if $LWCLevelmax < LWCLevelmin \rightarrow$ cloud and non-cloud phases are swapped, see pseudo LWC function)
- dust - (real, $\in [0,1]$) parameter for reducing the intensity of solar radiation, which is usually 1
- idate - (integer) format YYMMDD specifies the simulation date
- 10 – rlat - (real) latitude
- rlon - (real) longitude
- Temperature0 - (real) initial temperature in Kelvin
- Pressure0 - (real) initial pressure of the system (ONLY combustion, pressure for tropospheric mechanisms is always set to 1[atm])

15

&METEO

```
pHSet      = .T.
LWCLevelmax = 2.0d-8
LWCLevelmin = 3.0d-4
20 Dust      = 0.5d0
   idate     = 010621
   rlat      = 45.0d0
   rlon      = 0.0d0
   Temperature0 = 280.0d0
```

20

25

/END

The fifth part contains information for the numerical solver.

- RtolROW - (real) relative tolerance for integration scheme
- AtolGas - (real) absolute tolerance for all gaseous species
- 30 – AtolAqua - (real) absolute tolerance for all aqueous species (ONLY tropospheric systems)
- AtolTemp - (real) absolute tolerance for temperature (ONLY combustion systems)

- **Error_Est** - (integer, $\in \{1, 2\}$) error estimator, 1 = maximum norm, 2 = euclidean like norm
 - **LinAlg** - (character(2), $\in \{\text{cl}, \text{ex}\}$) linear algebra formulation (classic see: ??, extended see: ??)
 - **minStp** and **maxStp** - (real) minimum and maximum step size in seconds for integration scheme
 - **ODEsolver** - (character(80)) path to solver coefficients for Rosenbrock methods, also possible LSODE and LSODES,
- the Rosenbrock methods are stored in the METHODS/ folder and will be included at compile time

&NUMERICS

```

RtolROW  = 1.0d-3
AtolGas  = 1.0d-7
AtolAqua = 1.0d-7
Error_Est = 2
LinAlg   = 'cl'
minStp   = 1.0d-30
maxStp   = 600.d0
ODEsolver = 'METHODS/TSRosWRodas3.ros'

```

/END

The last part contains parameter for the output procedures.

- **NetCdfFile** - (character(80)) path to NetCDF output file, note: older files with same name will be overwritten
- **StpNetCDF** - (real) writing data to NetCDF file every s seconds, if **StpNetCDF** $< 0 \rightarrow$ write every time step
- **StpFlux** - (real) writing reaction rates data to binary file every s seconds, if **StpFlux** $< 0 \rightarrow$ write every time step (ONLY necessary for experimental reduction algorithm)
- **nOutP** - (integer) number of output points (ONLY necessary when LSODE or LSODES was selected)
- **DebugPrint** - (logical) printing additional information of the solver phase
- **MatrixPrint** - (logical) printing all matrices for the simulation run to formatted file (for investigation of sparsity patterns, see: /MATLAB/SparseInput.m)

&OUTPUT

```

NetCdfFile  = 'NetCDF/MCM32+C40_full.nc'
StpNetCDF   = 600.0d0
StpFlux     = -1.0d0
nOutP       = 1000

```

```
DebugPrint = .F.
```

```
MatrixPrint = .F.
```

```
/END
```

5 9 Simulation of combustion systems and atmospheric (multi-phase) chemistry mechanisms

mechanism	Chapman	RACM+CAPRAMv2.4	MCMv3.2+CAPRAMv4.0 α
class	pure gas phase	multiphase (gas, aqua)	multiphase (gas, aqua)
scenario	no emissions	urban	urban
droplets	no cloud	mono-disperse	mono-disperse
T_0	280 [K]	280 [K]	280 [K]
p_0	1 [atm]	1 [atm]	1 [atm]
n_s	7	250	10,196
n_r	10	787	23,098
tolerances	$\text{tol}_r = 10^{-3}$ $\text{tol}_a = 10^{-5}$ (gas)	$\text{tol}_r = 10^{-3}$ $\text{tol}_a = 10^{-5}$ (gas) $\text{tol}_a = 10^{-5}$ (aqua)	$\text{tol}_r = 10^{-3}$ $\text{tol}_a = 10^{-5}$ (gas) $\text{tol}_a = 10^{-5}$ (aqua)
reference	Sandu and Sander (2006)	Stockwell et al. (1997)	Jenkin et al. (2012)

mechanism	ERC <i>n</i> -heptane	LLNL <i>n</i> -heptane	LLNL methy-decanonate
class	gas phase combustion	gas phase combustion	gas phase combustion
environment	constant volume	constant volume	constant volume
T_0	750 [K]	750 [K]	750 [K]
p_0	2 [Bar]	2 [Bar]	2 [Bar]
n_s	29	160	2,878
n_r	104	1,540	16,831
tolerances	$\text{tol}_r = 10^{-10}$ $\text{tol}_a = 10^{-15}$ (gas) $\text{tol}_a = 10^{-1}$ (temp)	$\text{tol}_r = 10^{-10}$ $\text{tol}_a = 10^{-15}$ (gas) $\text{tol}_a = 10^{-1}$ (temp)	$\text{tol}_r = 10^{-10}$ $\text{tol}_a = 10^{-15}$ (gas) $\text{tol}_a = 10^{-1}$ (temp)
initial mixture	[C ₇ H ₁₆] = 15.3846 % [O ₂] = 17.7689 % [N ₂] = 66.8465 %	[C ₇ H ₁₆] = 15.3846 % [O ₂] = 17.7689 % [N ₂] = 66.8465 %	[C ₁₁ H ₂₂ O ₂] = 8.43882 % [O ₂] = 19.2275 % [N ₂] = 72.3337 %
reference	Patel et al. (2004)	Seiser et al. (2000)	Herbinet et al. (2008)

Table 3. Initial condition and scenarios of six different chemical mechanisms.

References

- Herbinet, O., Pitz, W. J., and Westbrook, C. K.: Detailed chemical kinetic oxidation mechanism for a biodiesel surrogate, *Combustion and Flame*, 154, 507 – 528, <https://doi.org/https://doi.org/10.1016/j.combustflame.2008.03.003>, <http://www.sciencedirect.com/science/article/pii/S0010218008000771>, 2008.
- 5 Jenkin, M. E., Wyche, K. P., Evans, C. J., Carr, T., Monks, P. S., Alfara, M. R., Barley, M. H., McFiggans, G. B., Young, J. C., and Rickard, A. R.: Development and chamber evaluation of the MCM v3.2 degradation scheme for β -caryophyllene, *Atmospheric Chemistry and Physics*, 12, 5275–5308, <https://doi.org/10.5194/acp-12-5275-2012>, 2012.
- Kee, R., Rupley, F., and Miller, J.: The Chemkin Thermodynamic Data Base, 87, 1990.
- Kee, R., Rupley, F., Meeks, E., and Miller, J.: CHEMKIN-III: A Fortran Chemical Kinetics Package for the Analysis of Gas
- 10 Phase Chemical and Plasma Kinetics," Sandia National Laboratories Report, 1996.
- Patel, A., Kong, S.-C., and Reitz, R.: Development and validation of a reduced reaction mechanism for HCCI engine simulations, SAE Paper 2004-01-0558, pp. 63–76, 2004.
- Sandu, A. and Sander, R.: Technical note: Simulating chemical systems in Fortran90 and Matlab with the Kinetic PreProcessor KPP-2.1, *Atmospheric Chemistry and Physics*, 6, 187–195, <https://doi.org/10.5194/acp-6-187-2006>, <http://www.atmos-chem-phys-discuss.net/5/8689/2005/{%}5Cnhttp://www.atmos-chem-phys.net/6/187/2006/>, 2006.
- 15 Seiser, R., Pitsch, H., Seshadri, K., Pitz, W., and Gurran, H.: Extinction and autoignition of n-heptane in counterflow configuration, *Proceedings of the Combustion Institute*, 28, 2029 – 2037, [https://doi.org/https://doi.org/10.1016/S0082-0784\(00\)80610-4](https://doi.org/https://doi.org/10.1016/S0082-0784(00)80610-4), <http://www.sciencedirect.com/science/article/pii/S0082078400806104>, 2000.
- Stockwell, W. R., Kirchner, F., Kuhn, M., and Seefeld, S.: A new mechanism for regional atmospheric chemistry modeling,
- 20 *Journal of Geophysical Research*, 102, 25 847, <https://doi.org/10.1029/97JD00849>, 1997.