# MC–ChemDB User's Manual
# v_1.0

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## Contents

# 1   Introduction

MC-ChemDB is a database of reactions rates and photoprocesses cross-sections for the simulation of cold chemical plasmas [1, 2]. The originality of MC-ChemDB is to encode uncertainty on the reaction rate parameters and cross-sections with specific attention to branching ratios. This additional feature makes that MC-ChemDB is not directly readable by simulation codes, but it must be processed to produce *samples* of readable databases (for instance in the KiDA-type format [3], with one line per reaction).

Running a simulation code over a set of these samples is known as *Monte Carlo uncertainty propagation* (MCUP)[4, 5], and enables to quantify the uncertainty on the predictions of chemical models due to the uncertainty on the chemical parameters. It also enables to perform *sensitivity analysis* to identify key reactions in need of better determination [6, 7, 8].

## 1.1   The MC-ChemDB system

MC-ChemDBUI (https://github.com/ppernot/MC-ChemDBUI) enables to edit the MC-ChemDB database and to generate random samples in the ChemDBPublic repertory. These samples are used by the plasma simulator through the reactorui interface (https://github.com/ppernot/ReactorUI) (see Fig 1). Note that ChemDBPublic contains all the chemical reactions encoded in MC-ChemDB. The chemical system under study is specified in reactorui which assembles a consistent subset of reactions and extract the relevant data from ChemDBPublic.
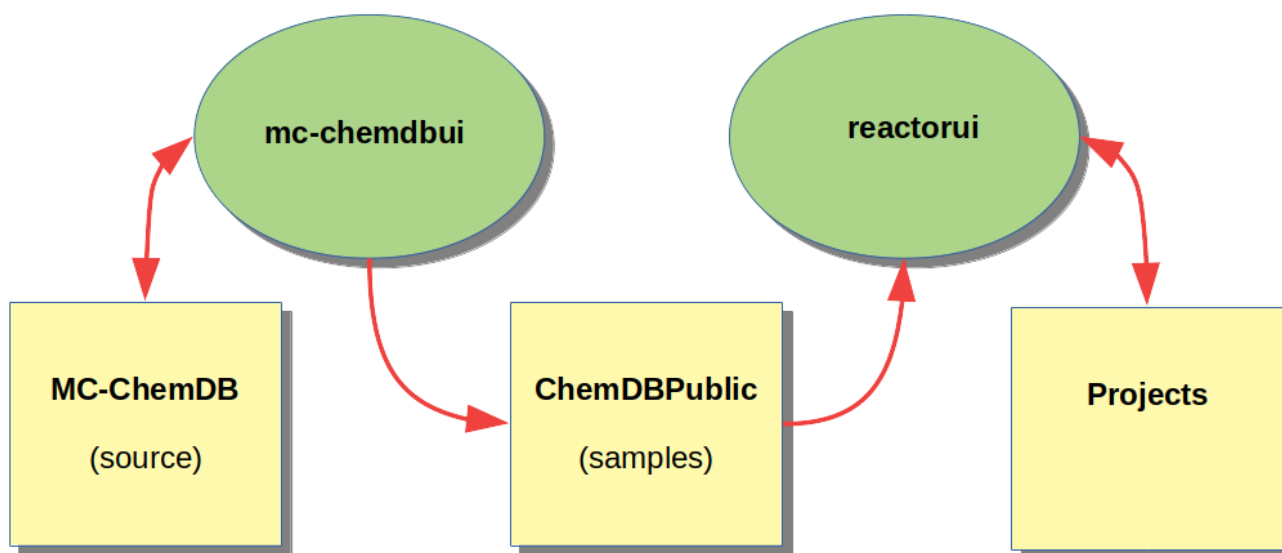


Figure 1: Principle scheme of MC-ChemDB and its articulation with Reactor.

## 1.2   Installation

1. Load the latest release of MC-ChemDB from the GitHub repository https://github.com/ppernot/MC-ChemDB and unpack it.

# 2   The data model

The database consists of three modules: one for the reactions between neutral species, one for the reactions involving ions, and one for the photo-processes (photodissociation and photoionization). This segregation reflects different approaches to describe reaction rates and handle uncertainty.

## 2.1   Rate constants

Following a common practice in atmospheric chemistry, one considers here a representation of a temperature-dependent uncertainty band by a specific function, called hereafter the "$f/g$ representation" [9, 10, 11].

The five parameters necessary to calculate the Kooij expression of a bimolecular rate constant $k(T)$ and its $T$-dependent multiplicative uncertainty $u_k(T)$ are $\{\alpha,\ \beta,\ \gamma,\ f,\ g\}$:

$$
\begin{aligned}
k'(T) &= k(T) \times u_k(T) & (1)\\
k(T) &= \alpha \times (T/T_0)^{\beta} \times \exp\left(-\gamma/T\right) & (2)\\
u_k(T) &= \exp\left(r \times \log\left(f \times \exp(g\left|1/T - 1/T_0\right|)\right)\right) & (3)
\end{aligned}
$$

where $r \sim N(0,1)$ is a standard normal random number, and $T_0$ is a reference temperature, typically 300 K.

With current databases, the user reads the values of $f$ and $g$ and generates random realizations of $u_k(T)$ curves. In the perspective of transferring the random number generation on the database/server side, one can take advantage of the fact that Eq. 3 can be rewritten as

$$
u_k(T) = f^r \times \exp\left(g \times r \left|1/T - 1/T_0\right|\right), \tag{4}
$$

which shows that random realizations of $u_k(T)$ curves can still be parameterized by only two numbers $f' = f^r$ and $g' = g \times r$. Without changing the initial database format, one can thus replace the nominal values in the database by random values

$$
\{\alpha,\ \beta,\ \gamma,\ f,\ g\} \longrightarrow \{\alpha,\ \beta,\ \gamma,\ f' = f^r,\ g' = g \times r\}. \tag{5}
$$

In order to benefit from this solution, the end user has only to adapt the rate expression in his code to include the $f' \times exp(g'\left|1/T - 1/T_0\right|)$ term.

### 2.1.1   Reaction rate expressions.

The temperature- and density-dependence of reactions rates between neutrals and ions are described by different rate laws. The dependence on temperature ($T$ in Kelvin) is typically expressed by the following laws, depending globally on three parameters ($\alpha, \beta, \gamma$):

`kooij`     $\alpha \times (T/T_0)^{\beta} \times exp(-\gamma/T) \equiv k(\alpha,\beta,\gamma,T_0)$

`dr`        $\alpha \times (T_0/T)^{\beta} = k(\alpha,-\beta,0,T_0)$

`ionpol1`     $\alpha \times (0.62 + 0.4767 \times \beta \times (T_0/T)^{0.5})$

`ionpol2`     $\alpha \times (1 + 0.0967 \times \beta \times (T_0/T)^{0.5} + \beta^2 \times T_0/(10.526 \times T))$

The density-dependence ($M$ in cm$^{-3}$) for reactions between neutral species is expressed as a combination of two or three `kooij`-type reactions for the high-density limit ($k_\infty$ in cm$^3.s^{-1}$), the low-density limit ($k_0$ in cm$^6.s^{-1}$), and the recombination rate ($k_R$ in cm$^3.s^{-1}$). This is globally parameterized by 10 values ($\alpha_{i=1,3}$, $\beta_{i=1,3}$, $\gamma_{i=1,3}$, $F_c$):

`3-body`       the Troe formula[3]

$k_\infty \times (R/(1+R)) \times F_c^{1/E}$

$R = k_0 \times M/k_\infty$

$E = 1 + ((\log_{10}(R) + C)/(N - 0.14 \times (\log_{10}(R) + C)))^2$

$C = -0.4 - 0.67 \times \log_{10} F_c$

$N = 0.75 - 1.27 \times \log_{10} F_c$

with $F_c = 0.64$, $k_0 = k(\alpha_1, \beta_1, \gamma_1, 300)$ and $k_\infty = k(\alpha_2, \beta_2, \gamma_2, 300)$

`assocVV`     a modified Troe formula for pressure-dependent association reactions[12]

$k_r + F_c^{1/E} \times (k_\infty - k_r) \times k_0 \times M/((k_\infty - k_r) + k_0 \times M)$

with $E$ defined above, $k_\infty = k(\alpha_1, \beta_1, \gamma_1, 1)$, $k_0 = k(\alpha_2, \beta_2, \gamma_2, 1)$ and $k_r = k(\alpha_3, \beta_3, \gamma_3, 1)$. Note the different parameterization of the Kooij formula ($T_0 = 1$) and the inverse order for parameters of $k_\infty$ and $k_0$.

`assocMD`     another expression for pressure-dependent association reactions,[13, 14] using also a simplified broadening factor

$k_\infty \times (k_0 \times M \times F_c^{1/E'} + k_r)/(k_0 \times M + k_\infty)$

$E' = 1 + (\log_{10}(R)/N)^2$

with $R$, $N$ as above, $k_0 = k(\alpha_1, \beta_1, \gamma_1, 300)$, $k_\infty = k(\alpha_2, \beta_2, \gamma_2, 300)$ and $k_r = k(\alpha_3, \beta_3, \gamma_3, 300)$

## 2.2   Branching ratios

When branching ratios (BR) have been measured instead of *partial* rate constants (which is the case for ion-neutral reactions or dissociative recombination of ions), one has to use a specific representation separating the global rate constant from the BRs.

Random values of the BRs, $b_i$, are sampled from probabilistic trees built from Dirichlet-type distributions [15]. This way, sets of BRs are generated consistently with the sum-to-one constraint ($\sum b_i = 1$), avoiding the spurious *uncertainty leak effect* demonstrated in [16, 6].

To derive a partial rate constant, one has thus to generate random parameters on the database side

$$\{\alpha' = \alpha \times b_i', \beta, \gamma, f', g'\}$$

(for instance), where $b_i'$ is a realization of the BR for the $i^{th}$ pathway. Here again, no change of database format is required. On the user side, the changes are the same as described above, depending on the description of the global rate's uncertainty.

## 2.3   Photo-processes

A special treatment has to be considered for photo-processes which are described by wavelength-dependent properties (cross-sections, branching ratios/quantum yields) [17]. The database has to provide random samples of wavelength-dependent cross-sections and branching ratios as sets of files.

### 2.3.1   Cross-sections

The uncertainty on the cross-section is defined by an uncertainty factor $XS\_F$. Samples of cross-sections are thus obtained by

$$\begin{aligned} \sigma_{MC}(\lambda; M) &= \sigma_0(\lambda; M) \times u_F \\ u_F &\sim LN(1, XS\_F) \end{aligned}$$

where $\sigma_0(\lambda; M)$ is the reference photo-absorption cross-section for species $M$ and $u_F$ is a random number with a log-normal distribution centered on 1 with uncertainty factor $XS\_F$. This scheme assumes only systematic, wavelength-independent, uncertainty.

### 2.3.2   Branching ratios

Probabilistic trees are used to get sum-to-one constrained random branching ratios. For most photodissociations, one does not have extensive information about the individual channel uncertainties, and the main partition is made between ionic channels and neutral channels because they are often issued from different experiments [2]. The proposed uncertainty scheme is therefore identical for all molecules.

A nested probabilistic tree was proposed in Ref. [2], on the basis that the sum of all ionic channels is less uncertain that individual channels. In this hypothesis, the probabilistic tree has two levels:

1. The first one deals with the neutrals/ions separation, with branching rations $b_N$ and $b_I$, respectively:

$$(b_N, b_I) \sim \mathrm{Dirg}\left(b_{N,0} < \mathrm{Neutrals} >, (1 - b_{N,0}) < \mathrm{Ionic} >; r_{NI} b_{N,0}, r_{NI}(1 - b_{N,0})\right)$$

    where one uses a generalized Dirichlet distribution with parameters $b_{N,0} = \sum_{i \in Neutrals} b_i$ and $r_{NI}$. $b_{N,0}$ is the sum of the reference branching ratios of the neutral channels at a given wavelength. $r_{NI}$ is the relative uncertainty on the total charged species measurement of about 3 % on $b_I$ [15, 2].

2. If one has more than one neutral channel, a secondary tree is specified by a generalized Dirichlet distribution with the corresponding branching ratios as parameters (renormalized) and a relative uncertainty $r_N$ of about 20 %. A similar sub-tree is designed for ionic channels ($r_I$).

This representation ensures that the sum of the ionic channels has a small uncertainty, while the branching ratios of individual channels might be more uncertain.

It turns out that this approach might produce strong uncertainty discontinuities along the wavelength, and an alternative one-level model based on partial cross-sections is now implemented.

One assumes that all neutral channels cross-sections are measured within 20 % ($r_N$) and all ionic channels within 10 % ($r_I$). The uncertainty on the branching ratios is derived by linear uncertainty propagation (LUP). Starting from

$$\sigma_T = \sum_i \sigma_i \tag{6}$$

and

$$b_i^0 = \frac{\sigma_i}{\sigma_T} \tag{7}$$

one gets

$$u_i = \sqrt{\frac{1}{\sigma_T^2}u_{\sigma_i}^2 + \left(\frac{\sigma_i}{\sigma_T^2}\right)^2 u_{\sigma_T}^2 - 2\frac{\sigma_i}{\sigma_T^3}u_{\sigma_i}^2} \tag{8}$$

where $u_{\sigma_i} = r_{N/I}\sigma_i$ is the uncertainty on the $\sigma_i$ cross-section (Neutral or Ionic), and $u_{\sigma_T} = \sqrt{\sum_i u_{\sigma_i}^2}$ is the uncertainty on their sum. The third term in the LUP expression results from the covariance between $\sigma_i$ and $\sigma_T$: $cov(\sigma_i, \sigma_T) = cov(\sigma_i, \sigma_i) = u_{\sigma_i}^2$, assuming independent measurement errors for all cross-sections.

One can then use a one-level generalized Dirichlet distribution based on the estimated uncertainties

$$(b_1, \ldots, b_n) \sim Dirg(b_1^0, \ldots, b_n^0; u_1, \ldots, u_n) \tag{9}$$

The sampling is done independently for each wavelength, leading to purely random errors. Several options are tested in Chem-DBUI to introduce some level of serial correlation.

# 3   The database

There is presently a discrepancy on the uncertainty representations of reaction rates for reactions involving neutrals and the ones involving ions. The sum-to-one of branching ratios has been extensively implemented in ionic reactions by Pernot and coworkers [4, 16, 15]. This has not yet been done for neutrals [18, 19]. Moreover, a special treatment has to be considered for photo-processes which are described by wavelength-dependent properties (cross-sections, branching ratios) [17].

The database consists therefore of three independent sections (Photoprocesses, Neutrals and Ions).

## 3.1   Photo-processes

The `PhoroProcs` database contains a repertory for each version (e.g., `v_1.3`), in which one finds all the necessary data files for the cross-sections and branching ratios (repertory `Data`) and the `photoDB.csv` file which makes the link between the partial processes and the associated data files. It contains the following fields (one line per channel):

`R1, R2`      the reactants (`R2 = HV`)

`P1, P2, P3, P4` the products

`CHANNEL`     the *index* of the channel for the current reaction

`XS_SOURCE` source for the cross-section (`typically either Leiden, SWRI or Hebrard`)

`XS_F`        uncertainty factor for the cross-section. The default value of `XS_F` depends on the data
              source: the `Leiden` database contains generally an estimate of `XS_F`; but for the `SWRI`
              or `Hebrard` cross-sections, a default value of 1.2 is used. These default values can be
              superseded by specifying a different `XS_F` value.

`BR_SOURCE` source for the wavelength-dependent branching ratios (typically `SWRI`, or `Plessis` for
              CH4)

`REFS`        semi-column-separated *bitex* keys of bibliographical references appearing in the `Doc/refsDR.bib`
              file. Considered only if "`CHANNEL = 1`"

`COMMENTS`  any useful information about the reaction. Considered only if "`CHANNEL = 1`"

`TIMESTAMP` the date and time of creation/modification of this line (format: `YYYY-MM-DD HH:MM:SS`)


## 3.2   Neutral reactions

The `Neutrals` database contains a repertory for each version (e.g., `v_1.4`), in which one finds
the `neutralsDB.csv` file. The actual format derives from M. Dobrijevic's implementation [14] for
neutral association reactions, with a few extra fields:

`R1, R2, R3` one reactant per field

`P1, P2, P3, P4, P5` one product per field (P5 is not used)

`TYPE`        reaction type (`kooij`, `assocMD` or `assocVV`)

`A1, B1, C1, F1, G1` parameters of a `kooij` rate $k(A1, B1, C1)$ and corresponding uncertainty
              factors for the $f/g$ model. See Sect. 2.1.1 for reaction-type-dependent definition ($k_0$ or
              $k_\infty$).

`A2, B2, C2, F2, G2` parameters of a `kooij` rate $k(A2, B2, C2)$ and corresponding uncertainty
              factors for the $f/g$ model. See Sect. 2.1.1 for reaction-type-dependent definition ($k_\infty$
              or $k_0$).

`A3, B3, C3, F3, G3` parameters of a `kooij` rate $k(A3, B3, C3)$ and corresponding uncertainty
              factors for the $f/g$ model. Defines $k_R$ in association reactions model (Sect. 2.1.1).

`FC`          broadening factor $F_c$

REFS         comma-separated *bibtex* keys of bibliographic references appearing in the `Doc/refsDR.bib` file

COMMENTS   any useful information on the reaction

TIMESTAMP the date and time of creation/modification of this reaction (format:  YYYY-MM-DD HH:MM:SS)

## 3.3   Ion reactions

The `IOns` database contains a repertory for each version (e.g., `v_1.4`). One describes separately the $T$-dependence of the global rate constant (kooij, dr or ionpol1/2), and the set of branching ratios (BR) which are assumed to be $T$-independent.[1] The database is stored in a `ionsDB.csv` file, in which one has one line per *global* reaction (meaning that each line might describe several partial reactions or channels) with 14 fields:

REACTANTS the reactants in 'A + B' form

The global reaction rate is defined by four main fields:

TYPE         the reaction type, either `kooij`, `dr`, `ionpol1` or `ionpol2`. See Sect. 2.1.1 for definitions.

ALPHA, BETA, GAMMA the probability density functions of the (independent) rate parameters, *i.e.* $p(\alpha, \beta, \gamma) = p(\alpha)p(\beta)p(\gamma)$. For the available distributions, see Table 1.

the next two fields encode the probabilistic tree describing the uncertain BRs

NBR          the number of channels. It is mostly used to ensure that the STRINGBR distribution is properly formatted and interpreted.

STRINGBR   is a string that encodes a probabilistic tree used to generate random samples of the BRs. To learn to build a probabilistic tree, see the article by Plessis *et al.* [5] and examples below. For the available distributions, see Table 2. Note that the syntax is slightly different from the mathematical notations of the article as it interleaves the identity of the products for each channel.

the four following fields contain the bibliographic references for the previous data

REF_ALPHA, REF_BETA, REF_GAMMA, REF_BR should contain semicolumn-separated *bibtex* keys appearing in the `Doc/refsDR.bib` file.

finally, the two last fields are

COMMENTS   any useful information on the reaction

TIMESTAMP the date and time of creation/modification of this reaction (format:  YYYY-MM-DD HH:MM:SS)

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[1]At the moment, there is practically no information on $T$-dependence of BRs, and no provision has been made in the database for this opportunity. The database contains thus only information to generate $T$-independent BRs.

| pdfNames | Note |
|---|---|
| `Delta`$(x_0)$ | fixed value $x_0$, no uncertainty |
| `Unif`$(x_{min}, x_{max})$ | uniform distribution over an interval |
| `Logu`$(x_{min}, x_{max})$ | log-uniform distribution over an interval |
| `Norm`$(x_0, u_x)$ | normal distribution, mean $x_0$, stdev $u_x$ |
| `Logn`$(x_0, f_x)$ | log-normal distribution, mean $x_0$, uncertainty factor $f_x$ |
| `Nort`$(x_0, u_x, x_{min}, x_{max})$ | truncated normal distribution |

Table 1: Available distributions for rate constant parameters used in the `ALPHA`, `BETA`, and `GAMMA` fields of the `ionsDB` database.

| pdfNamesBR | Note |
|---|---|
| `Diri`$(b_1, \ldots, b_N; \Gamma)$ | Dirichlet distribution with mean $b_1, \ldots, b_N$ and precision $\Gamma$. The uniform distribution is encoded as `Diri`$(1, \ldots, 1; 1)$. |
| `Dirg`$(b_1, \ldots, b_N; u_{b_1}, \ldots, u_{b_N})$ | Generalized Dirichlet distribution with mean $b_i$ and stdev $u_{b_i}$ |
| `Dior`$(k_1, \ldots, k_N)$ | Ordered uniform Dirichlet distribution respecting the order of $k_1, \ldots, k_N$ (integers). |
| `Diut`$(b_1^-, \ldots, b_N^-; b_1^+, \ldots, b_N^+)$ | Intervals-constrained Dirichlet distribution, with each component $i$ within $\left[ b_i^-, b_i^+ \right]$. |
| `Mlgn`$(b_1, \ldots, b_N; f_{b_1}, \ldots, f_{b_N})$ | Uncorrelated multivariate lognormal distribution, with mean $b_i$, uncert. factor $f_{b_i}$ |

Table 2: Available distributions for branching ratios used in the `STRINGBR` field of the `ionsDB` database.

### 3.3.1   `STRINGBR` examples

Products are encoded between brackets as terminal leaves of the tree.

`ArH+ + C2H4` there are two channels with measured BRs ($0.73 \pm 0.05$ for `C2H3+ + Ar + H2` and $0.27 \pm 0.05$ for `C2H5+ + Ar`). This is encoded via a generalized Dirichlet distribution:

```
Dirg(
    0.73<C2H3+ + Ar + H2>,
    0.27<C2H5+ + Ar>;
0.05,0.05)
```

which is compacted to

``"Dirg(0.73<C2H3+ + Ar + H2>,0.27<C2H5+ + Ar>;0.05,0.05)"``

`C2H2+ + E` a more involved case with several levels of information. One has five primary channels with measured BRs, and a secondary splitting for CH2 between singlet and triplet with no preferred value (uniform Dirichlet)

```
Dirg(
    0.5<C2H + H>,
    0.3<1C2 + H + H>,
    0.02<1C2 + H2>,
    0.05*Diri(
        1<1CH2 + C>,
        1<3CH2 + C>;
    1),
    0.13<CH + CH>;
0.06,0.05,0.03,0.01,0.01)
```

compacted to

`"Dirg(0.5<C2H + H>,0.3<1C2 + H + H>,0.02<1C2 + H2>,0.05*Diri(1<1CH2 + C>,1<3CH2 + C>;1),0.13<CH + CH>;0.06,0.05,0.03,0.01,0.01)"`

`C2H3+ + N4S` in this case, one has only limits for the BRs of two channels (e.g. $> 0.9$ for the first one, or $< 0.1$ for the second one). This is expressed by

```
Diut(
    0.9<CHCN+ + H2>,
    0.0<CHCNH+ + H>;
1.0,0.1)
```

or in compact form

`"Diut(0.9<CHCN+ + H2>,0.0<CHCNH+ + H>;1.0,0.1)"`

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