SPACK 1.0
Simplified Preprocessor for Atmospheric Chemical Kinetics

User's guide

CEREA – ENPC
January 2003
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Chapter 1

Introduction

SPACK is a chemical preprocessor. SPACK is written in FORTRAN77. Given a set of chemical reactions, SPACK writes FORTRAN routines to be used in chemistry-transport models.

This version of SPACK only deals with gas-phase chemistry.

1.1 Software structure and execution

SPACK has the following directories:

- code: the different subroutines.

  In order to run SPACK, type: make. SPACK is then generated in application.

- mechanism: the different chemical mechanisms that are currently available, that is RACM, RADM, MOCA, OZONE16 (a toy model) and CBM4 (a simplified version of CBM IV).

- application: the directory for running SPACK. Choose a chemical mechanism and the related set of chemical species (see next section). This has to specified in the file inSPACK. Then type: SPACK>result and the required subroutines are generated (see next section). Some comments can be found in result (whatever the name is): check WARNING and ERROR (the execution stop if an error occurs)

- usersguide: the files for this user's guide.

1.2 Inputs/outputs

1.2.1 Inputs

Two files are to be given as inputs for SPACK:

- The first file gives the names of chemical species to be used: let say ciMECHANISM (e.g. ciMoCA, ciRADM, ciRACM)).

- The second one details the chemical mechanisms: let say MECHANISM (e.g. MOCA, RADM, RACM).

The names of these 2 files are to be specified in the master file inSPACK (this is the only file for which the name has to be kept).

1.2.2 Outputs

- a file `kinetic.f`:

  This routines computes the kinetic rates for the chemical mechanism.

  The format is `SUBROUTINE kinetic(rk,temp,xlw,Press,azi,att,photk,coefphotk)` with:

  - **inputs:**

    `TEMP`: temperature (Kelvin).
    `XLW`: water massic fraction.
    `PRESS`: pressure (Pascal).
    `AZI`: zenithal angle (degree).
    `ATT`: cloud attenuation factor.
    `PHOTK, COEFPHOTK`: photolysis coefficients computed e.g. by `FASTJ`.

  - **outputs:**

    `RK(NR)`: kinetic rates for the `NR` reactions.

- a file `fexchem.f`:

  This routine computes the chemical production rates.

  The format is `SUBROUTINE fexchem(y,rk,ZCsourc,chem)` with:

  - **inputs:**

    `Y(NESP)`: concentrations of the `NESP` species.
    `RK(NR)`: kinetic rates for the `NR` chemical reactions.
    `ZCSOURC(NESP)`: volumic source terms for the `NESP` species.

  - **outputs:**

    `CHEM(NESP)`: chemical production rates for the `NESP` species.

- a file `jacdchemdc.f`.

  This routine computes the Jacobian matrix associated to chemistry.

  The format is `SUBROUTINE jacdchemdc(y,rk,JacC)` with:

  - **inputs:**

    `Y(NESP)`): concentrations of the `NESP` species.
    `RK(NR)`: kinetic rates for the `NR` chemical reactions.

  - **outputs:**

    `JACC(NESP,NESP)`: Jacobian matrix.

1.3 Description of the chemical mechanism MECHANISM

1.3.1 Commented lines

All lines starting with `%` or `!` are not read by `SPACK`.

1.3.2 Standart format for stoichiometry

SPACK needs chemical reactions to be written in a standarized format, as now explained. Examples are given in RACM ([1]), MOCA ([2]), RADM ([3] and CBM4 ([4]). Note that the names of all chemical species used need to be defined in a separate file (see next point).

A chemical reaction of the form $X_1 + X_2 \rightarrow X_3 + X_4$, where X_i are chemical species, should be written as:

```
X1+ X2 > X3 + X4
KINETIC KEYWORD
```

where KEYWORD speficies the kind of chemical reaction (e.g. photolytic) and the constants required to compute the rate coefficient of the reactions.

The word KINETIC may be replaced by KIN. > may be replaced by ->.

1.3.3 Keywords for set-up

Set-up commands are:

- The definition of units by `SET UNIT GAS X` with X is either MOLCM3 or PPB.
- The definition of tabulated zenithal angles for photolysis through:

  `SET TABULATION N DEGREES T1 T2 ... TN`

  where N is the number of tabulated angles and T_i is the value (in degrees) for the i-th angle. Notice that the sequence has to be strictly monotonic (increasing or decreasing).

1.3.4 Keywords for kinetic rates

Different keywords may be used. For each of the keyword recognized by SPACK, this paragraph details how many constants Ci are required to compute the rate coefficient k of the corresponding reaction.

- Arrhenius' law with one constant:

  `KINETIC ARR1 C1`

  This computes: $k = C_1$.

- Arrhenius' law with two constants:

  `KINETIC ARR2 C1 C2`

  This computes: $k = C_1\, exp(-C_2/T)$ where T is the temperature.

- Arrhenius's law with three constants:

  `KINETIC ARR3 C1 C2 C3`

  This computes: $k = C_1\, T^{C_2}\, exp(-C_3/T)$.

- TROE/Fall-off reactions with 4 coefficients:

  `KINETIC TROE4 C1 C2 C3 C4`

  This computes:

  $$k = \frac{k_0\, M}{1 + k_0 * M/k_\infty} 0.6^{\frac{1}{(1+[log10(k_0 * M/k_\infty)]^2)}}$$

  with $k_0 = C_1(T/300)^{-C_2}$ and $k_\infty = C_3\,(T/300)^{-C_4}$.

- TROE/Fall-off reactions with 5 coefficients:

  `KINETIC TROE5 C1 C2 C3 C4 C5`

  This computes:

$$k = \frac{k_0\, M}{1 + k_0 * M/k_\infty} C_5^{\frac{1}{(1+[log10(k_0*M/k_\infty)]^2)}}$$

  with $k_0 = C_1 (T/300)^{-C_2}$ and $k_\infty = C_3\,(T/300)^{-C_4}$.

- TROE/Fall-off reactions with 7 coefficients:

  `KINETIC TROE7 C1 C2 C3 C4 C5 C6 C7`

  This computes:

$$k = \frac{k_0\, M}{1 + k_0 * M/k_\infty} C_7^{\frac{1}{(1+[log10(k_0*M/k_\infty)]^2)}}$$

  with $k_0 = C_1\, exp(-C_2/T)\,(T/300)^{-C_3}$ and $k_\infty = C_4\, exp(-C_5/T)\,(T/300)^{-C_6}$.

- TROE/Fall-off reactions with 10 coefficients (e.g. in MOCA):

  `KINETIC TROE10 C1 C2 C3 C4 ... C10`

- Reactions calculated from equilibria:

  `KINETIC RCFE C1 C2 C3 C4 C5 C6`

  This computes:

$$k = C_5\, exp(-C_6/T) \frac{k_0\, M}{1 + k_0 * M/k_\infty} 0.6^{\frac{1}{(1+[log10(k_0*M/k_\infty)]^2)}}$$

  with $k_0 = C_1 (T/300)^{-C_2}$ and $k_\infty = C_3\,(T/300)^{-b4}$.

- Tabulated photolysis:

  `KINETIC PHOTOLYSIS C1 C2 C3 ... CN`

  The constants C_i are the photolytic constants corresponding to the zenithal angles $T(i)$ as defined by the command `SET TABULATION` (to be used before!).

  There is no photolysis at 90. Interpolation is made with a standard cubic spline (the first and second derivatives are set to 0 at 0 and 90).

- Reactions with variable stoichiometry (e.g. MOCA):

  `KINETIC CVAR C1 C2 ... C7`

  The stoichiometric coefficients of the produced species by the reactions may vary with temperature. Although the stoichiometric coefficients may vary with temperature, the coefficients of all the chemical produced are the same:

  - C_1, C_2, C_3 are the three Arrhenius coefficients of the reaction (as for ARR3).
  - C_4, C_5, C_6, C_7 are the stoichiometric coefficients at temperature 260K, 280K, 300K, 320K respectively.

- Special reaction of "EXTRA" type:

  These reactions are special reactions which require to provide some parameters.

- For the reaction $N_2O_5 \rightarrow 2\,HNO_3$:
  `KINETIC EXTRA0 C1`
- For the reaction $2HO_2 \rightarrow H_2O_2$:
  `KINETIC EXTRA1 C1 C2 C3 C4 C5`
- For the reaction $O_3 \rightarrow 2OH$:
  `KINETIC EXTRA2 C1 ... CN`
  where the constants C_i are the photolytic constants corresponding to the zenithal angles $T(i)$ as defined by the command `SET TABULATION` (to be used before!). An attenuation factor is then applied.

- Special reactions:
  `KINETIC SPEC I`
  The chemical reaction is not described by any of the keyword above. Because the rate coefficient may not be computed similarly to any other reaction, this reaction is treated explicitely in SPACK. The reaction is referenced with the integer . It does not required any constant as input. See next section how to add such a reaction.

  - Case `I=-1`:
    ```
    O3P -> O3
    KINETIC TB O2 SPEC -1
    ```
    This computes:
    $$k = 6.00\,10^{-34}(\frac{T}{300})^{-2.3}O_2\,M$$
  - Case `I=-2`:
    ```
    HO2 + HO2 -> H2O2 + O2
    KINETIC SPEC -2
    ```
    This computes:
    $$k = 2.3\,10^{-13}EXP(600./T) + 1.7\,10^{-33}M\,EXP(1000./T)$$
  - Case `I=-3`:
    ```
    HO2 + HO2 -> H2O2 + H2O + O2
    KINETIC TB H2O SPEC -3
    ```
    This computes:
    $$k = [3.22\,10^{-34}EXP(2800/T) + 2.38\,10^{-54}M\,EXP(3200./T)]H_20$$
  - Case `I=-4`:
    ```
    HO + HNO3 -> NO3 + H2O
    KINETIC SPEC -4
    ```
    This computes:
    $$a = 7.2\,10^{-15}EXP(785/T)\,,\;\; b = 4.1\,10^{-16}EXP(1440/T)\,,\;\; c = 1.9\,10^{-33}EXP(725/T)M$$
    and then $k = a + c/(1 + c/b)$.

- Case I=-5:

  ```
  CO + HO -> HO2 + CO2
  KINETIC SPEC -5
  ```

  This computes:

$$k = 1.5\,10^{-13}(1 + 2.439\,10^{-20}M)$$

- Case I=-6:

  ```
  NO2 + OH -> HNO3
  KINETIC SPEC -6
  ```

  This computes:

$$Rapk = 3.4\,10^{-30}(\frac{300}{T})^{3.2}M \ , \quad Effko = Rapk/(4.77\,10^{-11}(\frac{300}{T})^{1.4})$$

  and then:

$$k = (Rapk/(1. + Effko)) * 0.3^{\frac{1}{1+((dlog10(Effko)-0.12)/1.2)^2}}$$

- Case I=-7:

  ```
  N2O5 -> 2.  HNO3
  KINETIC SPEC -7
  ```

  This computes:

$$k = 2.\,10^{-39}H_20\,H_20$$

- Third body reactions:

  `KINETIC TB NAME KEYWORD`.

  `KEYWORD` may be any of the keywords described above. The name of the third body (`NAME`) may be `M`, `O2`, `N2`, `H2` or `H2O`. The kinetic rate is then multiplied by the concentration of the third body.

1.4 Description of the species ciMECHANISM

See the examples provided in `mechanism`. The number of gas-phase species has to be given and the list of species. The molar masses may (or not) be specified. This is not used in the gas-phase version of `SPACK`.

1.5 How to add a new keyword

To add a new keyword in `SPACK`:

- the subroutine `kinreac` in file `code/cinet.f` needs to be modified in order to define the keyword,
- a new subroutine that details how to compute rate coefficients according to this keyword needs to be added in the file `code/generator.f`.

  For example, such a routine may be written similarly to `WTROE`, if it requires four constants as inputs.

Bibliography

[1] W.R. Stockwell, F. Kirchner, M. Kuhn, and S. Seefeld. A new mechanism for regional atmospheric chemistry modeling. *J.Geophys.res.*, 1997.

[2] B. Aumont. *Modélisation de la chimie de la basse troposphère continentale: développement et tests d'un modèle chimique condensé.* PhD thesis, Université Paris VII, 1994.

[3] W.R. Stockwell, P. Middleton, J. Chang, and X. Tang. The second regional acid deposition model chemical mechanism for regional air quality modeling. *J.of Geophysical Research*, 95(D10):16343–16367, September 1990.

[4] M.W. Gery, G.Z. Whitten, J.K. Killus, and M.C. Dodge. A photochemical kinetics mechanism for urban and regional scale computer modeling. *J. Geophys. Research*, 94(D10):12925–12956, 1989.