Manual of code UBAC

Uncertainty Band of Arrhenius Curves

Code version 1.2 and manual version 1.2

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1. Scope

The program makes uncertainty parameter values of rate coefficients be consistent with the Arrhenius equation. It also provides the convex multi-dimensional uncertainty domain of Arrhenius parameters by defining its boundaries. The theory behind this code has been introduced in articles [1-2].

2. Usage

The code was written in Fortran 90 and is distributed in compiled forms: ubac.x for Linux and ubac.exe for Microsoft Windows operating systems. The input to the code is given in a single text file (name_of_the_input_file), which has to be prepared by the user. The executable code and the input file have to be in the same folder, where the program can be executed with the following commands in a Linux terminal or a Windows command window.

In Linux (case sensitive!):

```
./ubac.x name_of_the_input_file
```

In Windows:

```
ubac.exe name_of_the_input_file
```

If the program is executed without argument *name_of_the_input_file* or directly by clicking on it then file **`data.txt`** is taken as input.

3. Input

The input file contains title lines starting with an asterisk (highlighted lines below) and flag/data lines. The title lines are the same for all inputs and their order is fixed, whereas the flag/data lines are provided by the user for the specific problem and reaction. No empty lines or extra comment lines are allowed. The contents of the title lines are not checked during runtime, therefore they can be modified to include comments for the specific reaction or problem.

Example for file *name_of_the_input_file*

```
* Uncertain Arrhenius parameters [A/An/AE/AnE]
AnE
* Values of Arrhenius parameters of the central Arrhenius curve: A n E/R (omit missing)
1.264E16 -0.56 1350
* if n is uncertain, limits can be provided for n: n_min n_max
-2.56 1.44
* Number of data (1st row),data in rows: temperature-uncertainty pairs
25
300 0.15
400 0.15
500 0.15
600 0.15
700 0.15
800 0.15
900 0.15
1000 0.15
1000 0.3
1100 0.3
1200 0.3
1300 0.3
1400 0.3
1500 0.3
1600 0.3
1700 0.3
1700 0.2
1800 0.2
1900 0.2
2000 0.2
2100 0.2
2200 0.2
2300 0.2
2400 0.2
2500 0.2
```

Content and format of the input file:

Line 1:

```
* Uncertain Arrhenius parameters [A/An/AE/AnE]
```

Line 2:

The user has to provide one of the following string flags (case insensitive): A, An, AE, or AnE based on which Arrhenius parameters are considered uncertain in the extended Arrhenius expression ($k(T)=AT^n\exp(-E/RT)$). Note, it also means that α, αn, $\alpha\varepsilon$ or $\alpha n\varepsilon$ are uncertain, respectively. Accordingly, the number of uncertain parameters (N) can change between 1–3. Covariance matrix of these parameters will be determined.

Note that this set of parameters can be different from the list of Arrhenius parameters which are used for the description of temperature dependence of the reaction ($k=A$; $k(T)=AT^n$; $k(T)=A\exp(-E/RT)$; $k(T)=AT^n\exp(-E/RT)$). It is possible that the recommended rate expression has the form of a simple Arrhenius expression, which is equivalent of an extended Arrhenius expression with a recommended value of 0 for n, still one can provide 'AnE' by assuming that also the temperature exponent (n) has some uncertainty to explain accurately the complicated temperature dependence of the uncertainty of $k(T)$. It is also possible that we investigate the uncertainty of fewer Arrhenius parameters than their number in the Arrhenius expression, as we know one or more parameters with little uncertainty.

Line 3:

```
* Values of Arrhenius parameters of the central Arrhenius curve: A n E/R (omit missing)
```

Line 4:

The user has to provide the mean values of uncertain Arrhenius parameters. The unit of E/R has to be K. The unit of A can be chosen freely without restriction. In paper [1] and in the example A is expressed in units cm, mol, s. As many values have to be provided as the number of uncertain Arrhenius parameters was given in Line 2. If n or E/R is zero for the central Arrhenius curve while n or E appears in the list of uncertain Arrhenius parameters, then the user has to provide zero for these quantities.

Line 5:

```
* if n is uncertain, limits can be provided for n: n_min n_max
```

Line 6:

The range of the temperature exponent parameter n may be constrained by providing the allowed minimum and maximum values. If parameter n is defined as uncertain (see lines 1-2) and these limits are given symmetrically ($n_{max}-n=n-n_{min}$) around the central value of n, then the uncertainty range of the rate coefficient will be symmetric and the uncertainty parameter can be defined unambiguously as the new downward and upward uncertainties of the rate coefficient will be equal at all temperatures.

Line 7:

```
* Number of data (1st row),data in rows: temperature-uncertainty pairs
```

Line 8:

The user has to provide the number of temperature T – uncertainty parameter f pairs (M). If the number of uncertain Arrhenius parameters is N, then at least N data have to be provided for determining Arrhenius equation consistent uncertainty limits.

Line from 8+1 to 8+*M:*

The user has to provide the list of temperature T – uncertainty parameter f pairs (M) one-by-one in rows.

4. Output

The progress of code execution is monitored on the screen. The detailed results are provided in text files. The names of the output files are generated by taking the 'name_of_the_input_file' as prefix in their names and adding suffixes to it, therefore working on several reactions in one folder is possible if their input files are named differently. Files with the same names will be overwritten during program execution. The output files with their description are listed in the order of their creation.

File 1: *name_of_the_input_file*_copy.txt

It repeats the text of the input file after reading and checking its information content. Title lines are repeated as they are, whereas flag and data lines might be formatted differently (*e.g.* different number of decimal places and (de)capitalization of certain characters).

File 2: *name_of_the_input_file*_original_uncertainty_limits.txt

It contains the original uncertainty parameter f values, the central Arrhenius curve, the upper and lower uncertainty limits as a function of temperature.

File 3: *name_of_the_input_file*_extreme_uncertainty_limits.txt

It contains the central Arrhenius curve, the upper and lower extreme uncertainty limits, and the corresponding downward and upward uncertainty parameters at the input temperatures (see input file).

File 4: *name_of_the_input_file*_extreme_Arrhenius_parameter_sets.txt

It contains the sets of Arrhenius parameters ($\ln A$ n E/R if present) of the extreme Arrhenius curves. As many curves may coincide, the list may contain repeated items.

File 5: *name_of_the_input_file*_extreme_Arrhenius_parameter_sets2.txt

It contains the irredundant list of Arrhenius parameters sets (ln*A* *n* *E*/*R* if present) of the extreme Arrhenius curves. It is a subset of the list given in File 4.

File 6: ***name_of_the_input_file***_convex_hull_Arrhenius_parameters.txt

It contains the vertices of the convex hull of the uncertainty domain of Arrhenius parameters (ln*A* *n* *E*/*R* if present). It is a subset of the list in File 5.

File 7: ***name_of_the_input_file***_convex_hull_sides.txt

It contains the sides of the convex hull of the uncertainty domain of Arrhenius parameters. In the case of *AnE* it contains vertices of triangles. In the case of *An* and *AE* it contains the vertices of the segments, defined by their two endpoints. The triangles are given by their 3 vertices, and the 1st vertex is repeated to be able to draw a full triangle when the convex hull is visualized as a line plot in 3D in a data plotting application.

File 8: ***name_of_the_input_file***_convex_hull_Arrhenius_curves.txt

It contains the Arrhenius curves computed from the vertices of the convex hull of the uncertainty domain of Arrhenius parameters.

References

[1] T. Nagy, T. Turányi
Uncertainty of Arrhenius parameters
Int. J. Chem. Kinet. **43**, 359-378 (2011)

[2] T. Nagy, É. Valkó, I. Sedyó, I. Gy. Zsély, M.J. Pilling, T. Turányi
Uncertainty of the rate parameters of several important elementary reactions of the H_2 and syngas combustion systems
Combust. Flame, **162**, 2059-2076 (2015)