# Manual of code JPDAP

# Joint Probability Density of Arrhenius Parameters

Code version 2.1 and manual version 2.1

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## 1. Scope

The program calculates the covariance matrix of the transformed Arrhenius parameters ($\alpha$=ln{A}, $n$, $\varepsilon$=$E$/$R$) from the temperature dependence of the uncertainty of the rate coefficient. It assumes that the temperature dependence of the rate coefficient follows the Arrhenius equation and the uncertainty parameter $f$ has a probabilistic meaning, more specifically it is proportional with the standard deviation of the logarithm of the rate coefficient. The theory behind this code has been introduced in articles [1] and [2]. The original code JPDF (Joint Probability Density Function) published with article [1] was slightly improved and the determination of the covariance matrix based on the maximization of the integral of the square of the uncertainty function is omitted. The numerical algorithm used in the codes JPDF and JPDAP for the efficient determination of the covariance matrix by unconstrained fitting is discussed in article [3]. Article [3] proposes a further application of this code: the covariance matrix of the transformed Arrhenius parameters can be used for the efficient storage of the temperature dependence of uncertainty of the rate coefficient even if it does not have a probabilistic meaning.

## 2. Usage

The code was written in Fortran 90 and is distributed in compiled forms: jpdap.x for Linux and jpdap.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!):

```
./jpdap.x name_of_the_input_file
```

In Windows:

```
jpdap.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 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
* Uncertainty type [3slog10k/2slog10k/1slog10k/1slnk/2slnk/3slnk]
3slog10k
* Number of data (1st row),data in rows: temperature-uncertainty pairs
18
 298    0.28
 400    0.20
 500    0.21
 600    0.23
 700    0.25
 800    0.28
 900    0.29
1000    0.3
1100    0.32
1200    0.36
1300    0.39
1400    0.42
1500    0.45
1600    0.48
1700    0.51
1800    0.54
1900    0.56
2000    0.59
* Test sets: number of sets (1st row),sets in rows [sa,sn,se,ran,rae,rne, omit missing]
1
5.01757 0.685287 389.858 -0.998686 0.997497 -0.992562
```

**Content and format of the input file:**

<u>Line 1:</u>

```
* 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 $\alpha$, $\alpha n$, $\alpha\varepsilon$ 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:

```
* Uncertainty type [3slog10k/2slog10k/1slog10k/1slnk/2slnk/3slnk]
```

Line 4:

The user has to provide one of the following string flags (case insensitive): 3slog10k, 2slog10k, 1slog10k, 1slnk, 2slnk, 3slnk. It determines whether the uncertainties (see Lines 6+1 – 6+$M$) correspond to the 1, 2, or 3 multiple of the standard deviation of the natural logarithm (ln) or the decimal logarithm ($\log_{10}$) of the rate coefficient $k$.

Line 5:

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

Line 6:

The user has to provide the number of temperature-uncertainty pairs ($M$). If the number of uncertain parameters is $N$, then at least $N\cdot(N-1)/2$ data have to be provided for the unambiguous determination of the covariance matrix. If this condition is not fulfilled, the program stops with error.

Line from 6+1 to 6+$M$:

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

Line 6+$M$+1:

```
* Test sets: number of sets (1st row),sets in rows [sa,sn,se,ran,rae,rne, omit missing]
```

Line from 6+$M$+2

The user have to provide the number of test sets of standard deviations and correlations of transformed Arrhenius parameters for which the program will reconstruct the covariance matrix of the transformed Arrhenius parameters and evaluate the temperature dependence of the uncertainty at the input temperatures. The user optionally can provide any non-negative integer $L$. If $L$=0 then no trial sets will be investigated and no further input is expected by the program.

Line from 6+$M$+2+1 to 6+$M$+2+$L$

The list of $L$ trial sets of standard deviations and correlations of the transformed Arrhenius parameters has to be provided (one set per line). Depending on the list of uncertain Arrhenius parameters, the program expects certain number of values in certain order.

1 value is expected for A: $\sigma_\alpha$

3 values are expected for An: $\sigma_\alpha$ $\sigma_n$ $r_{\alpha n}$

3 values are expected for AE: $\sigma_\alpha$ $\sigma_\varepsilon$ $r_{\alpha\varepsilon}$

6 values are expected for AnE: $\sigma_\alpha$ $\sigma_n$ $\sigma_\varepsilon$ $r_{\alpha n}$ $r_{\alpha\varepsilon}$ $r_{n\varepsilon}$

## 4. Output

The progress of the fitting procedure 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). The standard deviations and correlations of the newly determined covariance matrices are added to the end of this file.

**File 2: *name_of_the_input_file*_fit_minRMSD.txt**

The output file contains the optimized statistical quantities obtained by the minimization of the root-mean-square-deviation (RMSD) between the simulated uncertainty and the input data by using global optimization Fortran IMSL-routine ZXMWD [4]. Once this optimization is finished, it is refined with a Nelder-Mead simplex optimization algorithm [5] and the content of the file is updated. It has the same format as the input file: title lines start with asterisk (highlighted lines) which are followed by flag/data lines.

**Example for file *name_of_the_input_file*_fit_minRMSD.txt**

```
* Uncertain Arrhenius parameters [A/An/AE/AnE]
AnE
* Uncertainty type [3slog10k/2slog10k/1slog10k/1slnk/2slnk/3slnk]
3slog10k
* Covariance matrix [(a,n,e)x(a,n,e)], where a=lnA, e=E/R
  25.1760234765781      -3.43396079909944       1951.24334939671
 -3.43396079909944      0.469618802700424      -265.177703978430
  1951.24334939671      -265.177703978430       151989.276656553
* Standard deviations(sa,sn,se), where a=lnA, e=E/R
  5.01757147199500      0.685287386941000       389.858021152000
* Correlations (ran,rae,rne), where a=lnA, e=E/R
-0.998686150339800      0.997496531715700     -0.992562340812100
* Root mean square error of slnk values
 0.421777636008221E-02
* Number of input data
 18
* T_K   Input_uncertainty       Input_sigma_lnk        Simulated_sigma_lnk     Simulated_uncertainty
  298.0  0.280000000000000       0.214907942012778       0.215222156132795       0.280409384375379
  400.0  0.200000000000000       0.153505672866270       0.151839395133468       0.197829034325978
  500.0  0.210000000000000       0.161180956509583       0.163651969070060       0.213219441359187
  600.0  0.230000000000000       0.176531523796210       0.178898966383185       0.233084501755237
  700.0  0.250000000000000       0.191882091082837       0.191874552073243       0.249990177549203
  800.0  0.280000000000000       0.214907942012778       0.204930685685390       0.267000797897444
  900.0  0.290000000000000       0.222583225656091       0.219695923249828       0.286238181492122
 1000.0  0.300000000000000       0.230258509299405       0.236662485495120       0.308343634572117
 1100.0  0.320000000000000       0.245609076586032       0.255659536855628       0.333094578307020
 1200.0  0.360000000000000       0.276310211159286       0.276250973109957       0.359922819726174
 1300.0  0.390000000000000       0.299336062089226       0.297960041186495       0.388207205144882
 1400.0  0.420000000000000       0.322361913019166       0.320366821700495       0.417400628548223
 1500.0  0.450000000000000       0.345387763949107       0.343136026986100       0.447066249186806
 1600.0  0.480000000000000       0.368413614879047       0.366013924180798       0.476873482714427
 1700.0  0.510000000000000       0.391439465808988       0.388814822260132       0.506580395369307
 1800.0  0.540000000000000       0.414465316738928       0.411406155602502       0.536014269597591
 1900.0  0.560000000000000       0.429815884025555       0.433695446966263       0.565054618332037
 2000.0  0.590000000000000       0.452841734955496       0.455619917724149       0.593619648338434
```

The file contains the list of uncertain Arrhenius parameters and the uncertainty type repeated from the input file. Furthermore, it contains the covariance matrix of the transformed Arrhenius parameters, their standard deviations and correlations, the RMSD between the input and simulated standard deviations of ln $k$. In addition, it contains the number of uncertainty data and their list with input temperatures extended with the input (calculated from $f$ input) and simulated standard deviations of ln $k$ values and the simulated uncertainty values at the input temperatures.

**Files 2+1 … 2+*M*:**

***name_of_the_input_file*_sim_001.txt … *name_of_the_input_file*_sim_00M.txt**

These files have exactly the same structure as that of file ***name_of_the_input_file*_fit_–minRMSD.txt**, however here the covariance matrix is determined from the user provided test sets of standard deviations and correlations, and not from a fitting procedure.

**File 2+*M*+1: *name_of_the_input_file*_denseT.txt**

This file contains the simulated uncertainty values obtained from both the fitted covariance matrix and the sets of standard deviations and correlations at 100 temperature points distributed evenly. It can be used for smooth plotting of the simulated uncertainty curves even in cases when the input data are given at sparsely distributed temperatures.

## References


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

[2] T. Nagy, T. Turányi
Determination of the uncertainty domain of the Arrhenius parameters needed for the investigation of combustion kinetic models
*Reliability Engineering and System Safety*, **107**, 29–34 (2012)

[3] 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)

[4] http://www.netlib.org/list/imsl

[5] http://www.nist.gov/pml/div684/grp03/upload/NelderMeadMinimizer.f90