



Thermokinetic analysis using open-source THINKS software

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Dr. Nikita V. Muravyev

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Preface

Kinetic analysis of the real-life processes is a challenging task. It is highly influenced by the design of the experiment, selection of the computational method, and the interpretation of the results including the building of the physicochemical model. Significant amounts of data concerning these topics have been published over the years. Nevertheless, the analysis of modern papers devoted to thermokinetic analysis in different types of materials shows that the critical evaluation of the various aspects of thermokinetics is still challenging.

One of the main ideas of the project is to announce the ready-to-use set of tools for the thermoanalytical data pre- and postprocessing, thermokinetic analysis and thermal stability prediction. This package, called THINKS, comprises the main modern approaches proposed in the literature so far. The set of applications released as the freeware open-source computer code written in R language.¹ This language and the environment to work with it (i.e., RStudio²) are free and open-source, provide advanced mathematical tools and user-friendly graphical interface, and widely used nowadays in various fields of science and business.

All information about THINKS software can be found on the website <http://chemphys.space/thinks>. The original codes (to run offline on the local computer) are available on the project homepage – <https://www.researchgate.net/project/THINKS>. For feedback, leave comments on the homepage or mail to thinks@chemphys.space.

I would like to thank my family for support, Dr. Alla Pivkina motivating and directing me, my friends and colleagues, Konstantin Monogarov and Dr. Vitaly Kiselev for fruitful discussions, Anatoly Bragin and Arina Akulova helped with design, and Prof. Nobuyoshi Koga for the strong motivation of my kinetic research. The financial support from Russian Foundation for Basic Research is acknowledged under grant 16-33-60162 mol_a_dk.

How to run offline:

- (1) Go to <https://cran.r-project.org> and download the latest version of R (base) for your operating system (Windows, Linux, or Mac OS).
- (2) Download the free version of RStudio from <https://www.rstudio.com/products/rstudio/download/>.
- (3) Run RStudio and load the target application: from the main menu in RStudio select "Open project", then choose the file inside the folder with the respective app (e.g., Isoconversional), it has the same name. Once you do this, you will see two tabs with ui.R and server.R appeared.

- (4) If the tabs didn't open, click on it from the "Files" window (see Figure 1), open "ui.R" and "server.R" files.
- (5) At the first running of the application, you will need to install some required packages.³⁻⁸ Follow the recommendations if they appear in the top of the file (see Figure 1).
- (6) If necessary packages from both ui.R (the graphical part of application) and server.R (the part with script) are installed, you can run the app by pressing the "Run App" (see Figure 1).

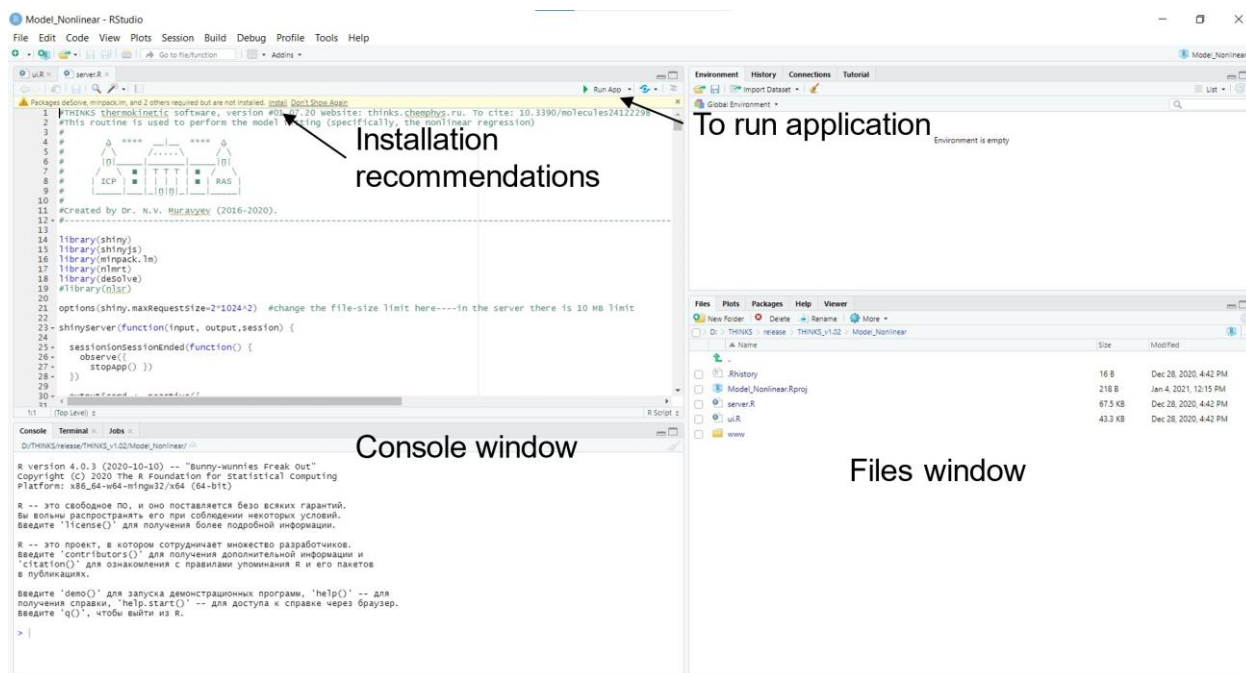


Figure 1.

1. Short Introduction: Thermokinetics and overview of THINKS

What we measure? Contrary to the gaseous homogeneous kinetics, the value of the concentration is not readily available during decomposition of solids. Instead, we measure the changes in some macroscopic parameter, either integral or differential in nature. Accordingly, it is accepted to use the conversion degree parameter, which can be formalized as:⁹

$$\alpha = f(T, t, V, N, S_{sp}, R, P, \dots) , \quad (1)$$

where V is the reaction volume, N – number of nuclei, S_{sp} – specific surface area, R – characteristic geometric size, P – partial pressure of gaseous products. The conversion degree is determined experimentally in the case of integral signal (e.g., thermogravimetric analysis, TGA; thermomanometry; dilatometry) as a ratio of the change in the measured quantity W compared to that in the whole process:

$$\alpha = \frac{W_t - W_0}{W_f - W_0}, \quad (2)$$

where indices 0, t , and f denote the initial, final, and at time t values. Note that in the case of isothermal experiment, the value of W_∞ is used, while in non-isothermal runs the final value is W_f , the difference can be appreciable.¹⁰ Alternatively, for differential signals (differential scanning calorimetry, DSC; differential thermal analysis, DTA; evolved gas analysis, EGA) the measured data is accepted to be proportional to the conversion rate.¹¹ The understanding of the physico-chemical background of the involved experimental signal is required for distinguishing of the true conversion degree of the process¹² and facilitates the kinetics analysis.¹³

Approaching to the kinetic analysis itself, the first step is evidently, the acquisition of thermoanalytical data. Since the experimental data is the base of the further analysis, it has to be reproducible and the main affecting factors have been controlled. These experimental parameters, e.g., sample mass and particle size,¹⁴ partial pressure,¹⁵ composition of gas flow,¹⁶ sample holder type,¹⁷ can be varied to probe the investigated process. It is very important to understand and account the influence of the experimental conditions, to minimize the situations, when the obtained kinetic data is “the characteristics of the experimental conditions rather than of the thermal reaction itself”¹⁸.

What do we need from thermokinetics? Two general goals can be formulated: (i) understanding of the physico-chemical mechanism of the studied process, and (ii) description of the measured signals in terms of temperature/time functions under the conditions of experiments and possible extrapolation outside. Both tasks are highly interconnected (e.g., the insights into the mechanism allow to choose the appropriate reaction model) and must keep in mind when performing the kinetic research.

How can we perform the kinetic analysis? The basic equation of thermokinetics (e.g.,¹⁹) uses the dependence of reaction rate on temperature T (which, in turn, depends on time via a predefined time program) and the conversion degree α :

$$\frac{d\alpha}{dt} = k(T)f(\alpha), \quad (3)$$

where $k(T)$ stands for the rate constant and $f(\alpha)$ corresponds to a kinetic model function. Note, that equation (3) is not a fundamental law, it is just our **assumption** that the temperature and conversion functions can be thus separated (see also discussion about the applicability of this equation to non-isothermal experiments²⁰). The next assumption usually applied is that the rate constant is described by:

$$k(T) = AT^m \exp(-E_a/RT), \quad (4)$$

where the exponent m lies within $[0, 1]$. Usually m is set to 0, leading to well-known Arrhenius equation, that is widely and successfully applied to various solid-state processes.

The determination of the complete **kinetic triplet**, i.e., preexponential factor, activation energy, and the reaction model function, is the goal of thermokinetic analysis since only the combination of these three parameters²¹ allow to perform the kinetic predictions.

What is THINKS? THINKS combines a set of applications for kinetic analysis of thermal data. After critical analysis²² of the proposed in literature methods, several techniques have been selected and implemented in THINKS software differing by its fundamental assumptions, capabilities and merits. The available applications as well as its interconnections are illustrated in Figure 2. In short, the “Purity analysis” and “Import” work with a raw thermal analysis data. The first allows performing the purity determination from DSC data according to standard procedures.²³ “Import” application is used to convert a set of thermoanalytical data from separate experiments into a single kinetic project data. This kinetic project data is a necessary input in the applications performing the kinetic analysis (denoted by blue boxes in Figure 2). “Prediction” (shown in green) aims to use the obtained kinetic parameters for the simulation of reaction profiles under certain temperature-time programs.

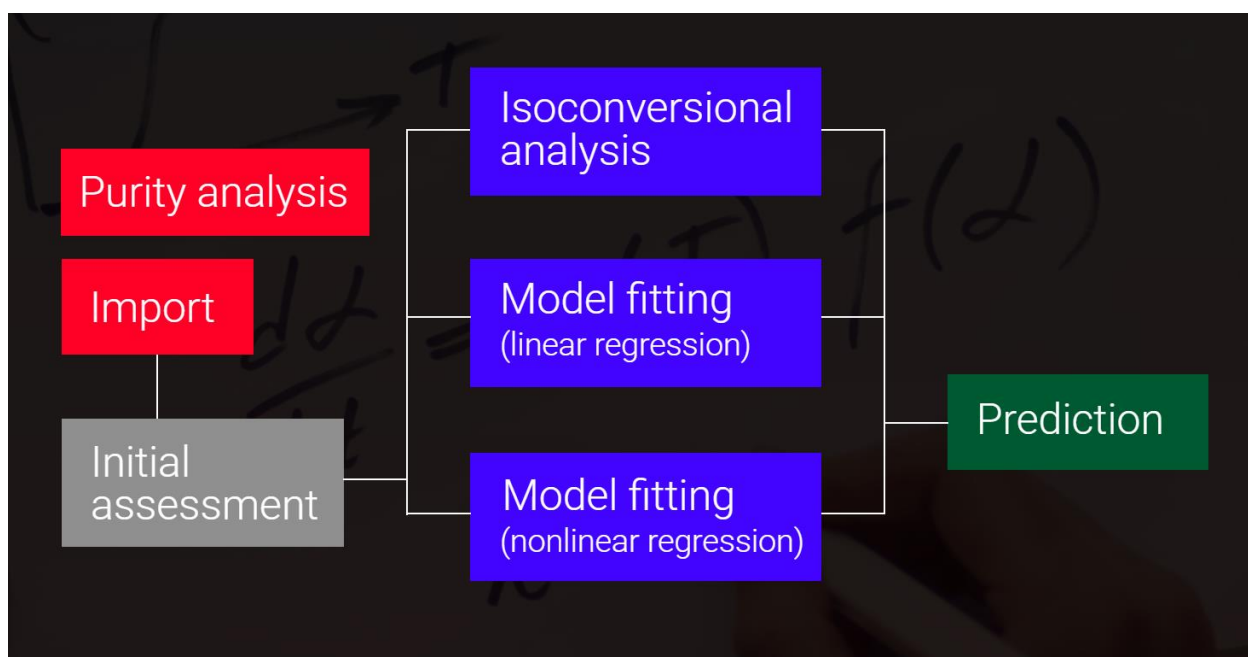


Figure 2. An overview of THINKS set of applications (snapshot from <http://chemphys.space/thinks>). In red boxes the applications for the treatment of the raw thermal analysis data are shown. Gray box discloses the application that is under development. Blue boxes denote the applications for performing the kinetic analysis. Green box represents a postprocessing application for prediction and simulation.

In conclusion of this short introduction, I'd like to cite Sewry and Brown²⁴: “Describing experimental data by some conversion function with an increased number of adjustable parameters is of little value unless these parameters can be given some physical significance”. As the rest of the Manual discusses the details of the kinetic analysis, it always should be kept in mind that performing (art?!) of thermokinetic analysis involves not only finding of the statistically best fit of the experimental data, but the understanding of the mechanism of the process.

2. “Import” application: Creating a kinetic project data

The purpose of this application is to convert the raw thermal analysis data into a series of equal size columns of the form (time, temperature, conversion degree, conversion rate). First, the “File Info” has to be properly set following the file structure (i.e., the length of the header, separator, order of columns, and units of quantities). **If you see the error once uploaded the file, please make sure that there are no blank or non-digit lines at the end of file and all parameters in block 1 (Figure 3) are set correct.** Once the file is selected and everything is ok, the plot with loaded data is shown (under number 2, Figure 3).

Creating the kinetic project

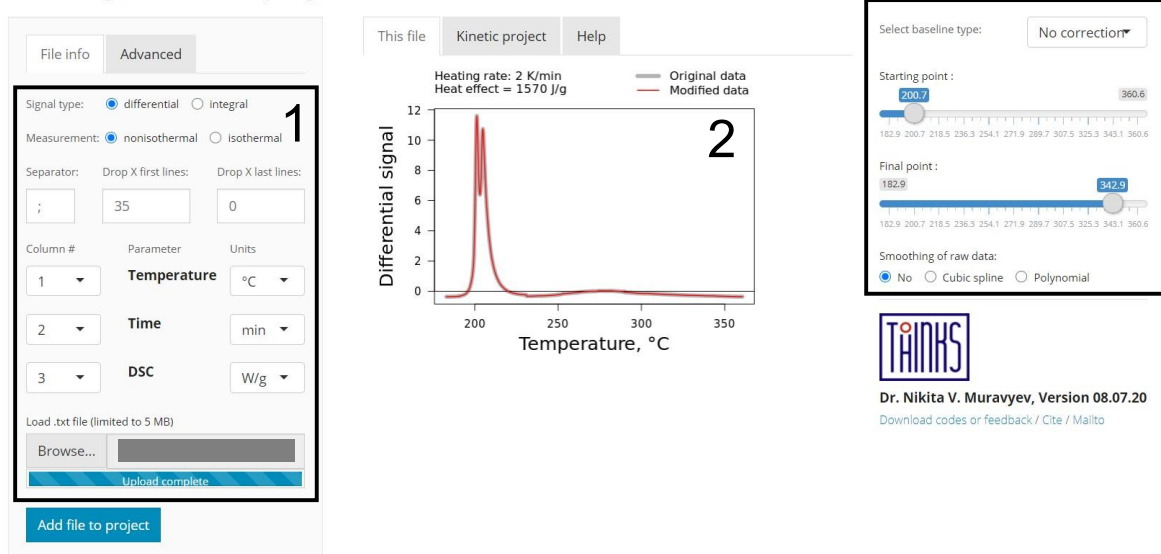


Figure 3.

Check out the loaded data. Above the plot, some information is shown, viz., the heating rate value for nonisothermal runs, the “heat effect” value for the differential type of input signal (more precisely, the area under curve at a selected baseline), the “mass loss” value (more precisely, the change of the input integral data). For the differential data, the options for baseline appear

(under number **3** in Figure 3). For integral data, two sliders appear to define the range where the conversion degree changes.

For the specific case considered here, we are mostly interested in the process with the main exothermic peaks. Therefore, the right portion of the data can be omitted (drop X last lines is set, under number **4**, Figure 4). Then, for the interested event by DSC, the baseline has to be specified (dropdown list **5**). In the current version, the following options are available:

- No correction. Clearly, if no baseline subtraction is needed.
- Linear. The linear fit is performed using the data located on left from the “starting point” (specified with slider **6**, also denoted as a left blue circle in plot **7**) and on the right from the “final point” (specified with the appropriate slider, denoted by the right blue circle in the plot **7**).
- Linear-2. Very specific case, the baseline of three pieces: the left portion is the linear fit of data located on left from the starting point, the central portion – the same linear fit as in “Linear” type above, the right portion – the linear fit of data between the “final point” and the right end.
- Tangential. The tangential baseline has to be applied for a processes with a change of the heat capacity. In THINKS, the routine for tangential baseline is taken from Takos⁸ package. Note that the procedure uses a single definition of the number of points used for the baseline construction for both sides, therefore, the minimal length of data located on left from the “starting point” and on the right from the “final point” is taken and used actually.
- Spline. The spline fit is performed using the data located on left from the “starting point” and on the right from the “final point”.
- Spline-2-center. Very specific type of baseline, useful for broad processes with a return to baseline in some central region. Then, a third adjustable point is available, acting as a “magnet” for the spline fit.

Note, that the linear and tangential baselines have a certain physical background (consult the literature, e.g.,^{25,26}). During the optimization of the baseline, use the plot shown under **7** in Figure 4. It shows a magnified on Y-scale, the original loaded data, the points used for baseline construction, and the baseline. The magnitude of its Y-axis can be tuned with slider **8**. Two types of smoothing are available, with the parameter that controls the degree of smoothing. The red curve in the upper plot **2** shows the data after all modifications (e.g., with a subtracted baseline).

Creating the kinetic project

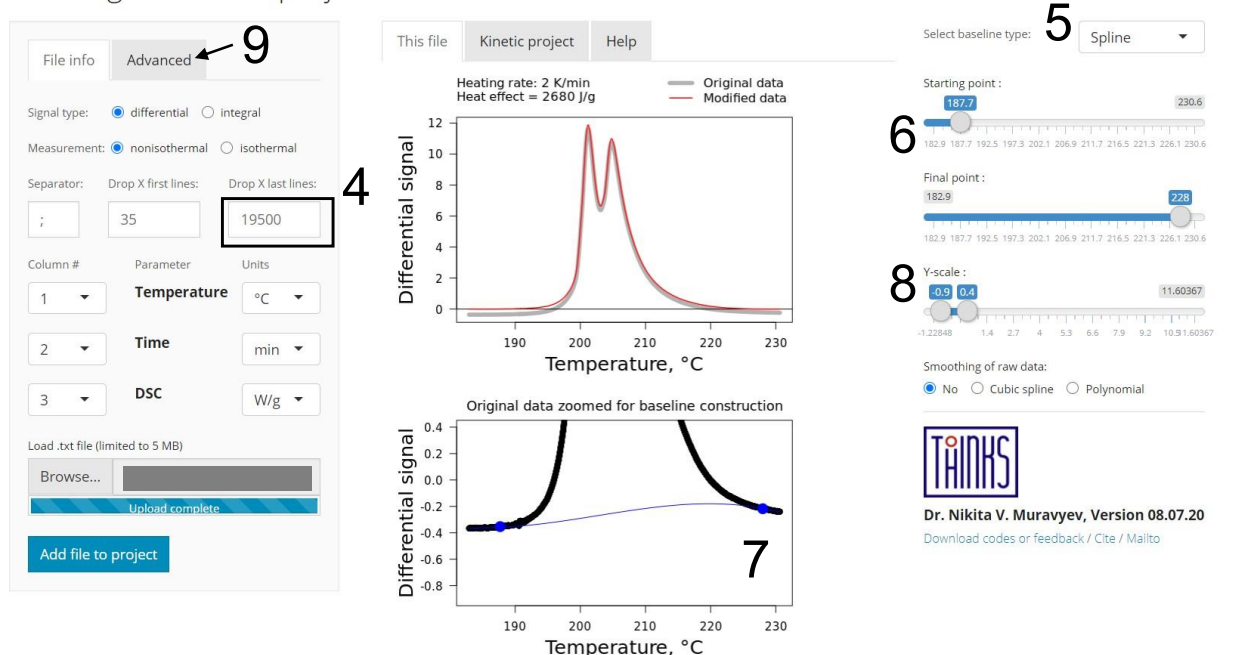


Figure 4.

The “Advanced” tab **9** contains some advanced options for input data and some graphical parameters (slight tuning of the plot’s representation). The first parameter in box **10** is a global parameter. It defines how many points will be in the array with (time, temperature, conversion degree, conversion rate) columns. This parameter can be set only before the first file is loaded into the project! Usually, 1000-2000 points is enough, an increase over it (possible in the offline version) adds nothing, but significantly complicates the calculations. The second parameter in box **10** determines a number of subdivisions in numerical integration. It has to be increased only if you see that the modified data do not follow the original data in the regions of sharp changes (very-very rare situation).

When the file is ready for inclusion into the kinetic project, you can have a look on the conversion and conversion rate in tab “Kinetic project” using plot **12**. If everything is ok, press “Add file to project” button **13**. In tab “Kinetic project”, the bottom plot **14** will appear with loaded into the project all kinetic data. The quantities on X- and Y-axis and some graphical parameters of plot **14** can be changed using options from the section in box **11**. The list of the loaded into kinetic project data is shown in box **15**. Note that the filenames within the project are truncated to 15 symbols, so they have to be different within this piece.

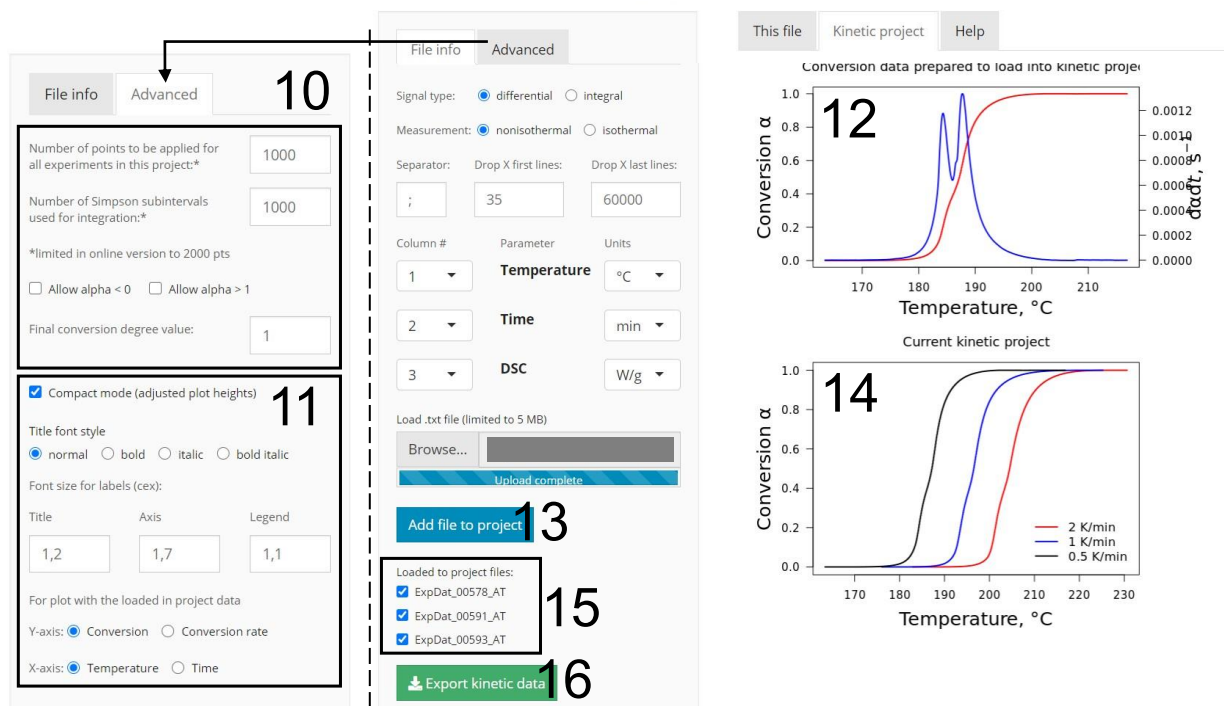


Figure 5.

Finally, by pushing the button “Export kinetic data” **16**, the output kinetic project data is downloaded. This file has to be used as input for the following kinetic analysis with “Isoconversional”, “Model fitting (Linear regression)”, “Model fitting (Nonlinear regression)”. Note, that kinetic project file contains the data from the files that are selected (by default all loaded files). Some general guidelines for the kinetic data necessary for the kinetic analysis can be found elsewhere.^{19,27,28} In very short, more than three different heating rates or isothermal temperatures is recommended, the ratio maximal to minimal heating rate within dataset at least a factor 10 should be considered as a mandatory requirement.

The direct link to Import application – <http://chemphys.space/shiny/Import/> or simply click on the box in scheme from the title webpage.

3. “Isoconversional analysis” application: Obtaining the isoconversional kinetic parameters

The isoconversional group of thermokinetic methods supposes the kinetic parameters as a function of the conversion degree. As an a priori knowledge on the reaction model $f(\alpha)$ is not necessary, the isoconversional methods are often called the “model-free”. The theoretical background of this approach and its application to various processes have been summarized recently in a book by Prof. Vyazovkin²⁹. Note that although the isoconversional methods are

relatively easy to use and interpret,³⁰ fundamental isoconversional hypothesis being valid for the single-step reaction can be not fulfilled in processes with successive and parallel reactions.^{31,32}

THINKS allows to perform the calculations via the differential Friedman³³ and integral advanced Vyazovkin³⁴ techniques, which give the results undistorted by approximation of the temperature integral unlike the common integral routines.^{19,35,36} Friedman method³³ is a typical *differential* isoconversional method, where the effective Arrhenius parameters A and $E_a(\alpha)$ are derived at various conversion degrees from a series of measurements:

$$\ln \left(\frac{d\alpha}{dt} \right)_{\alpha,i} = \ln(f(\alpha)A_\alpha) - \frac{E_a}{RT_{\alpha,i}}, \quad (5)$$

where i refer to a particular measurement. A set of equations is then solved for every particular value of α , and numerical values of $A_\alpha f(\alpha)$ and E_a for every particular α are obtained. In contrast to differential methods, the integral isoconversional techniques are based on the integral form of the kinetic equation (3):

$$\int_0^\alpha \frac{d\alpha}{f(\alpha)} = A \int_0^t \exp \left(-\frac{E_a}{RT} \right) dt \quad (6)$$

Since the right-hand side of the integral equation (6) does not have a simple analytical form for an arbitrary temperature program, several further approximations are introduced in common isoconversional methods. Contrary, the advanced Vyazovkin method³⁴ is based on the numerical integration of the equation over small time intervals.

Start working by loading the kinetic project data prepared with an “Import” application **1**. Then press “Calculate” button **2**, and the results will appear on plots **3**, **5**. Plot 3 illustrates the dependency of the apparent activation energy on the conversion degree. Conversion degree changes from “ $\alpha(\min)$ ” to “ $\alpha(\max)$ ” with a step “ $\Delta\alpha$ ”. Note that the minimization procedure utilized for the advanced Vyazovkin method can be time-consuming when the conversion degree is very detail. The histogram **4** on its left illustrates the distribution of E_a values (to showcase the plateau regions). The lower plot 5 represents the apparent $\ln\{A \cdot f(\alpha)\}$ term and the correlation coefficient R^2 of the linear fits for Friedman method. The correlation coefficient clearly should be close to 1 for trustful fit. In case of the advanced Vyazovkin isoconversional method, instead of R^2 , the Ω value is plotted. It should be as much closer to the $N \cdot (N+1)$ value as possible³⁷ (N is the number of experiments in kinetic project). Section **6** provides the general governing equation for the selected method and first references to the relevant literature.

Isoconversational analysis

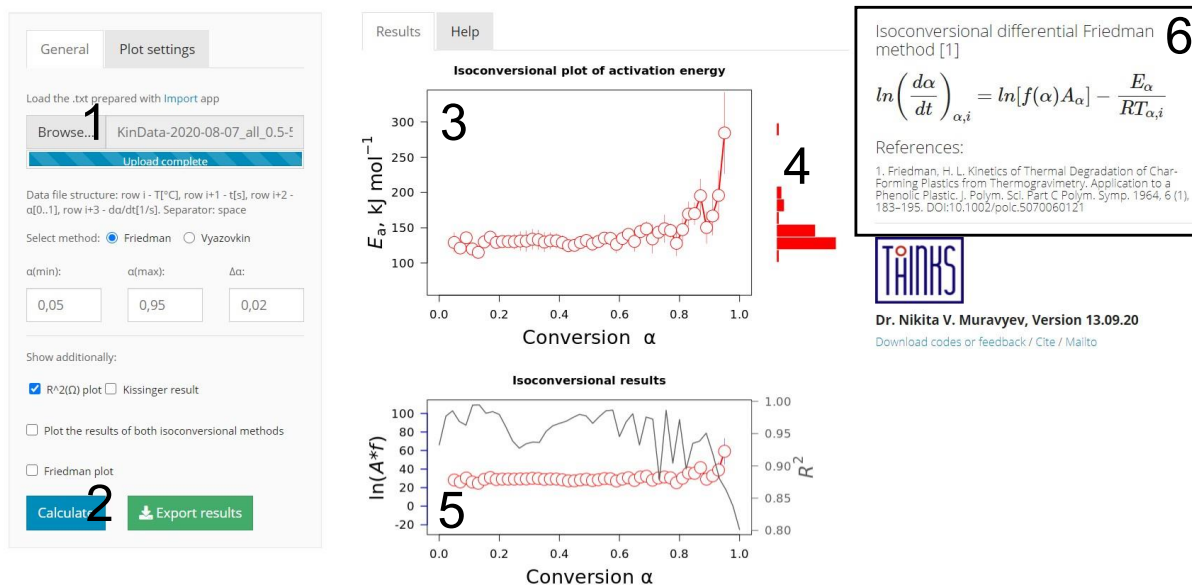


Figure 6.

Section 7 offers some advanced options:

- show/hide R^2 (Ω) plot.
- Show Kissinger method results. The widely used Kissinger method³⁸ allows obtaining E_a from a series of experiments at various heating rates β .⁴⁸ Note, however, that unlike of the above discussed isoconversational methods, Kissinger method uses only a small piece of kinetic information (the peak data). Moreover, it implicitly assumes the same extent of reaction (conversion degree) at a maximum rate (typically, at the DSC peak), this condition has to be examined. In total, the application of the Kissinger method to complex multistep processes is not recommended.^{22,39} THINKS software uses it only to provide a rough estimate of the kinetic parameters of the dominant reaction near the peak region. Results of Kissinger method are summarized in box 8, the original plot 9 is also shown.
- The results of both isoconversational methods (Friedman and Vyazovkin) can be plotted altogether in plot 3, once the respective checkbox is selected.
- Show an original Friedman plot (experimental option).

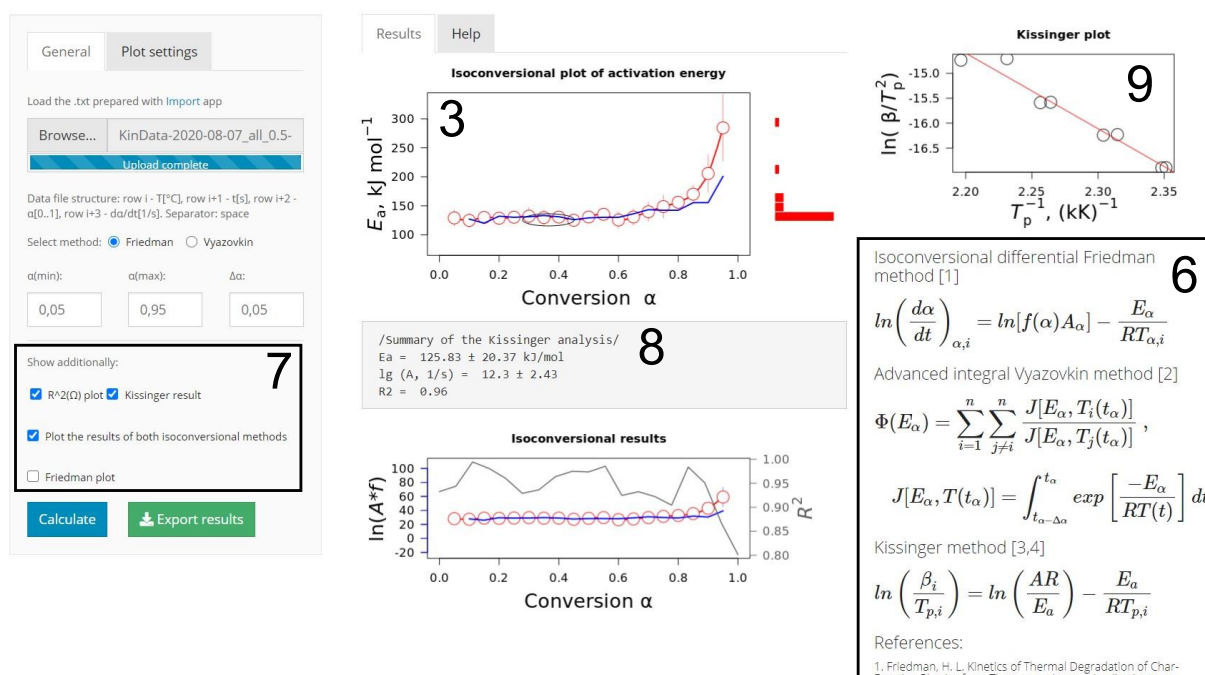


Figure 7.

The direct link to “Isoconversional analysis” application – <http://chemphys.space/shiny/Isoconversional/> or simply click on the box in scheme from the title webpage.

4. “Model fitting (Linear regression)” application

The combined kinetic analysis method⁴⁰ (proposed originally by Zimmerman⁴¹) is a kind of model-fitting thermokinetic technique based on the assumption of the single-step reaction. The kinetic parameters are optimized from the kinetic data according to:

$$\ln \frac{d\alpha}{dt} - \ln[(1 - \alpha)^n \alpha^m] = \ln(cA) - \frac{E_a}{RT} \quad (7)$$

Figure 8 shows the typical results (plots 3, 5) for a single-step process, a case of liquid-state thermal decomposition of tetranitroacetimidic acid.⁴² The calculated dependency of Eq. (7) exhibits high linearity proving the hypothesis of the dominant single-step reaction. With the calculated n and m exponents the reduced master plot⁴³ have been drawn along with the ideal reaction models. As can be seen, the first-order reaction type (F1 in Sharp⁴⁴ notation) closely resembles the obtained reaction profile.

Start with uploading the kinetic project data prepared with an “Import” application 1, press “Calculate” button 2. Plot 3 shows the linearization of data according to Eq. (7). The range of conversion degree values used in linear regression is defined by the inputs in section 4. Often an initial and final portions of data introduce errors, and therefore are not considered. A bottom plot 5

allows comparing of the reaction type with some proposed ideal reaction models (e.g., listed in ¹⁹). To add/remove the curves for ideal reaction types use the checkbox from list **6**. In some cases, the constraints to the parameters $\ln(cA)$, E_a , n , m of regression can be defined, using the tab “Advanced” and appropriate section **7**.

Model fitting (linear regression)

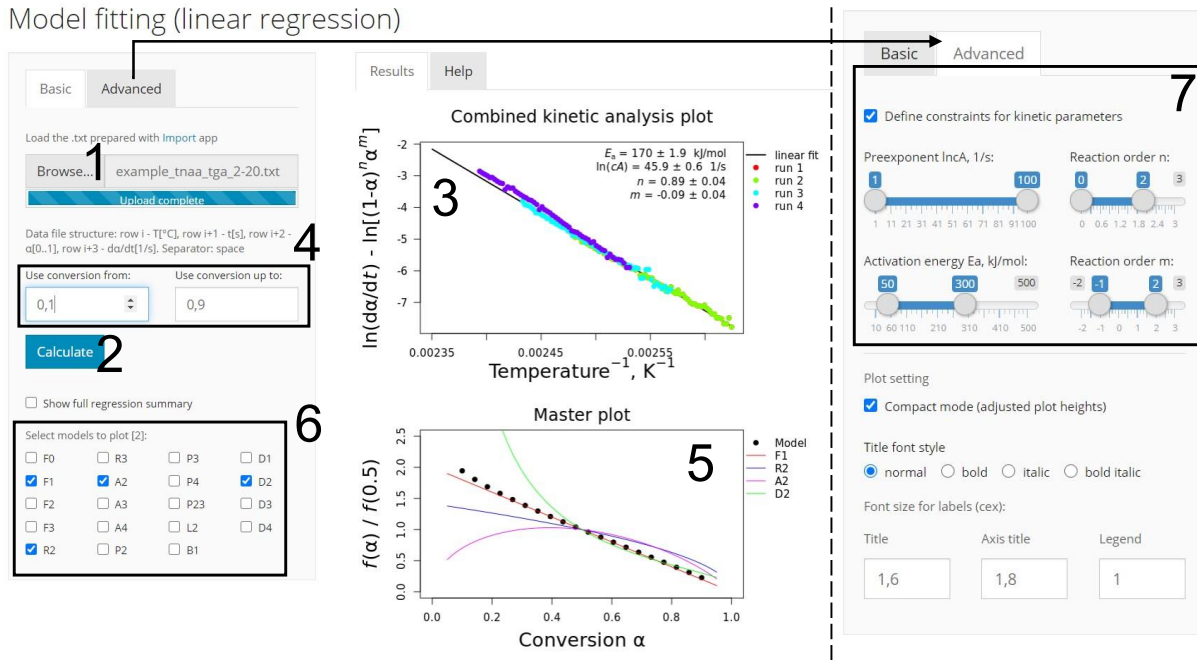


Figure 8.

The direct link to “Model fitting (Linear regression)” application – <http://chemphys.space/shiny/Model Linear/> or simply click on the box in scheme from the title webpage.

5. “Model fitting (Nonlinear regression)” application

Attempts to describe thermoanalytical data in terms of formal physically grounded kinetic models (the term $f(\alpha)$ of Eq.(3)) have a long history. E.g., zero- and first-order reaction models were probed in the course of kinetic analysis by Doyle,⁴⁵ the amount of considered reaction models was increased later up to 18,⁴⁶ and some modern papers discuss even more reaction types. Looking at the diversity of the proposed theoretical models and keeping in mind some factors resulting in deviations of the real reaction patterns from the ideal ones, it seems logical to develop some type of reaction model which will include various $f(\alpha)$ as a special case. Apparently, the first researcher who proposed such a general equation was Erofeev.⁴⁷ Not going deep into the proposed equations, just mention them. The equation recommended by Chornet et al.:⁴⁸

$$f(\alpha) = c \cdot \alpha^m \cdot (1 - \alpha)^n \quad (8)$$

is also known under names of the extended Prout-Tompkins equation (we will call under this name Eq.(11), however) and reduced SB equation. Another, even more flexible reaction function was proposed by Sestak and Berggren (SB):⁹

$$f(\alpha) = \alpha^m \cdot (1 - \alpha)^n \cdot [-\ln(1 - \alpha)]^p \quad (9)$$

The application available at <http://chemphys.space/shiny/UmbrellaSB> can be used to see how Eqs. (8), (9) describe the ideal reaction types.

The serious drawback of Eqs.(8), (9) is that the function $f(\alpha)$ should provide some finite values at the beginning of the reaction. Hence, Varhegyi et al. add the z -factor to overcome the issue:⁴⁹

$$f(\alpha) = (\alpha + z)^m \cdot (1 - \alpha)^n / F \quad (10)$$

where z is constrained to be higher than zero ($\geq 10^{-5}$ in particular), F is the normalizing factor. Another way to deal with the “kick-off issue” is the so-called extended Prout–Tompkins equation (ePT) proposed by Burnham:⁵⁰

$$f(\alpha) = (1 - \alpha)^n \cdot [1 - q \cdot (1 - \alpha)]^m \quad (11)$$

with q -factor approaching to 1, but generally a bit lower. THINKS adopts this ePT formalism with $q = 0,999$ by default. However, the value of q can be defined by user, and if no serious effect, Eq. (11) can be reduced to Eq. (8) by setting of $q = 1$.

An alternative form of the flexible reaction model is:

$$f(\alpha) = p(1 - \alpha)[- \ln(1 - \alpha)]^{(p-1)/p}, \quad (12)$$

Derived first by Kolmogorov⁵¹ and later on developed by Johnson and Mehl,⁵² Avrami,⁵³ and Erofeev⁴⁷ this equation is denoted in THINKS as KJMAE(n) equation with exponent $n (=p)$. For a nucleation-growth reaction, n is usually supposed to take an integer value in the range of 1 – 4. However, KJMAE equation is also used as a flexible reaction function, when the exponent n value is an adjustable parameter (e.g.,⁵⁴). Indeed, as was shown by Erofeev⁵⁵ for a certain combination of exponents, Eq. (8) reduces to KJMAE(n). The formalism of KJMAE(n) is a second way of introduction of the flexible reaction model implemented in THINKS.

The overall logics of the performing of the model fitting kinetic analysis accepted by the present author and implemented in THINKS is a sort of “top-down” approach (Figure 9). The analysis starts from the optimization in a single-step flexible ePT/KJMAE form (called in THINKS as **v1** model). If the fit is sufficient, we try to reduce the ePT model to some of the theoretical ideal reaction types (available in **v2** model in THINKS). This reduction is mainly driven by the values of (n , m) exponents and our perception on the investigated process. If the profiles are more complicated than the available single-step models, another stage is introduced. Again, we start

from two-step reactions in a flexible ePT/KJMAE form and then try to reduce them to ideal reaction types. In the case of two and more stages, the connectivity between stages has to be taken into account. That is, model **v6** describes two independent reactions (this approach is widely used under different names, e.g., “kinetic deconvolution”), model **v5** – two consecutive reactions, model “v4” – two parallel reactions. Note that for multistep kinetic schemes, the KJMAE form can be set only for a first stage. For three-step kinetic schemes, the single model **v9** is available in THINKS so far. It is the flexible ePT/KJMAE reaction followed by parallel ePT reactions (an example of its application can be found in *).

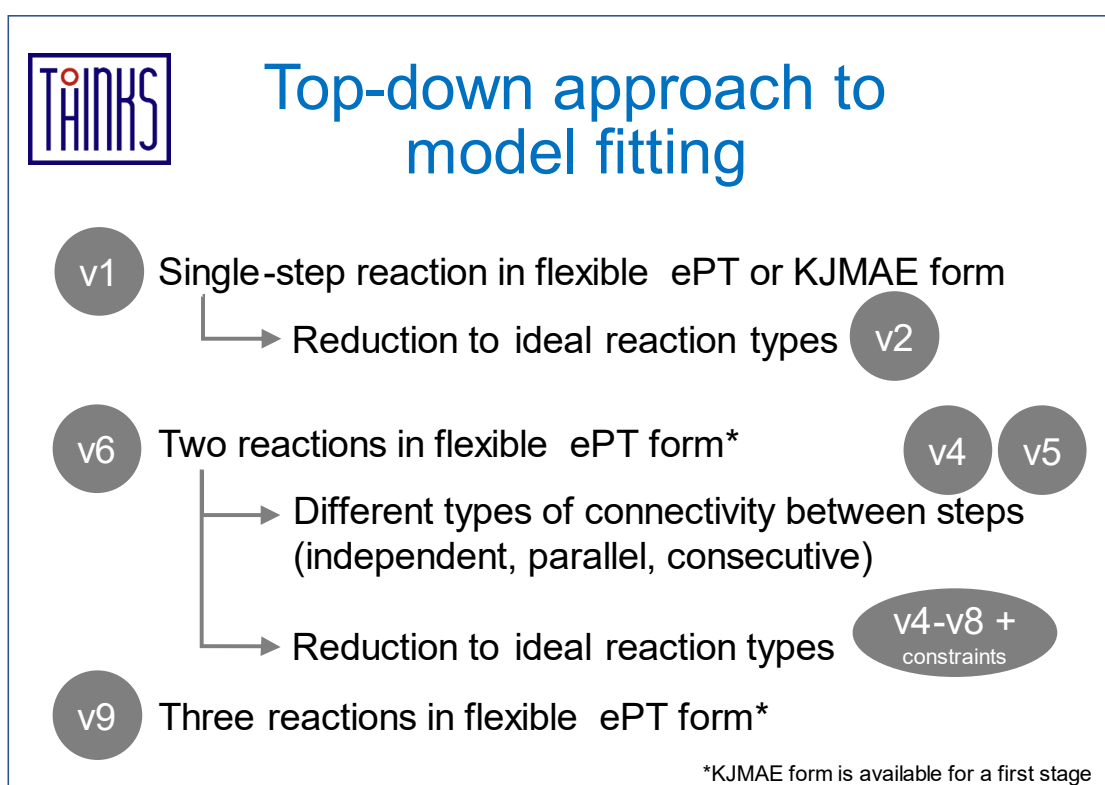


Figure 9.

The reaction model under the name **v3** is developed specially for autocatalytic reactions.⁵⁶ The original paper is available at http://chemphys.space/shiny/Model_Nonlinear/DAN_58.pdf. This model proposed by Dubovitskii, Manelis, and Merzhanov (DMM model)⁵⁶ is given by equation:

$$\frac{d\alpha}{dt} = k_1(1 - \alpha) + k_2(1 - \mu) \frac{\alpha(1-\alpha)}{1-\mu\alpha}. \quad (13)$$

where μ – the volume change at the complete decomposition, k_2 – the rate constant for the autocatalytic reaction, k_1 – the rate constant for the noncatalytic reaction. When the volume change can be neglected, i.e., $\mu = 0$, the DMM model reduces to a scheme with two parallel first-order and

first-order autocatalytic reactions.⁵⁷ This scheme is routinely applied to describe the reactions with acceleration.^{57–59} A model **v8** comprises the DMM model followed by ePT reaction, an example of its application can be found in recent study on decomposition of energetic triazines.⁶⁰

The practical work in THINKS starts from the uploading of the investigated kinetic project **1** (a file that has been created with Import application). The initial guesses of the kinetic parameters should be set using the sliders in box **2**. Plot **3** illustrates the input data (circles), and the results of the selected kinetic model with the defined in box **2** kinetic parameters. The main settings of the model fitting procedure are located in box **4**. From top to bottom, first, we should specify the type of signal that will be considered, i.e., the integral differential, and weighted differential. It is generally recommended to work with the same type of signal that was actually measured (to minimize the errors due to numerical differentiation/integration). Third option (“weighted differential”) should be selected to minimize the difference in amplitude of the differential signals at highly differing heating rates (weight = $1/(Y_{\max} - Y_{\min})$). The next selection is the type of solver for system of differential equations. Here, the names are shown that are names of widely used methods for approximate solution of ordinary differential equations (the deSolve⁶ package is used for methods higher than Euler). Not going deep into the mathematics, from left to right the accuracy is increased with several important notes: (i) the more complex method, the greater computation time is (remember that you share the server with other users, so perform demanding computations on the local machine), (ii) simpler methods have a better converging (more forgiving to the initial guesses), (iii) for a rigid systems of ODEs (e.g., **v5** with both nonzero exponents), only the high order methods will give a solution (use them for plotting of the initial guess **9** too). In short, the best way is to start from a simpler and robust method, like Euler and Runge-Kutta of 2nd order, and optimize the final model with a more accurate method. The last selection in box **4** is a list of kinetic models. In the current version, the kinetic models **v1–v6**, **v8**, **v9** are available (vide supra). For the selected kinetic model, the governing equations and first references appear in box **5**.

Once the kinetic model is selected, the optimization settings and initial guesses for the kinetic parameters are specified, press the button “Run analysis” **6**. The results of nonlinear regression will appear as a red curve in plot **3** and the regression summary will be shown below in box **7**. The summary includes the optimized values for the kinetic parameters, its standard errors, and other details. To set the initial guess of the kinetic parameters to the optimized values, use the “Set the current results” button **8** (clickable only after the nonlinear regression results are available).

Model fitting (nonlinear regression)

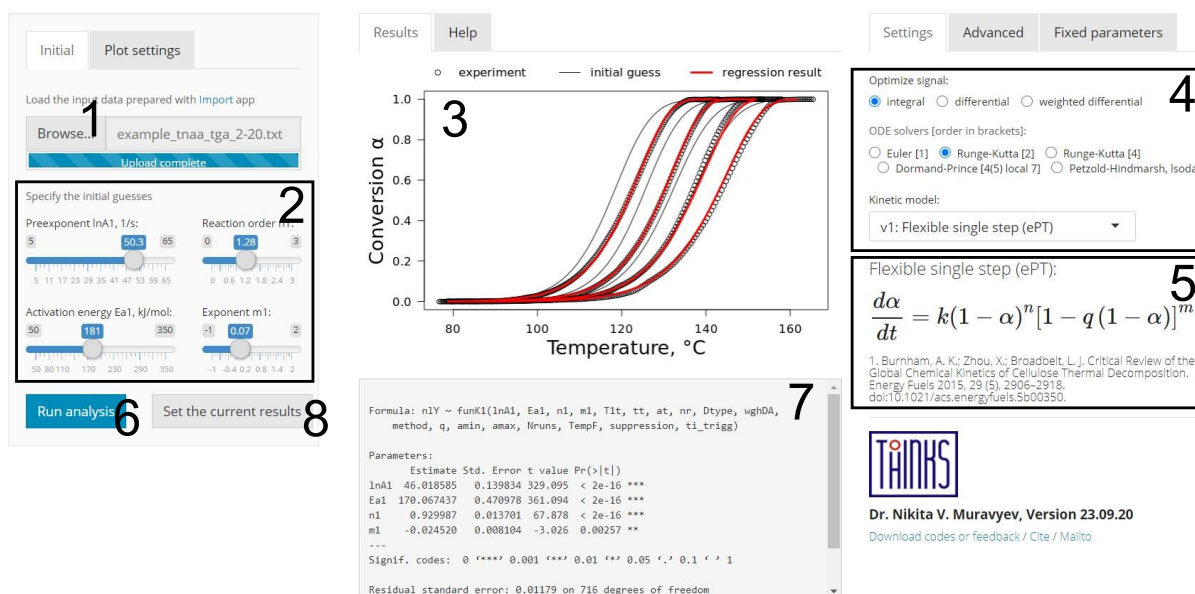


Figure 10.

Tab “Plot settings” controls the way the results are drawn in plot 3 (e.g., for preparing the picture for report). These options are located in box 9. E.g., in Figure 11 the X-axis is set to be a temperature in Celsius, the points of raw data are rarefied (every 3 points are shown), and the curves with initial guess are hidden. A checkbox “Normalize curves” is used for normalization of the data (for integral signals with conversion going to unity it is done by default, for optimization of weighted differential signals, the data is normalized by multiplying to the weights, but for differential signals, the normalization is applied solely for plotting, not during the optimization).

The statistical quality of the fit of input data with an optimized kinetic model are presented in box 10. In THINGS for this purpose, the recently proposed^{61,62} Akaike or Bayes information criteria (AIC and BIC, respectively) are available, along with the residual sum of squares (RSS). Using of the AIC and BIC values aims to introduce some penalty factors for the model, thus compensating the fit quality increase for a model with greater number of adjustable parameters. Of these two, the BIC is more stringent. An example of using of BIC criteria for selecting the best model is reported.⁵⁷

Tab “Advanced” also includes the possibility 11 to change of the ODE solver for computing of the initial guess in plot 3. It is generally a weaker method than that for the optimization itself, since the initial guess has to be drawn immediately after the slider with the guess on the kinetic parameters is changed (it is called “reactive” in R). However, for some rigid kinetic models (e.g., v5 with both nonzero exponents), the method has to be changed from the default “Euler” to give a meaningful result.

Model fitting (nonlinear regression)

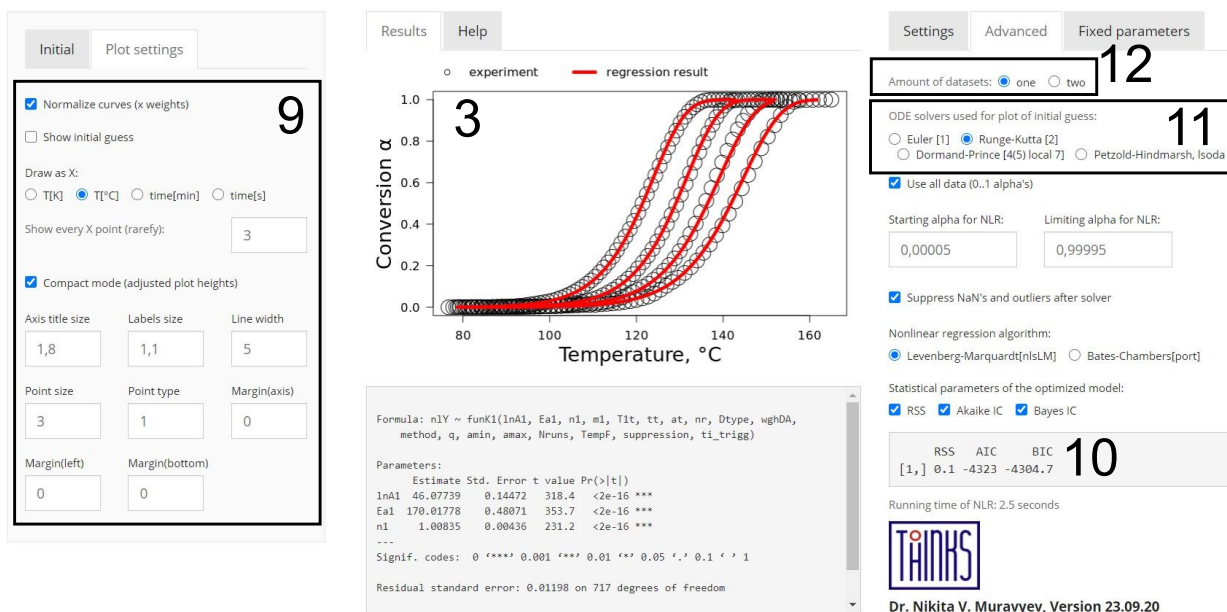


Figure 11.

Another advanced option located in this tab is the selection of two datasets for analysis. If this selector **12** is set to “two”, the second dataset can be uploaded with idea of building of the joint kinetic model on both sets of data. An example of the application of this option can be found in ¹³. Thermal decomposition of ammonium dinitramide has been investigated with a simultaneous thermal analyzer, thus, in a single measurement, the caloric (DSC) and mass loss (TGA) data are recorded. Two sets of DSC and TGA data were described by a two-step joint reaction scheme. Since the contributions of the first stage in total heat effect and total mass loss are not the same, in the kinetic model, these contributions were allowed to be different (called “cd1” and “cd2” in THINKS).

Finally, let us discuss some details of the definition of the kinetic model. For models **v1**, **v4-v6**, **v9**, the first reaction step, that is by default in ePT form, can be changed to a KJMAE form by fixing an exponent $m_1 = 10$ (shown under **13** in Figure 12). The change of the model is visible by another theoretical equation in the bottom. When a model **v2** is selected **14**, the additional list **15** appears, and after the selection of a certain ideal reaction type, its governing equations and literature references appear below. For the two-step reaction models **v4-v6**, **v8**, the contribution of the first stage by default is confined within 0.01..0.99 range, but the limits can be extended. This option is useful for a process comprising the exothermic and endothermic reactions.²² In certain cases, the constraint of activation energy of one stage equal to E_a for another stage can be set **17**. An example in Figure 13 illustrates the liquid-state thermal decomposition of energetic triazine,⁶⁰ where the beginning of the mass-loss process is governed by an autocatalytic reaction (DMM model). Within this DMM model (Eq. (13) with $\mu = 0$), the autocatalytic step appeared to be much

faster, so that forced to apply the constraint $E_{a1} = E_{a2}$ to the kinetic model.⁶⁰ Another (experimental) feature implemented in THINKS is a “triggering temperature” **18**. Setting of this temperature (marked as a dashed vertical line in plot **3**) aims to mimic the increase of the reaction in the liquid phase compared to the solid. The retardation coefficient K_T is nearly constant for common energetic materials: $K_T = k_{liq}/k_{sol} \approx 100 \pm 50$.^{63,64} Thus, below the triggering temperature T^* (set as a melting temperature), the preexponential factor is reduced in 100 times, imitating the retardation by the crystal lattice.⁶⁰

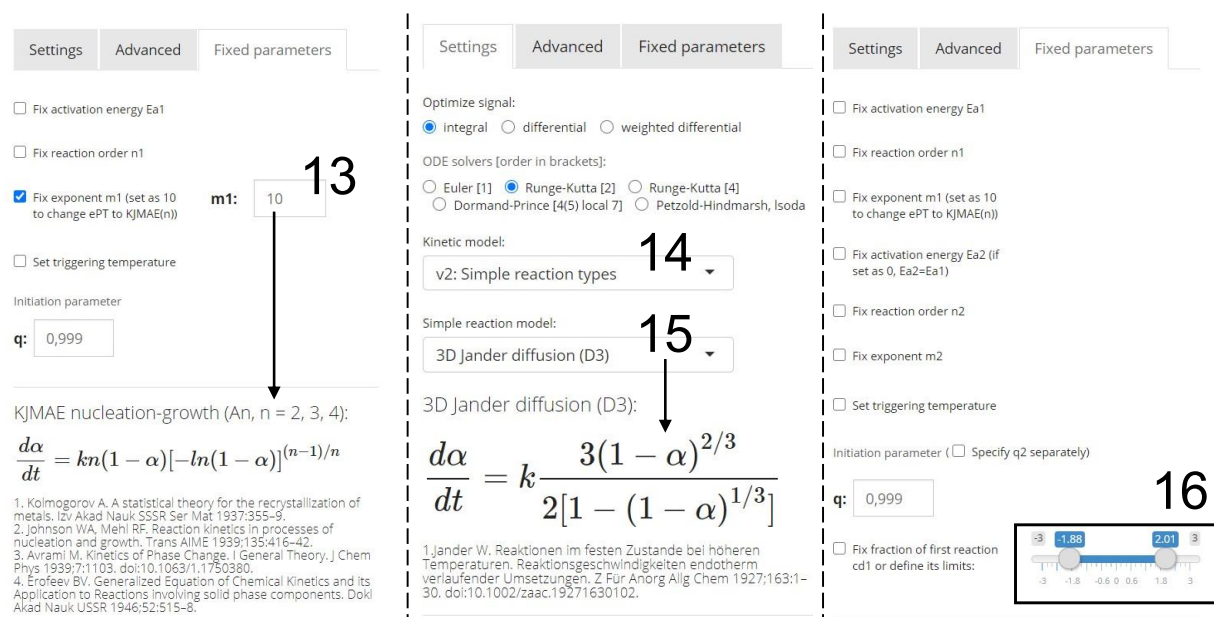


Figure 12.

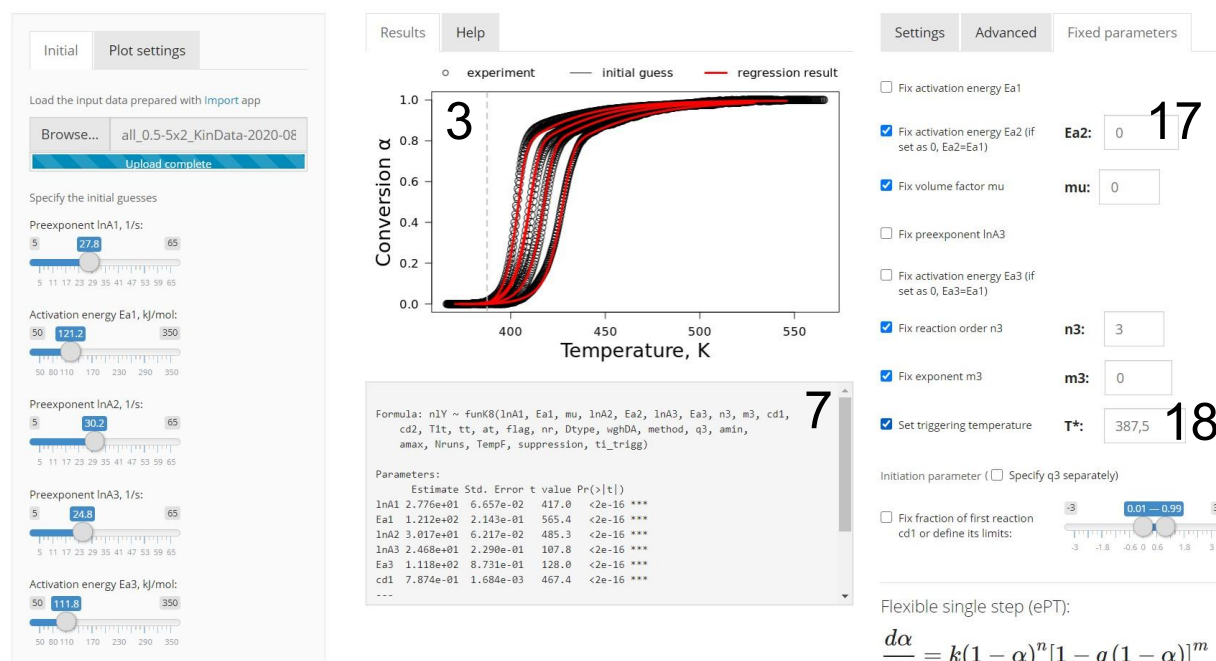


Figure 13.

The direct link to “Model fitting (Nonlinear regression)” application – http://chemphys.space/shiny/Model_Nonlinear/ or simply click on the box in scheme from the title webpage.

6. “Prediction”: Simulation of reaction profile under the selected temperature program

The prediction of the conversion profiles under a certain temperature-time condition is often desirable. Mainly it is applied to predict the behavior at lower temperatures and longer times that are attainable in the thermal analysis experiment. Herein, we will consider only a so-called “kinetic prediction”, i.e., extrapolation using only the Eq. (3), without considering the heat balance equation. For extrapolation purposes, the kinetics by isoconversional methods or model fitting with flexible reactions are extremely useful.^{36,65,66} Importantly, that the kinetic parameters above the phase transition, in general, cannot be applied to predict thermal behavior below the phase transition.

The interested temperature program has to be defined using the parameters from box **1** (Figure 14). For a linear heating program, the initial and final temperatures should be set, as well as the heating rate. For isothermal runs, the temperature and duration of the measurement should be specified. The third option is the “user-specified” program, it will be taken from the input text file with the following structure: row 1 - $T[^\circ\text{C}]$, row 2 - $t[\text{s}]$, row 3 (optional) - $\alpha[-]$, row 4 (optional) - $da/dt[1/\text{s}]$ (separator: space). In this case, if the conversion data is available from the input file, it can be plotted along with the kinetic prediction once the appropriate checkbox is selected. Note that the structure of this file is the same as the output of the “Import” application of THINKS.

Then, the type of the kinetic data is selected **2**. If the isoconversional kinetics will be used, it has to be uploaded **3** (the output file of “Isoconversional” application of THINKS). By pressing “Calculate” button **4**, two plots **5**, **6** will appear. Plot **5** represents the uploaded isoconversional activation energy as a function of conversion degree. Plot **6** is the predicted conversion data. Box **7** encloses the selection of parameters that are shown at Y and X axis. In rare situations (usually far extrapolations), the very beginning of the isoconversional data affects the result, and the type of curve that approximates this data can be varied **8**. Finally, the prediction results are downloaded using the “Export prediction” button **9**.

Kinetic prediction

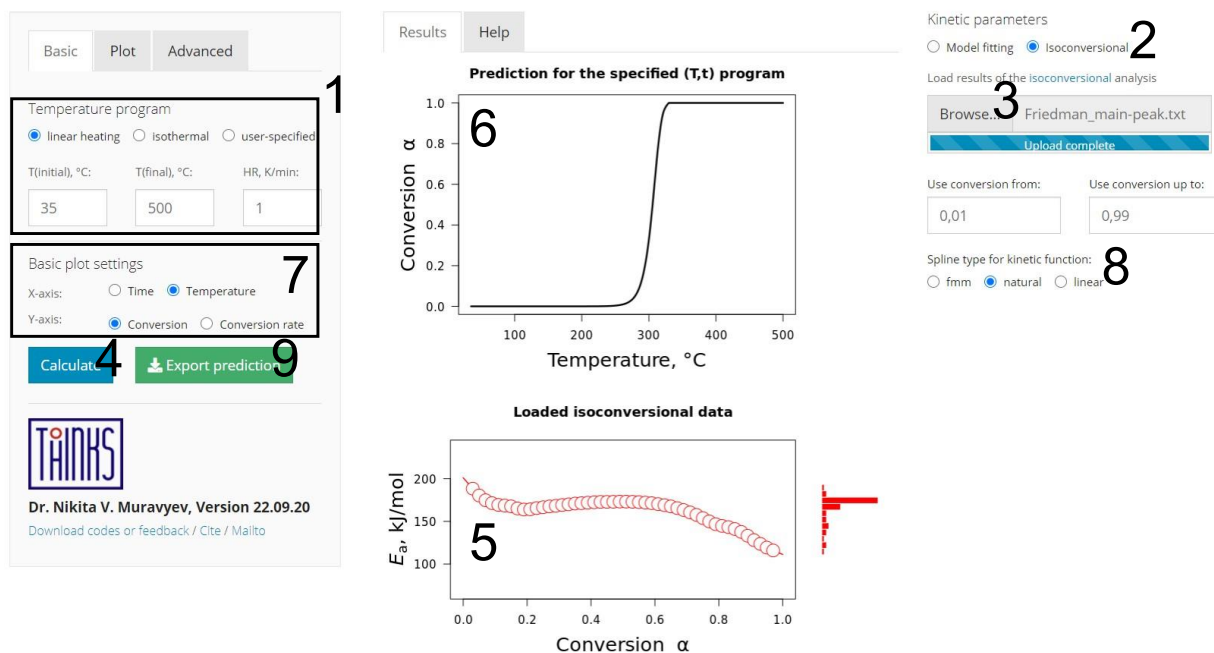


Figure 14.

Alternatively, the model fitting kinetics can be use by defining of the respective kinetic parameters in box 10. For models with more than two reaction steps, plot 12 shows the change of the concentration of brutto-products (e.g., A, B, and C for the v5 model, $A \rightarrow B \rightarrow C$). The graphical parameters are located under “Plot” tab. If the scale of concentration for some of the products differs from the others, it can be drawn on the secondary Y-axis (by selection 13). Checkbox 13 forces the graphs to fit a single screen, if it is not selected, the height of plots can be defined explicitly.

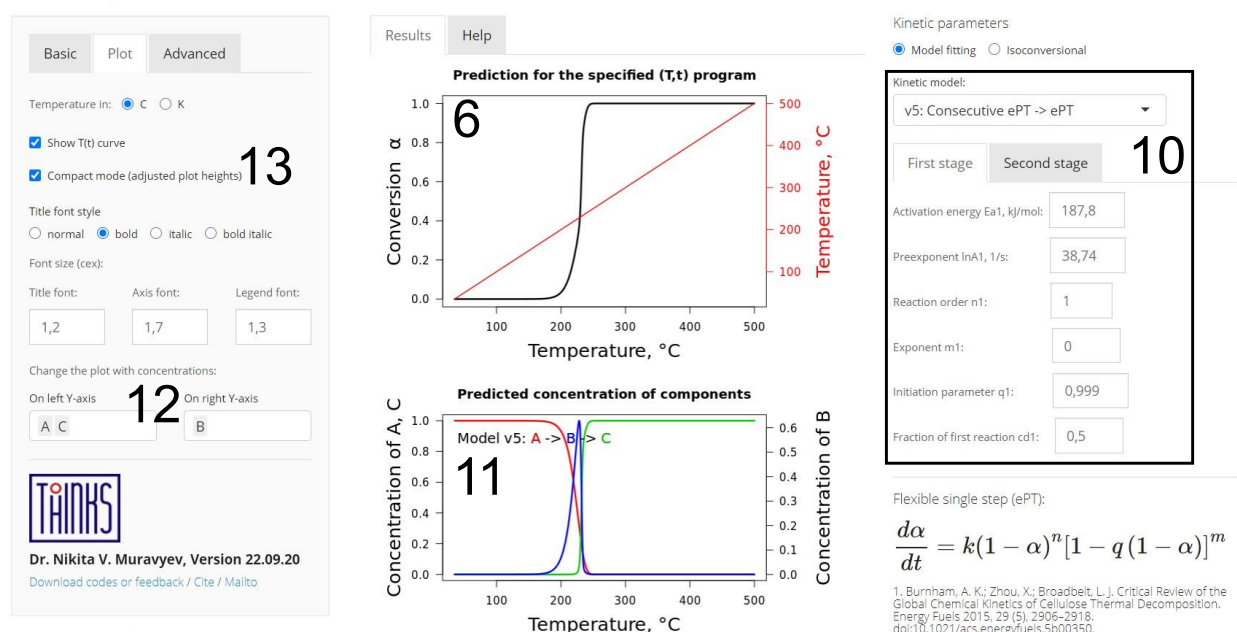


Figure 15.

Some advanced options are hidden at “Advanced” tab. It is possible to change the number of points in the predicted profile **14**, starting conversion degree **15** (e.g., useful for prediction of the isothermal ageing⁵⁷), the type of time series **16** (a logarithmic step can be selected to cover the long isothermal runs with less data points). The ODEs solver type can be varied **17**, for details see the discussion above in Section 5. Sometimes, usually in parallel with the model fitting using nonlinear regression, the output of two solvers may be compared. The two solvers are selected using **17, 18**, and its difference is shown in plot **19** (again, to unlock the fitting to the single screen and enlarge the plots, use checkbox **13**).

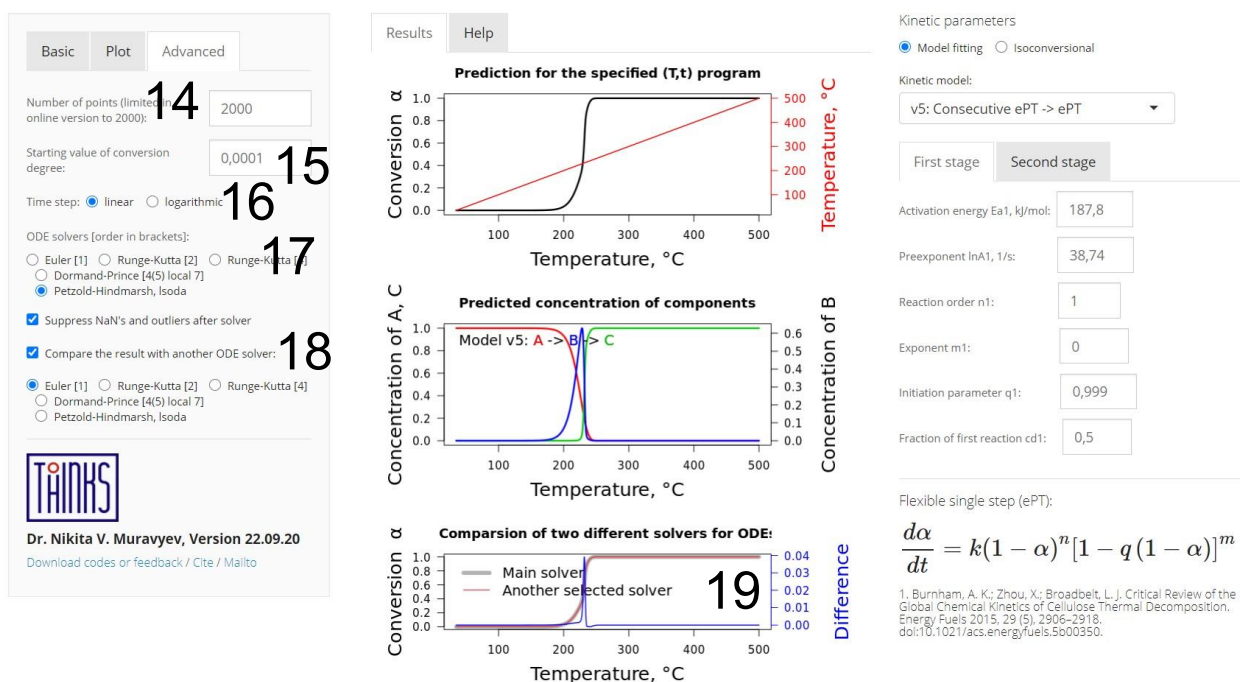


Figure 16.

The direct link to Prediction application – <http://chemphys.space/shiny/Prediction/> or simply click on the box in scheme from the title webpage.

Concluding remarks

I'd like to thank you for the interest to THINKS. My idea was to share with the community of the modern tool, to shift the focus of researchers from struggling with the methods to the interpretation of the results (mechanistic insights of the studied process). Many other communities have their free and open-source research tools, I hope that THINKS will be adopted by thermal analysis researchers. The only way to make THINKS better is having any feedback or comments, feel free to write within the project page in RG (<https://www.researchgate.net/project/THINKS>) or by e-mail.

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