

# THERMOKINETICS Software (TK)

Evaluation of Kinetic Parameters  
from Conventional Thermoanalytical Data

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AKTS E-Learning

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## PREDICTIONS

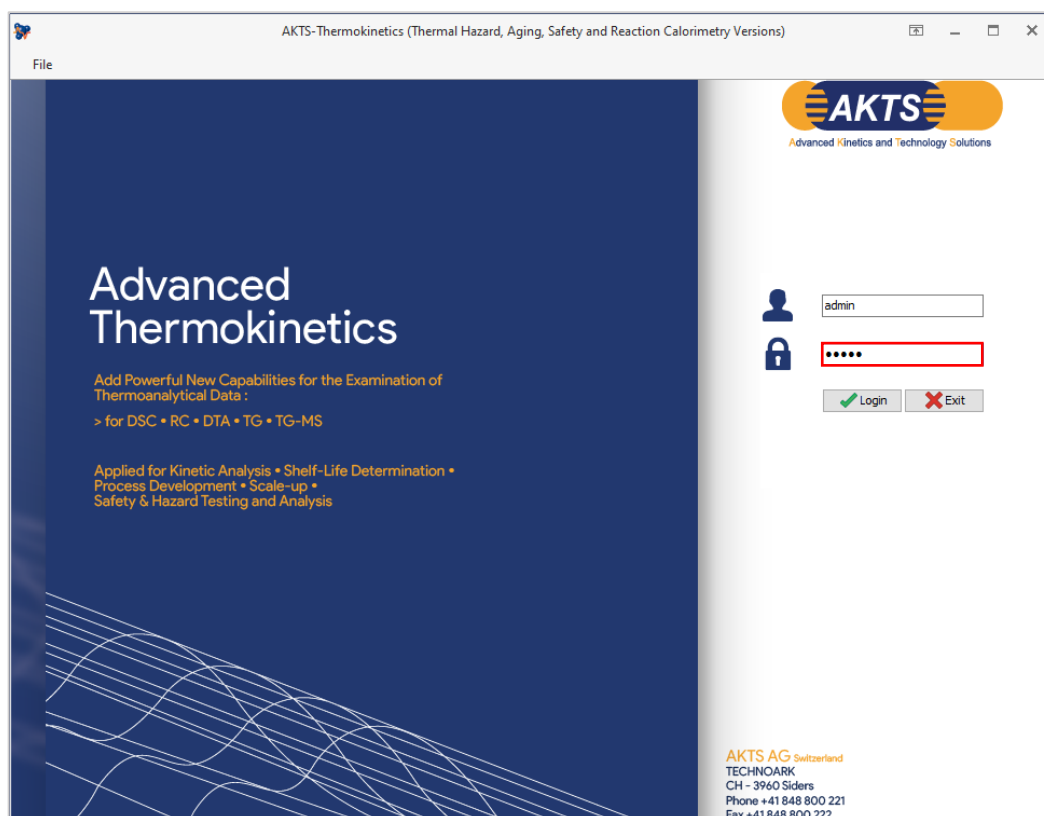
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# AKTS E-LEARNING DATA ANALYSIS

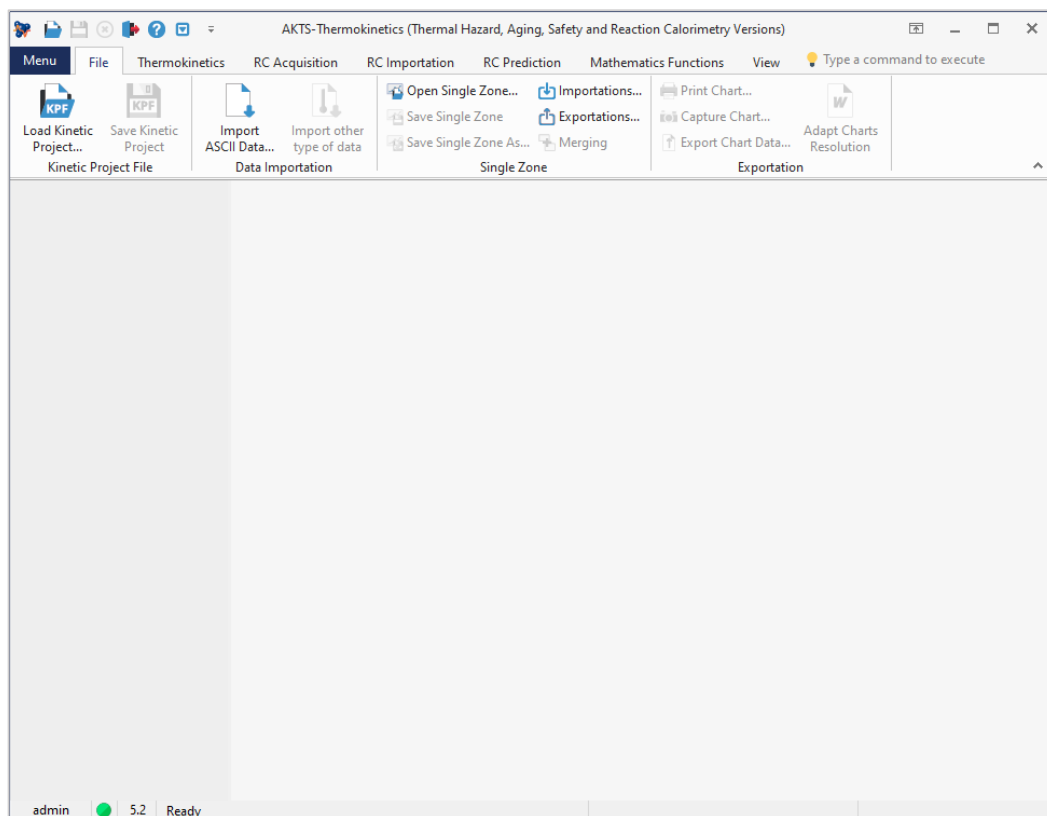
## DATA COLLECTION AND IMPORTATION

The THERMOKINETICS software (TK) permits the evaluation of kinetic parameters from thermoanalytical data. TK allows the kinetic analysis of the variety of chemical reactions and physical processes from the simplest one-step to multi-step reactions. TK has been developed to offer advanced treatment of any thermoanalytical data independent of its kind. The software can work with the data collected by all types of thermoanalyzers of reputable manufacturers available on the market. With TK it is possible to correctly describe kinetics of complex reactions within few minutes only.

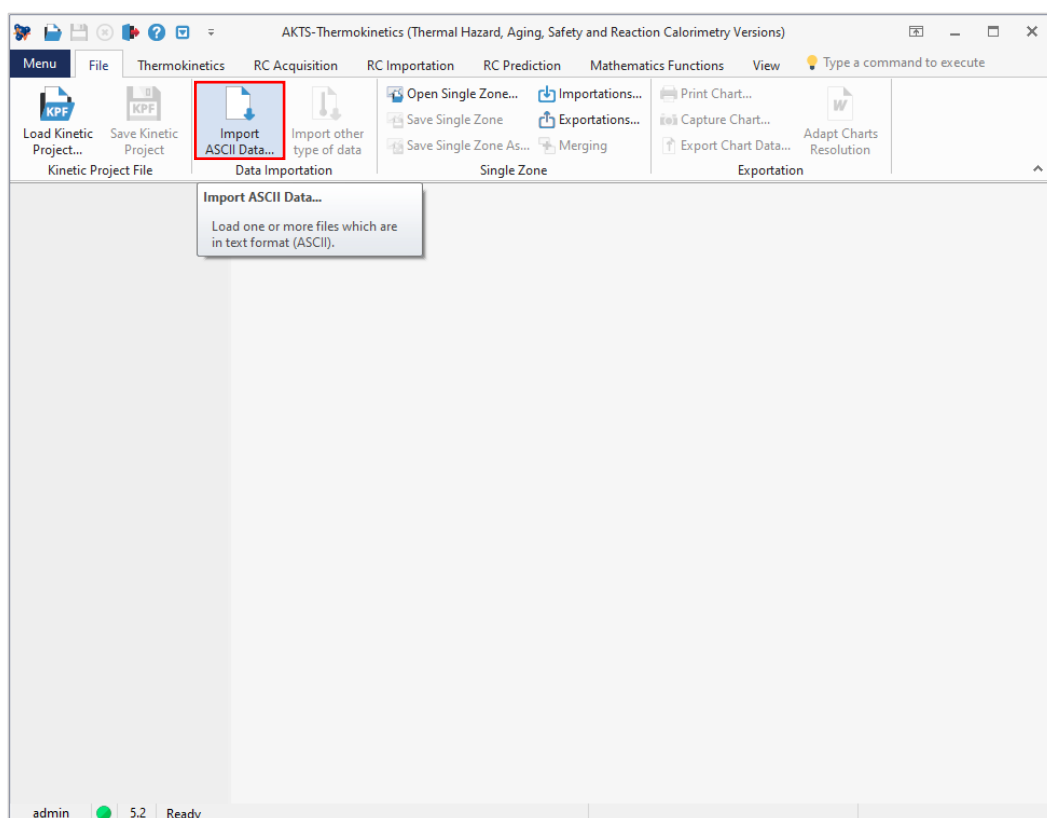
The following screen captures and notes present the workflow of the kinetic analysis based on DSC experiments carried out in non-isothermal conditions.



**FIG. 1** - Enter password to start the AKTS-Thermokinetics software (TK).



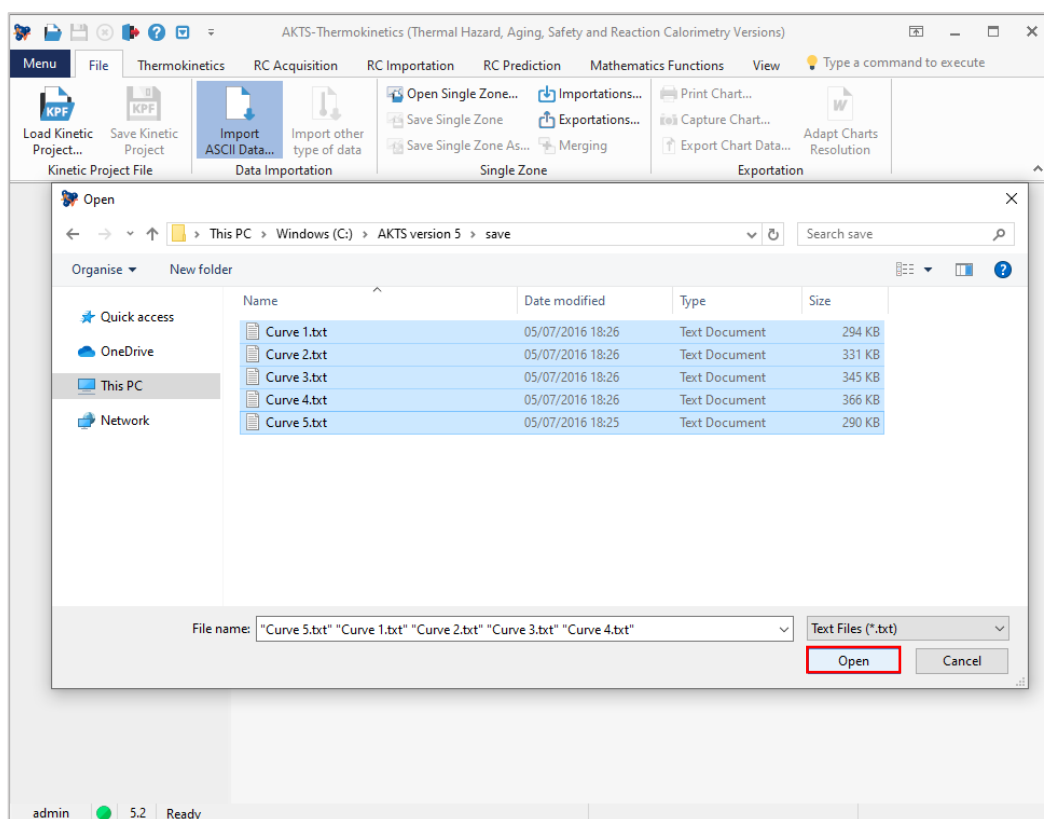
**FIG. 2** - Opening screen of TK.



**FIG. 3** - Importation of thermoanalytical data (DSC, TGA, etc.) in ASCII-format (.txt).

(1) The meaningful kinetic analysis requires performing four-five DSC experiments measured at e.g. 0.5, 1, 2, 4 and 8 K/min followed by the construction of the baseline. (Remark: DSC runs under isothermal conditions (i.e. 0K/min) can be also evaluated by the TK Software).

(2) The option 'Import ASCII Data' allows the importation in ASCII-format of any thermoanalytical data independent of its kind.



**FIG. 4** - Selection of the required data files.

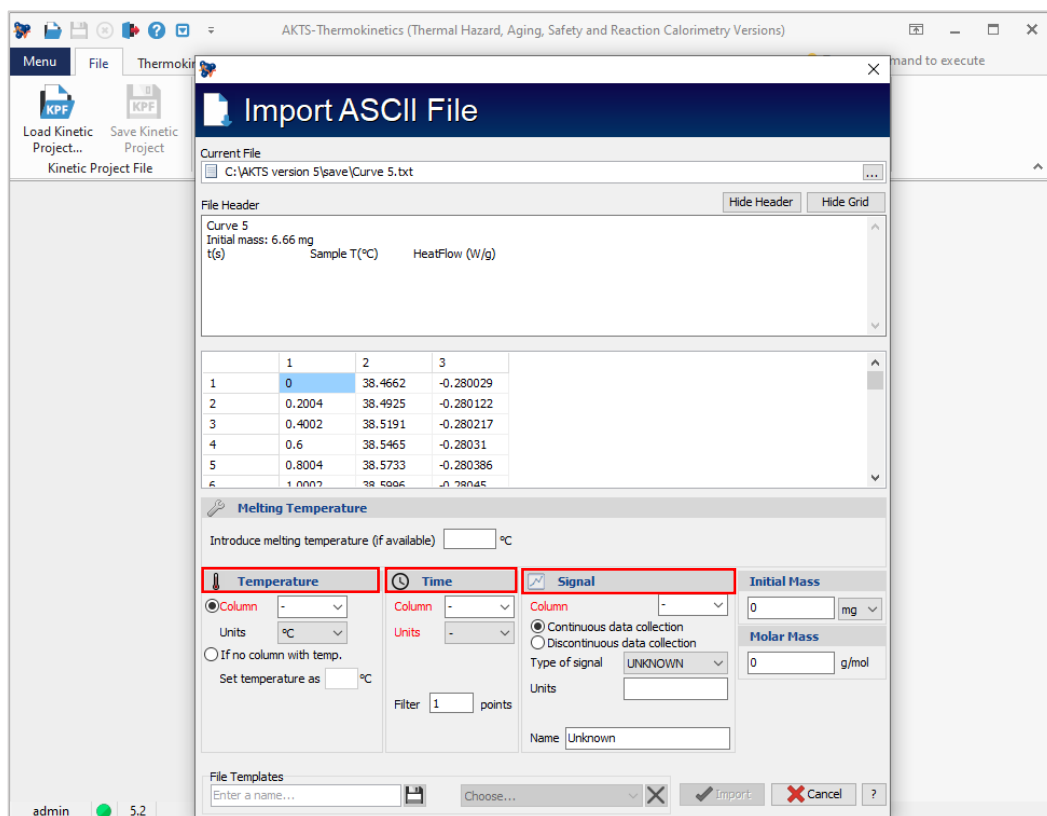


FIG. 5 - Selection of the properties.

After selection of the data files for further elaboration, one has to specify the properties of temperature and time columns and the type of the measured signals.

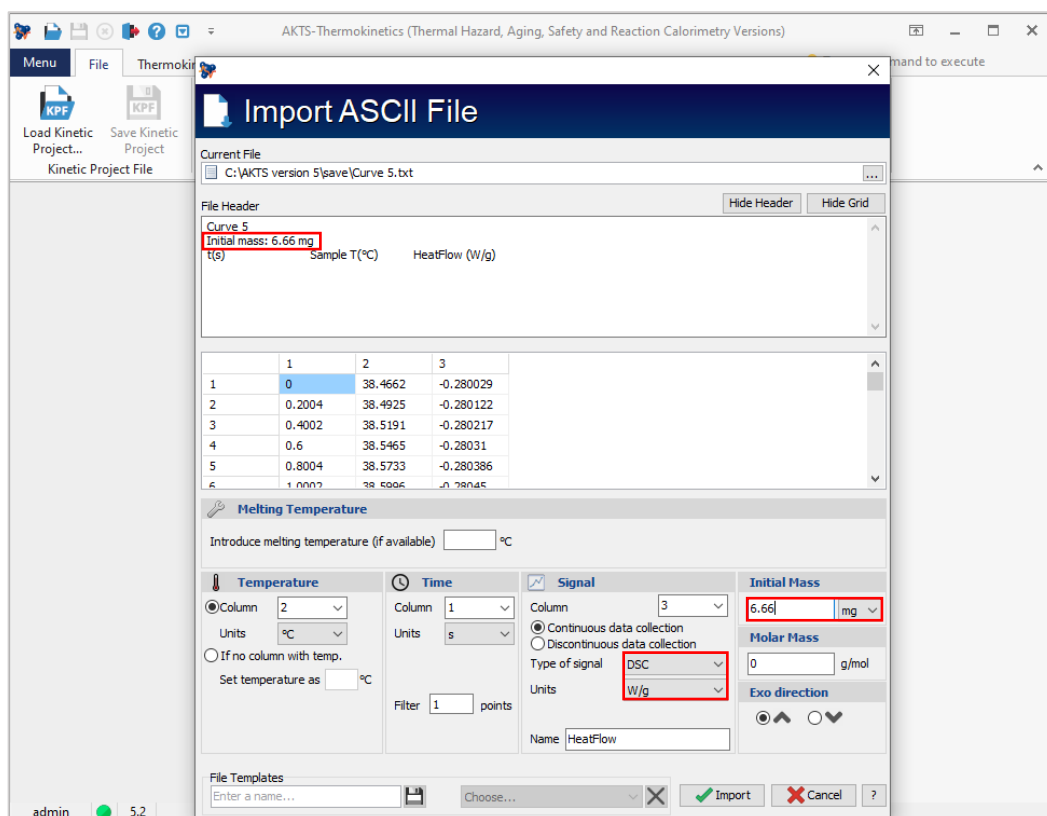


FIG. 6 - Indication of signal type and input of sample mass.

Finally, the type of signal and an initial sample mass has to be introduced. (Remark: As shown in the next figures, the input of further data can be facilitated by just updating the sample mass only).

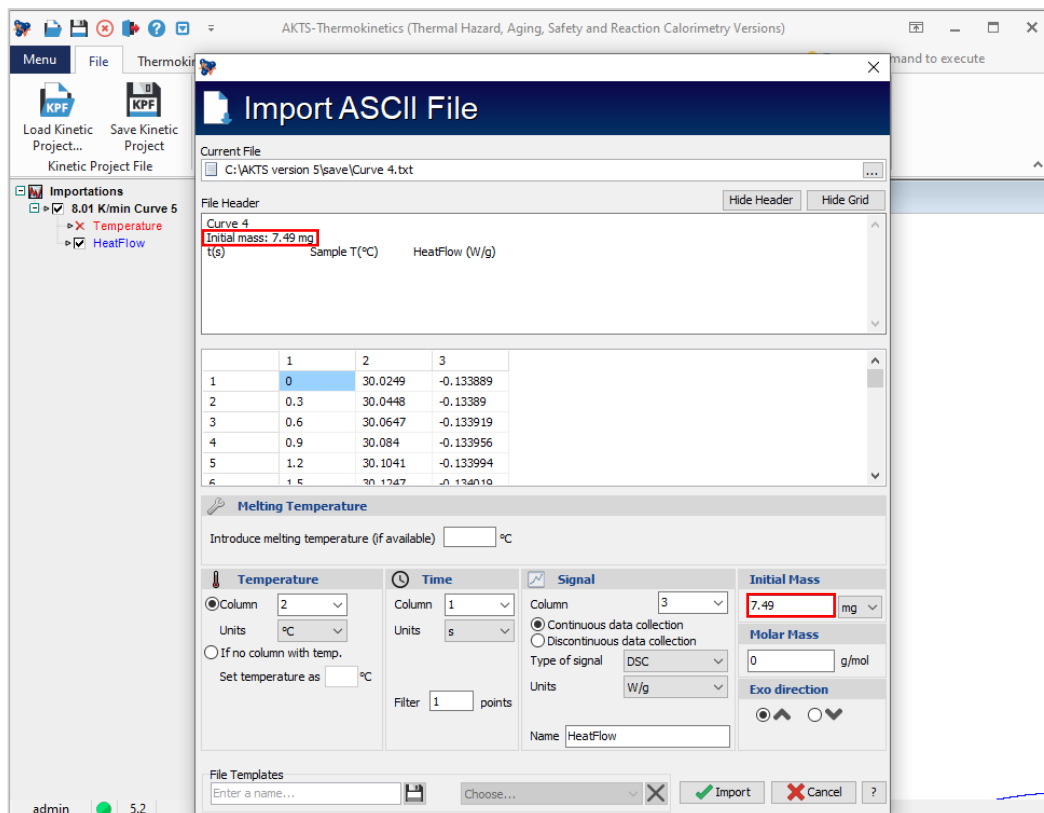


FIG. 7 - Introducing sample mass.

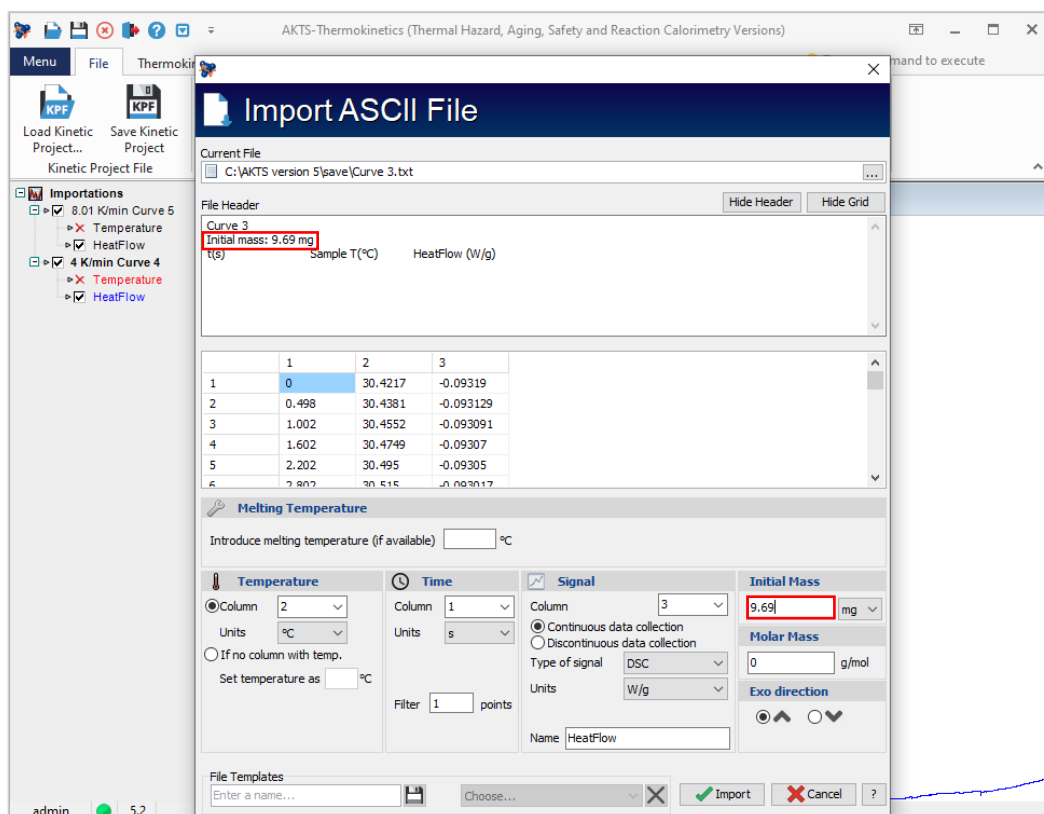


FIG. 8 - Introducing sample mass.

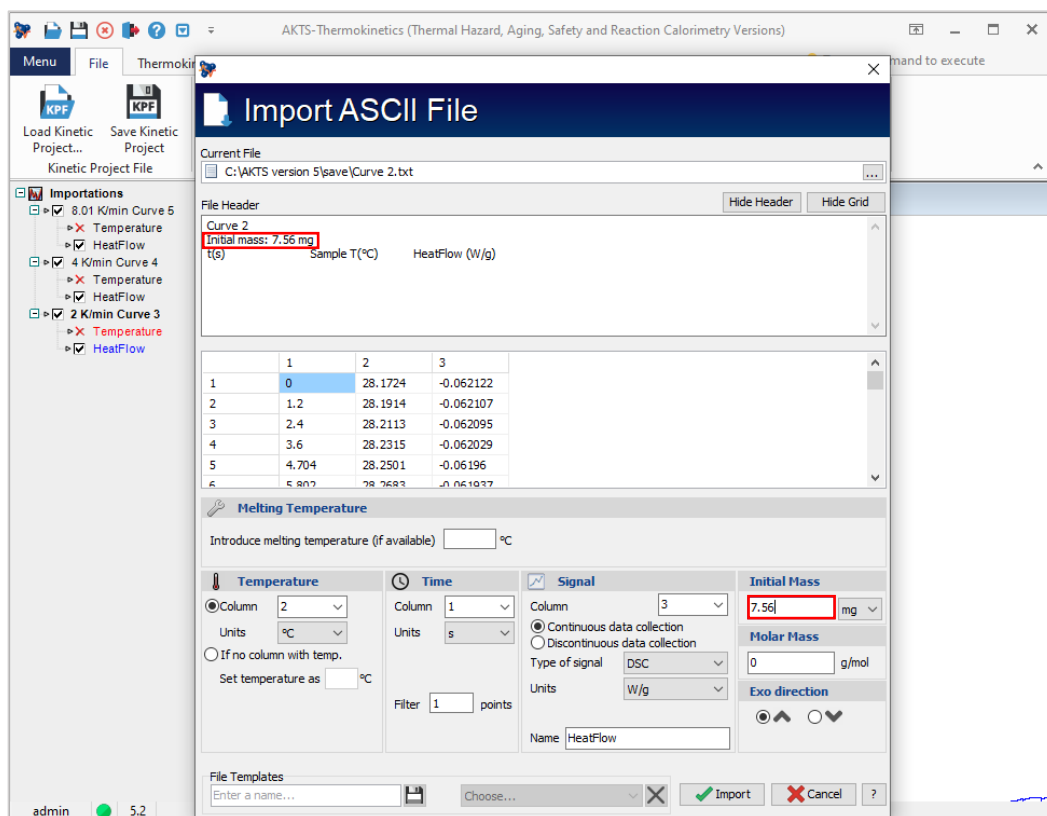


FIG. 9 - Introducing sample mass.

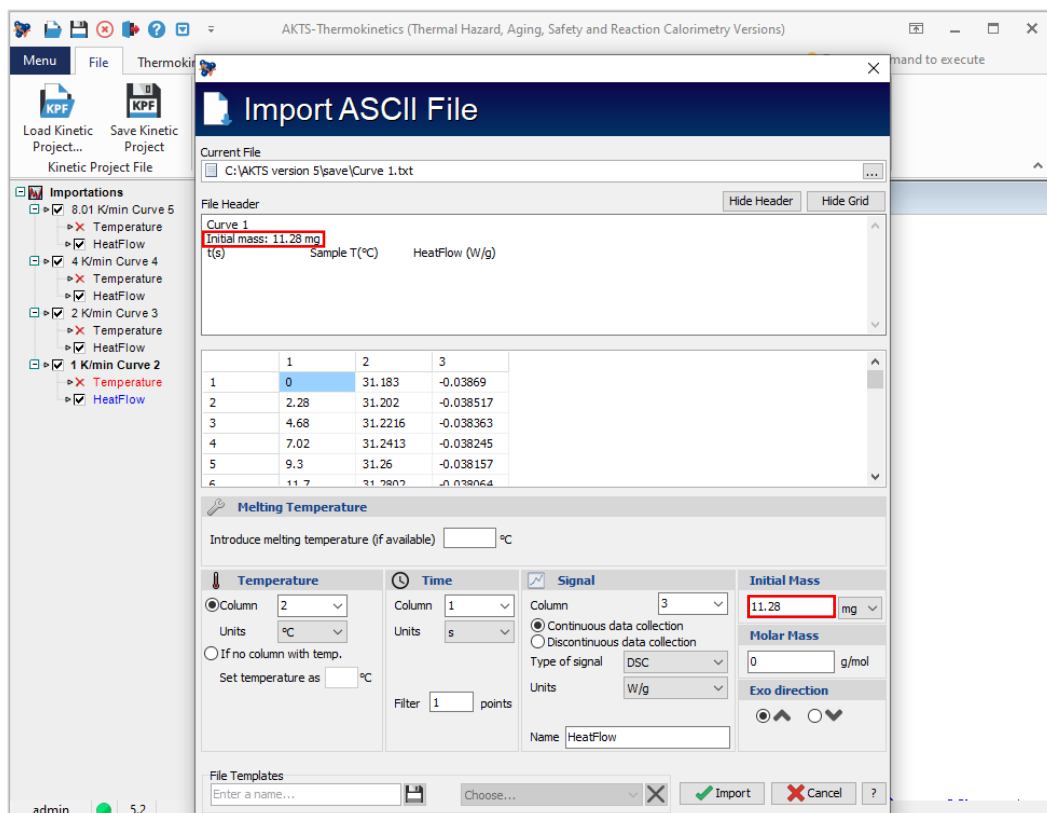
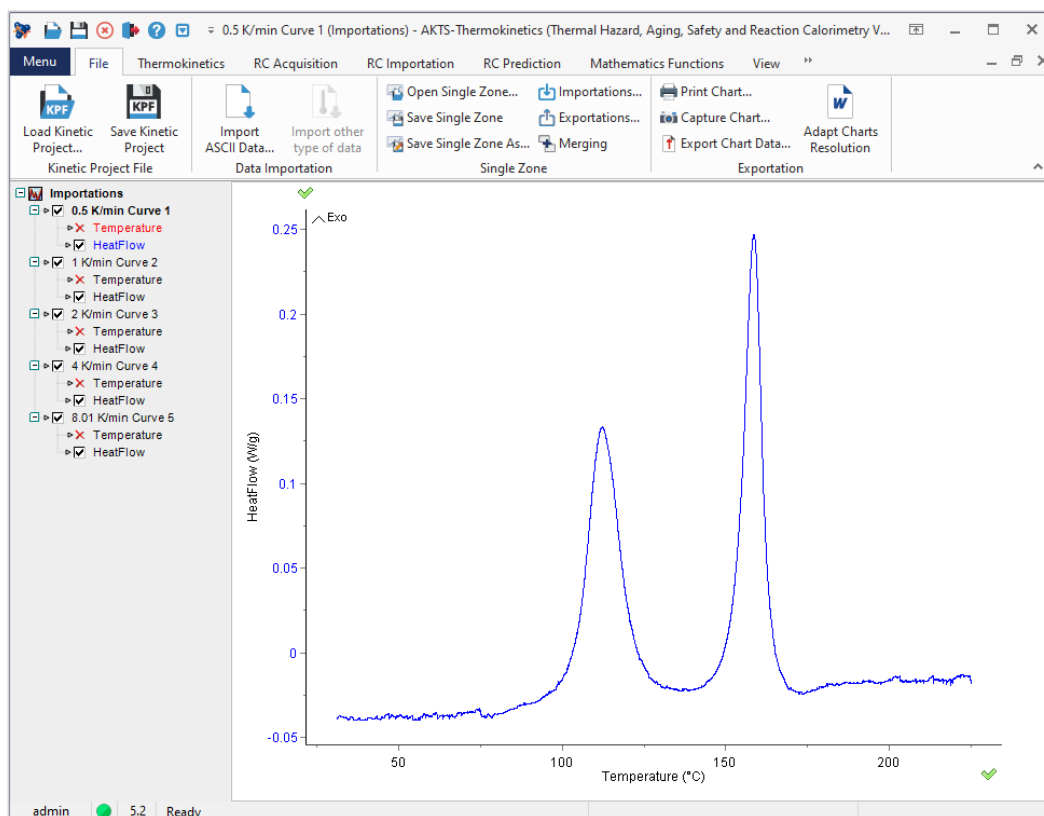


FIG. 10 - Introducing sample mass.





**FIG. 11** - DSC curve at 0.5 K/min.

After finishing data import, the labels of the curves are visible in the tree view under 'Importations' and the required signals can be selected to construct the baseline. The user has to construct two baselines only (generally for the first and last curve), for the remaining curves an automatic procedure can be applied.

## BASELINE CONSTRUCTION

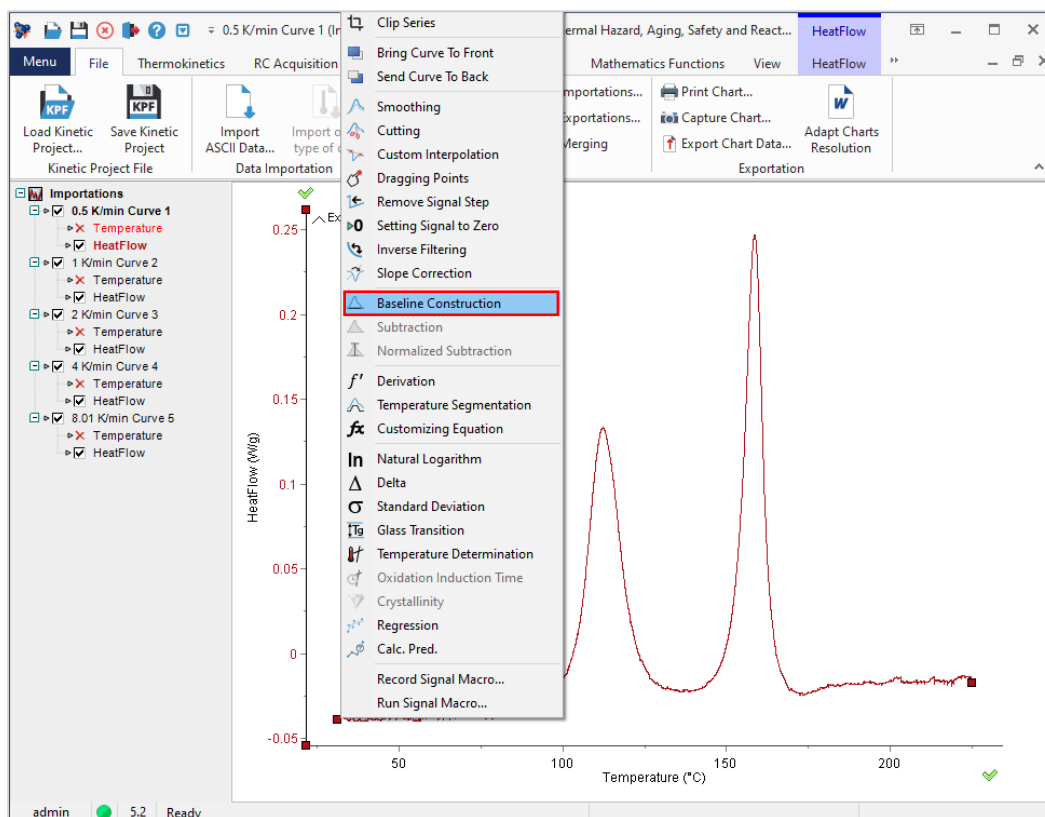
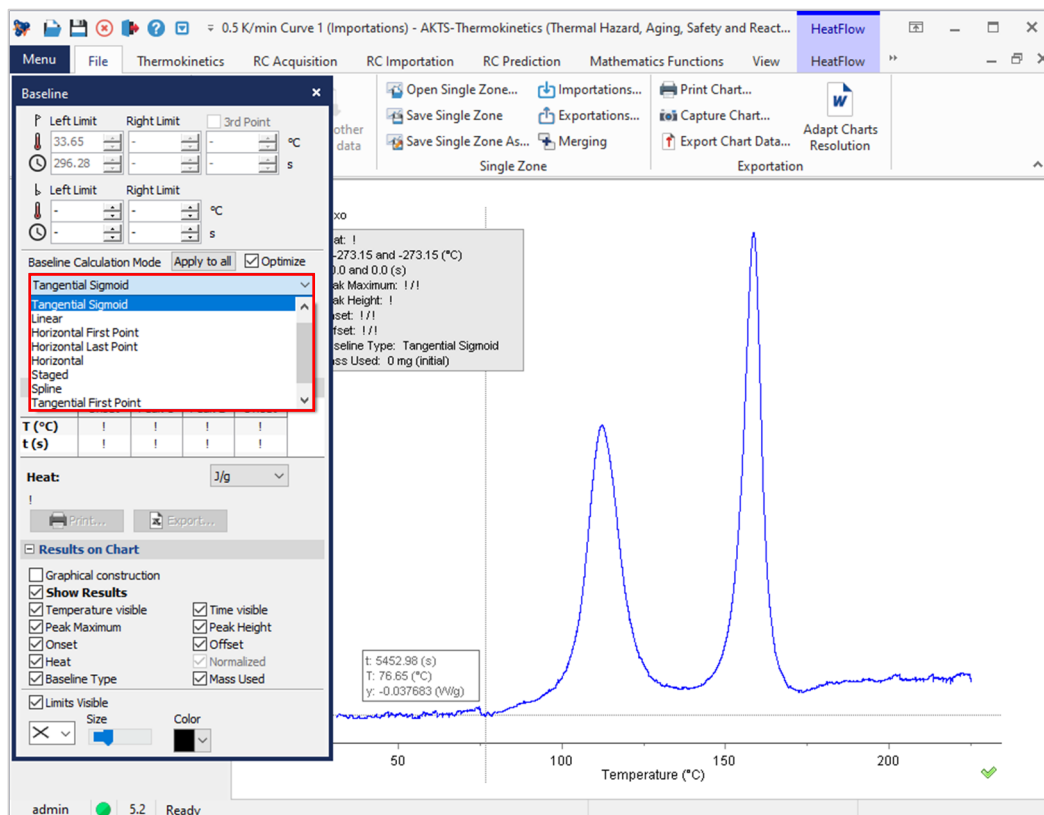


FIG. 1 - Baseline construction.

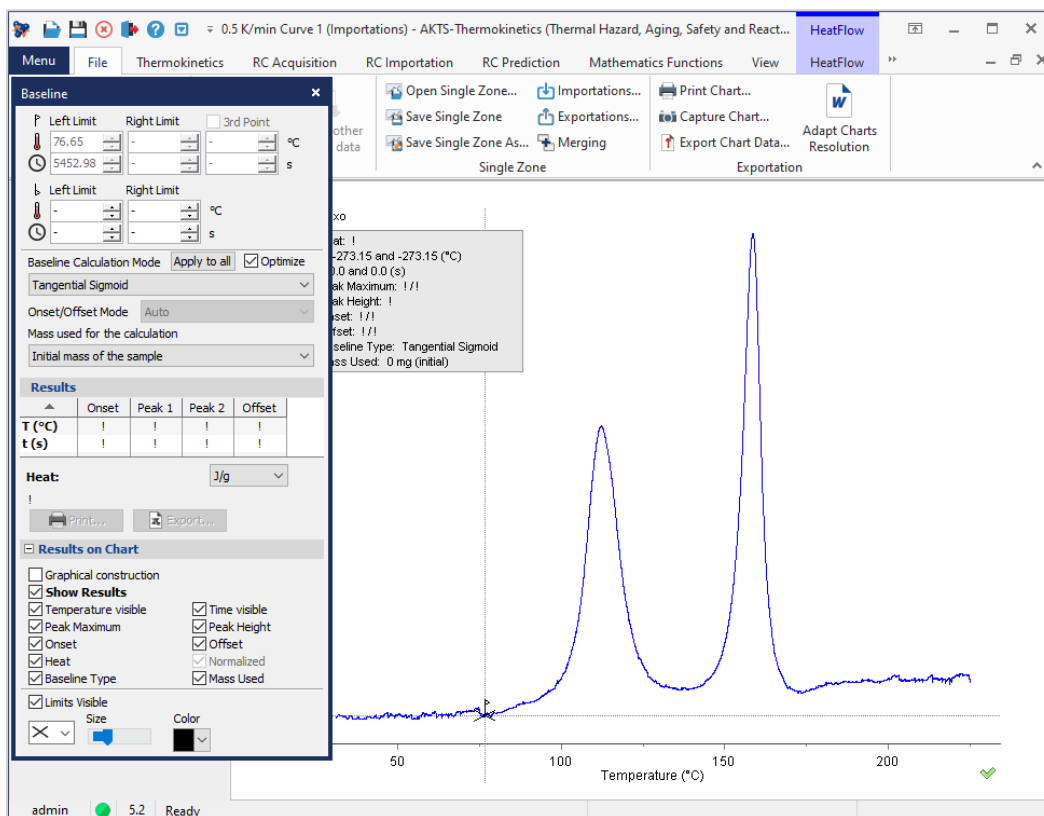
The baseline construction starts with a placing the cursor on the signal (the cursor icon should switch to a hand symbol) followed by the right click on the graph and selecting the option 'Baseline construction'.



After selecting '**Baseline Construction**' the window '**Baseline**' opens and the type of baseline can be chosen. (Remark: it is recommended to use the Baseline type '**Tangential Sigmoid**' for non-isothermal runs and '**Horizontal**' or '**Horizontal last point**' for isothermal runs).

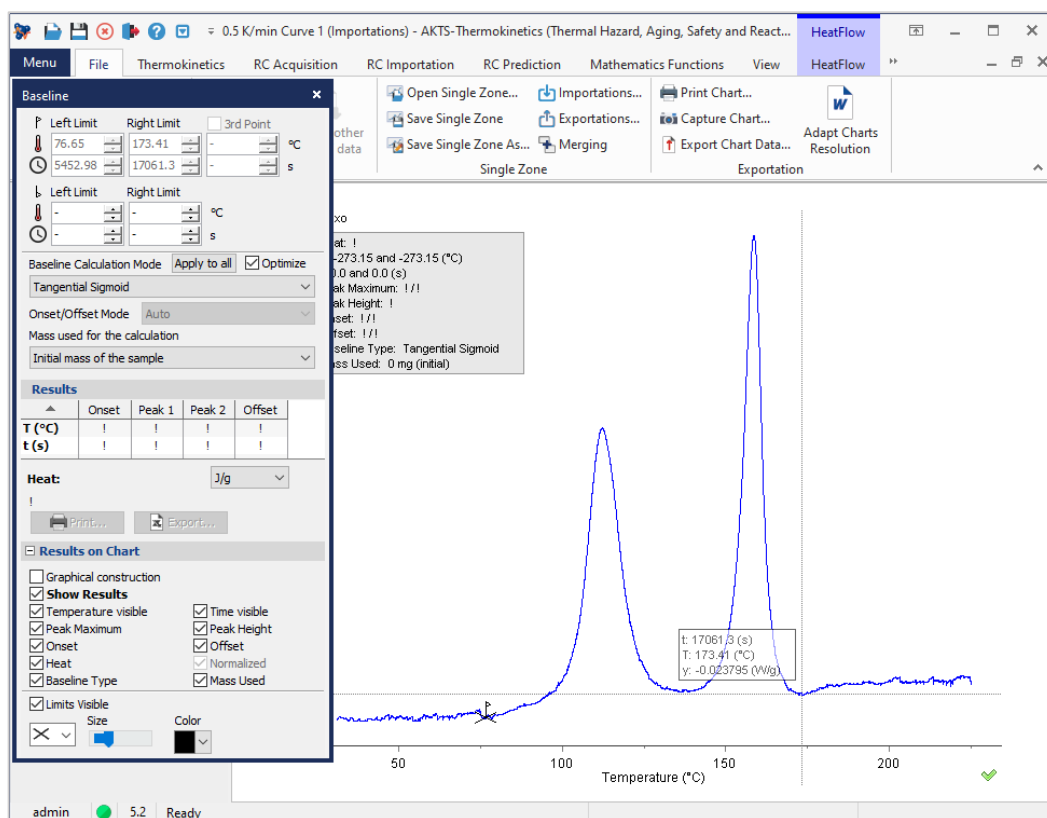
Next one has to select the left and right temperature limits between which the baseline will be constructed (integration limits).

The calculation of the baseline course proceeds automatically.



**FIG. 3** - Left temperature limit.

The left temperature limit indicates the point at which the heat flow curve starts to climb or descent in exo- or endothermic signals, respectively, and begins to deviate from the baseline. The choice of the left limit significantly depends on the sensitivity of the thermoanalytical device and shape of the measured signal.



**FIG. 4 - Right temperature limit.**

The right temperature limit should be placed at the end of the peak(s), where the signal returns to the baseline. A partial integration of the signal is also possible by choosing arbitrarily the right temperature limit at any temperature higher than left temperature limit.

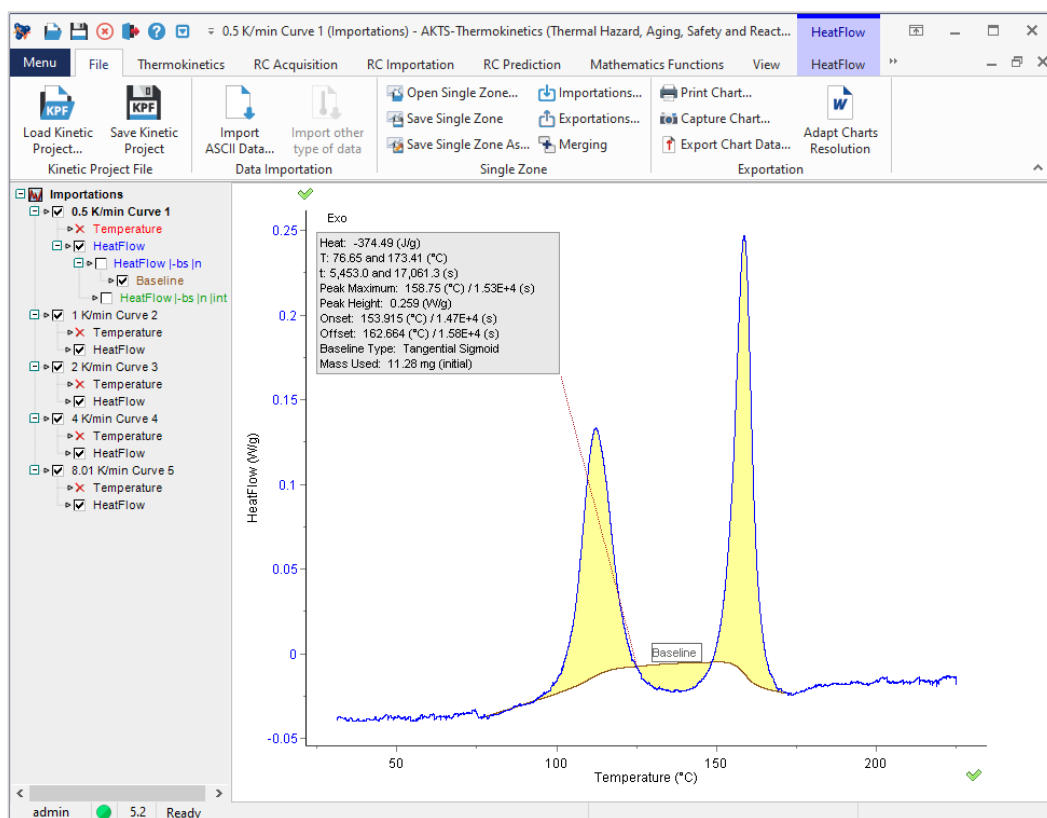


FIG. 5 - Improper baseline construction.

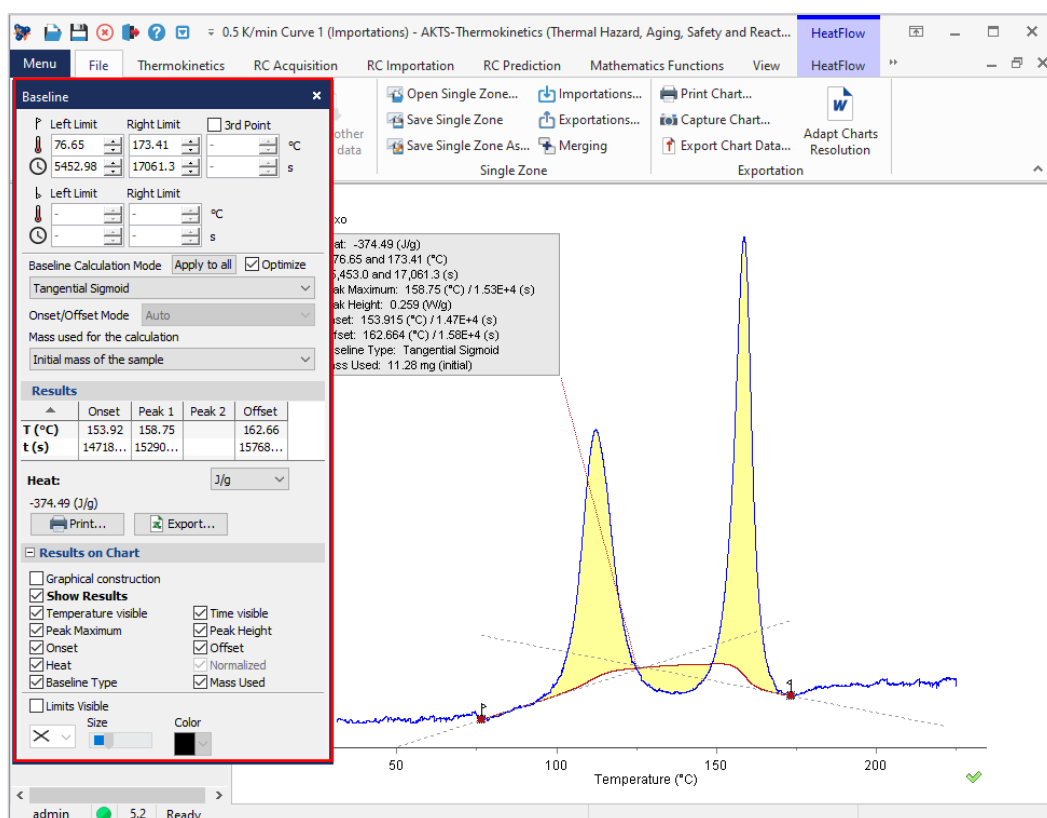


FIG. 6 - Opening the 'Baseline' window for manual baseline adjustment.

In case of applying 'Tangential Sigmoid' a double check of the tangents is required before continuing because it can happen that a manual adjustment is needed (see above). In this case, one has to select the baseline (double click) and change the tangents at chosen left and right temperatures accordingly. (Remark: the tangents can be only modified if the window 'Baseline' is visible).

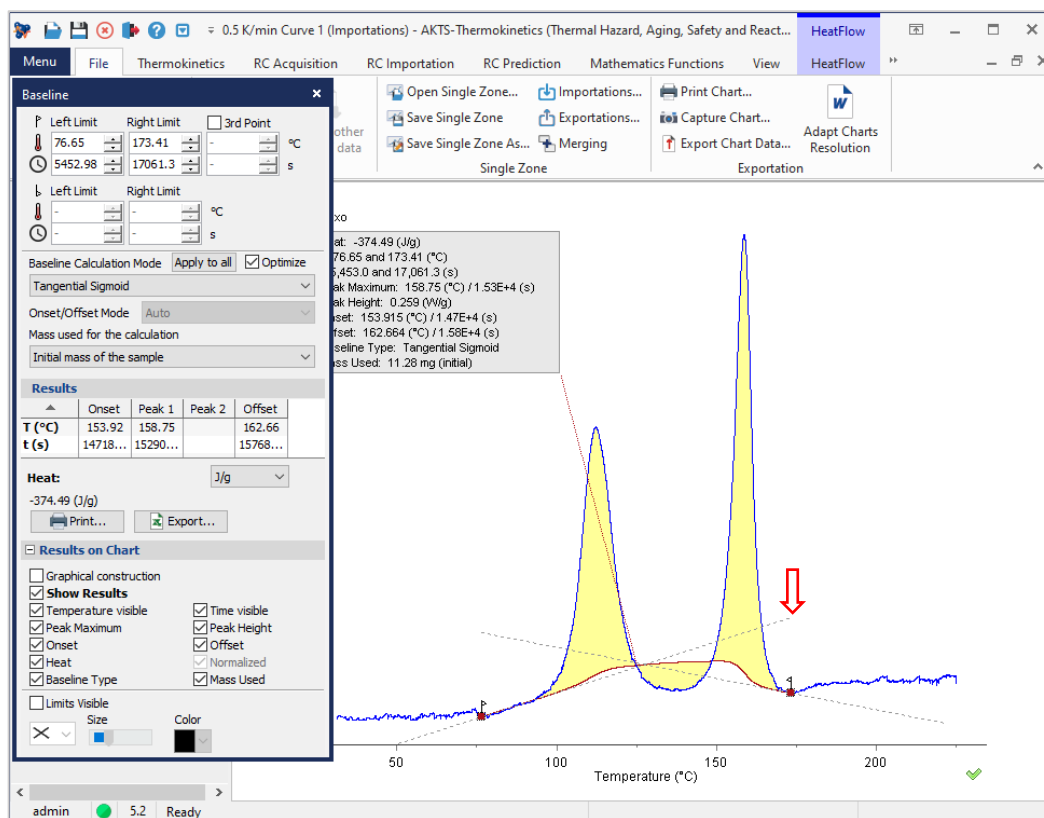


FIG. 7 - Adjustment of the tangent at left temperature limit.

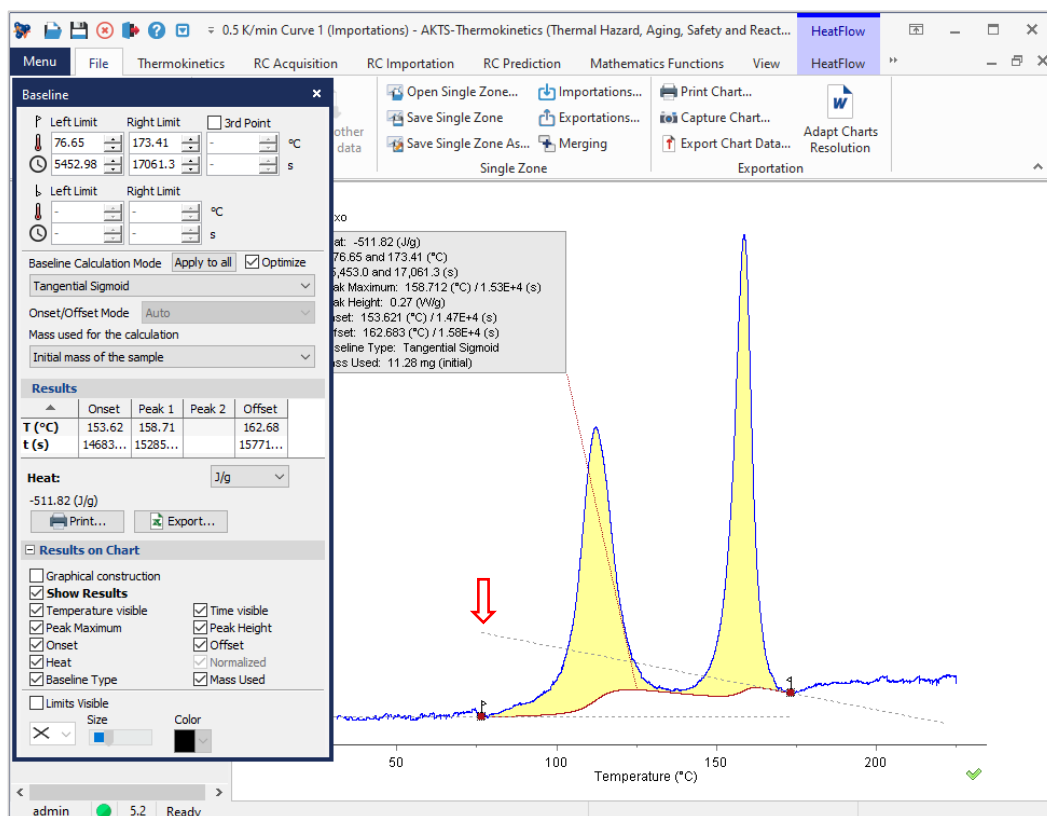


FIG. 8 - Adjustment of the tangent at right temperature limit.

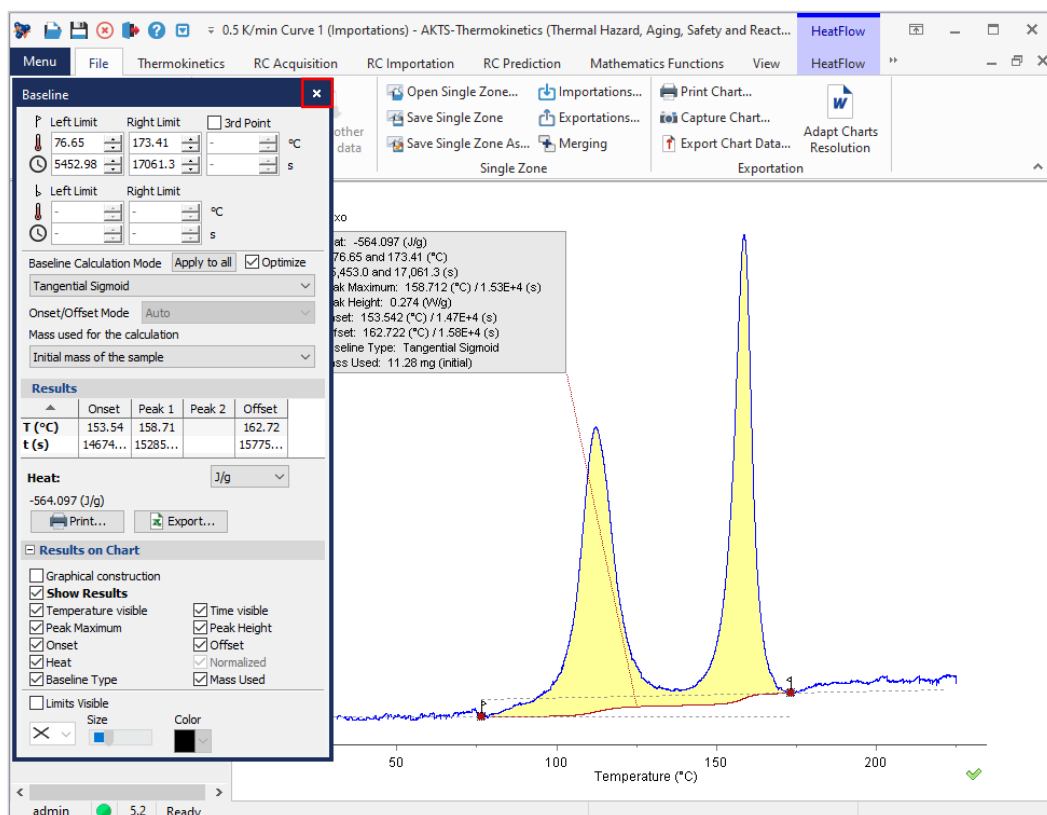
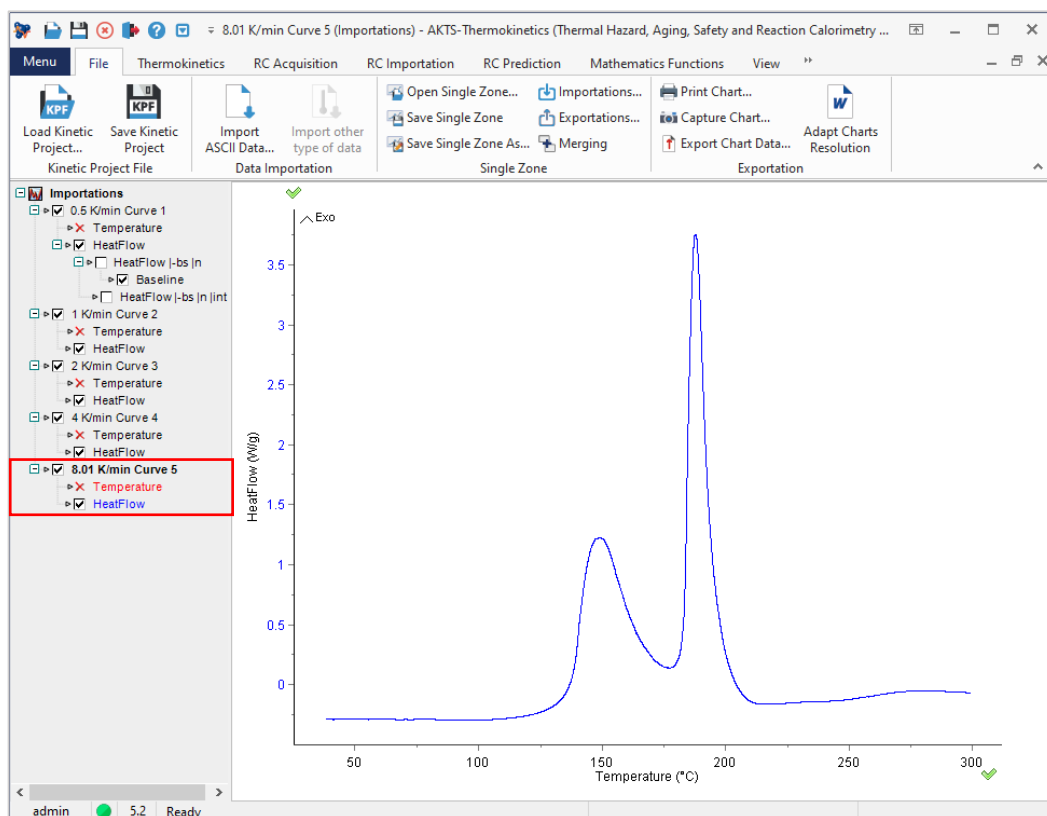


FIG. 9 – Final course of the baseline.

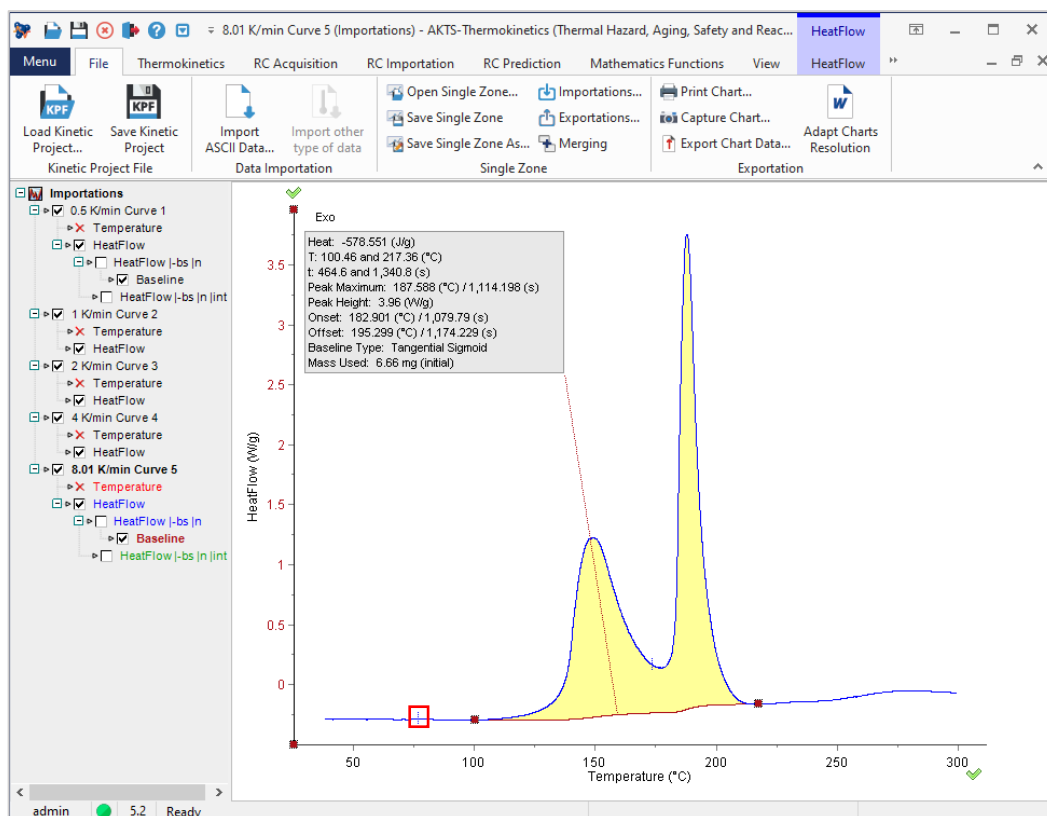
After final adjustment of the baseline, the window 'Baseline' can be closed.





**FIG. 10** - DSC curve at 8 K/min.

Next step is the construction of the second baseline, usually for the curve recorded with the fastest heating rate, i.e. in this example 8 K/min.



**FIG. 11** - Evaluation of left temperature limit at 8 K/min.

The construction of the baseline is performed in the same way as already explained before. The blue tick mark (see red square) placed on the signal represents the temperature of the left limit of the baseline chosen for the lowest heating rate of 0.5 K/min. The position of this limit helps to select the left temperature limit for 8 K/min, which has to be placed at temperature higher than for signal recorded at 0.5 K/min. (Remark: in general, by increasing scanning rates the temperature ranges of the reaction are shifted to higher temperatures. Therefore, the left and right temperature limits for the remaining signals should be placed between those chosen for the lowest and highest heating rates i.e. 0.5K/min and 8 K/min, respectively).

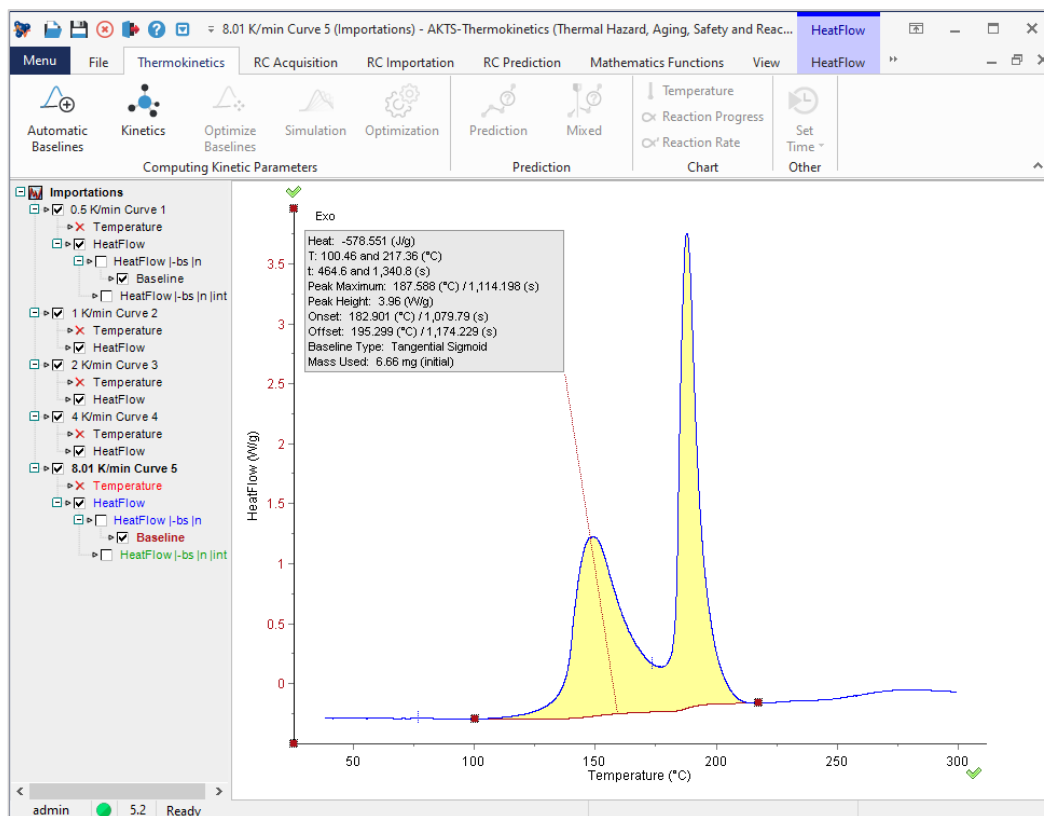
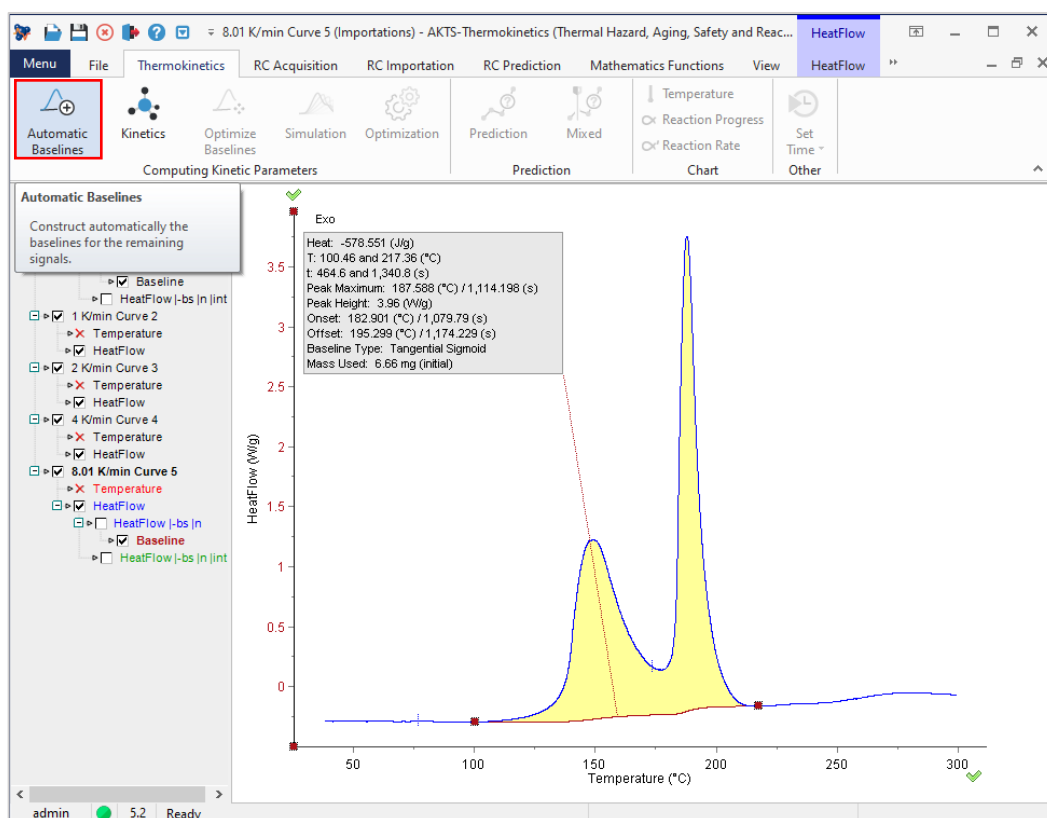


FIG. 12 - Final course of the baseline at 8 K/min.



**FIG. 13** - Automatic baseline construction.

For the remaining signals the option 'Automatic Baselines' is applied to construct the missing baselines automatically. However, it is necessary to check all curves after automatic option if an additional manual adjustment is required or not. It is necessary to check visually the constructed baselines if the tangents at left and right limits are in-line with the signals. Secondly, the standard deviation of the reaction heat determined at all heating rates should not exceed 10% because higher deviations may indicate or poor data quality or incorrect baseline construction.

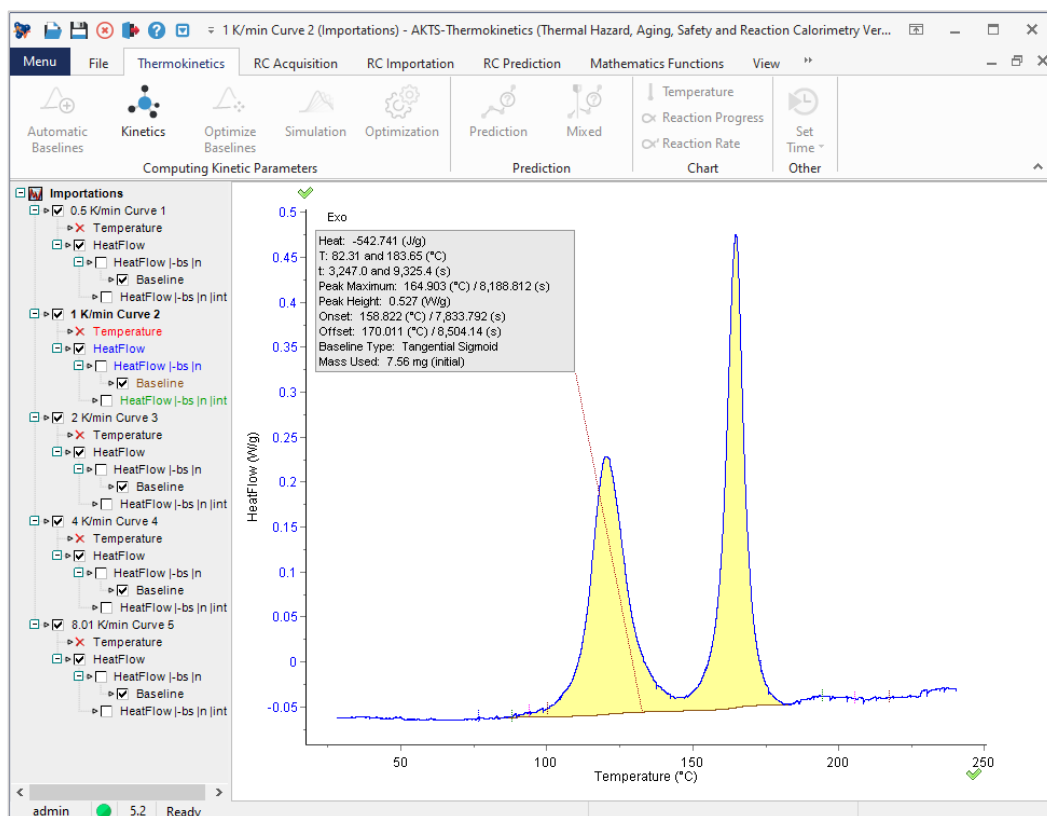


FIG. 14 - Baseline construction at 1 K/min.

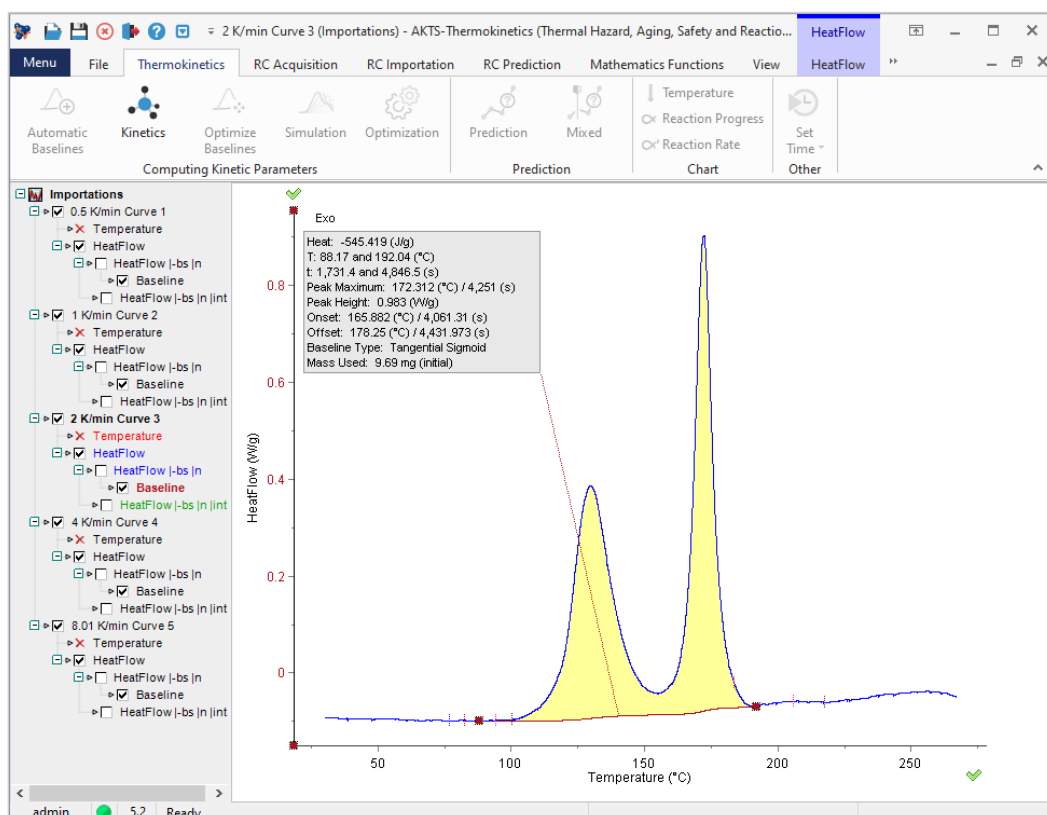
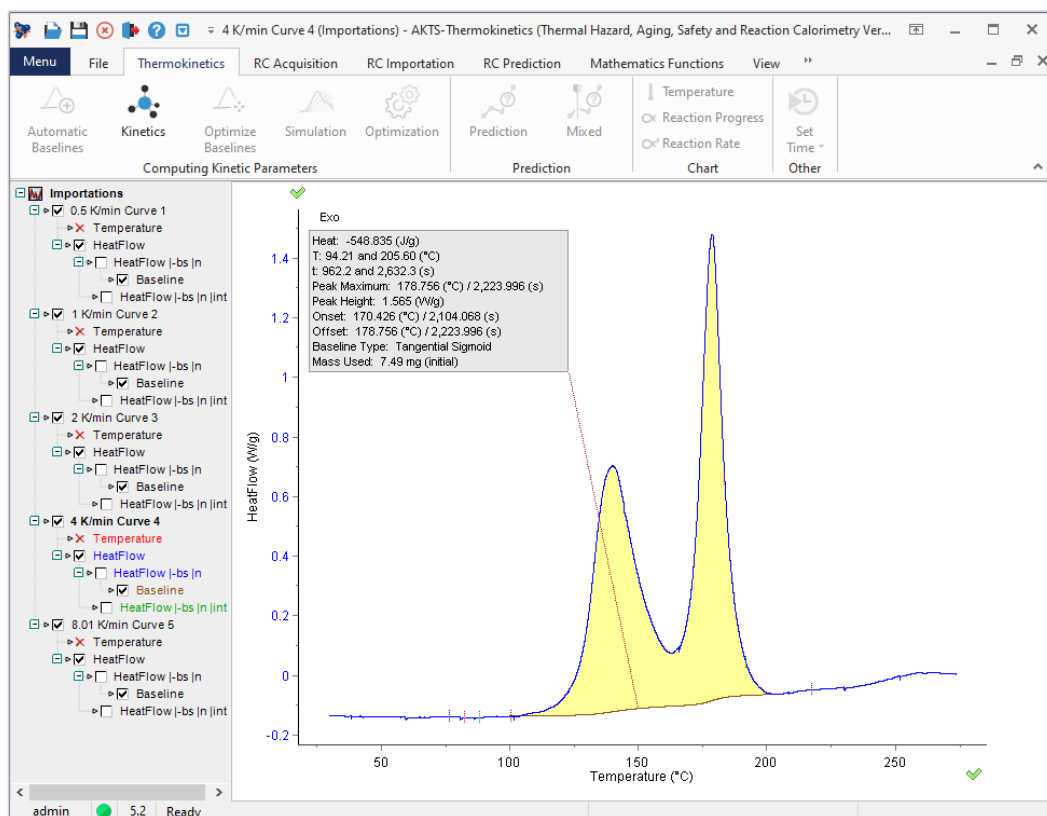


FIG. 15 - Baseline construction at 2 K/min.



**FIG. 16** - Baseline construction at 4 K/min

## DIFFERENTIAL ISOCONVERSIONAL KINETIC ANALYSIS

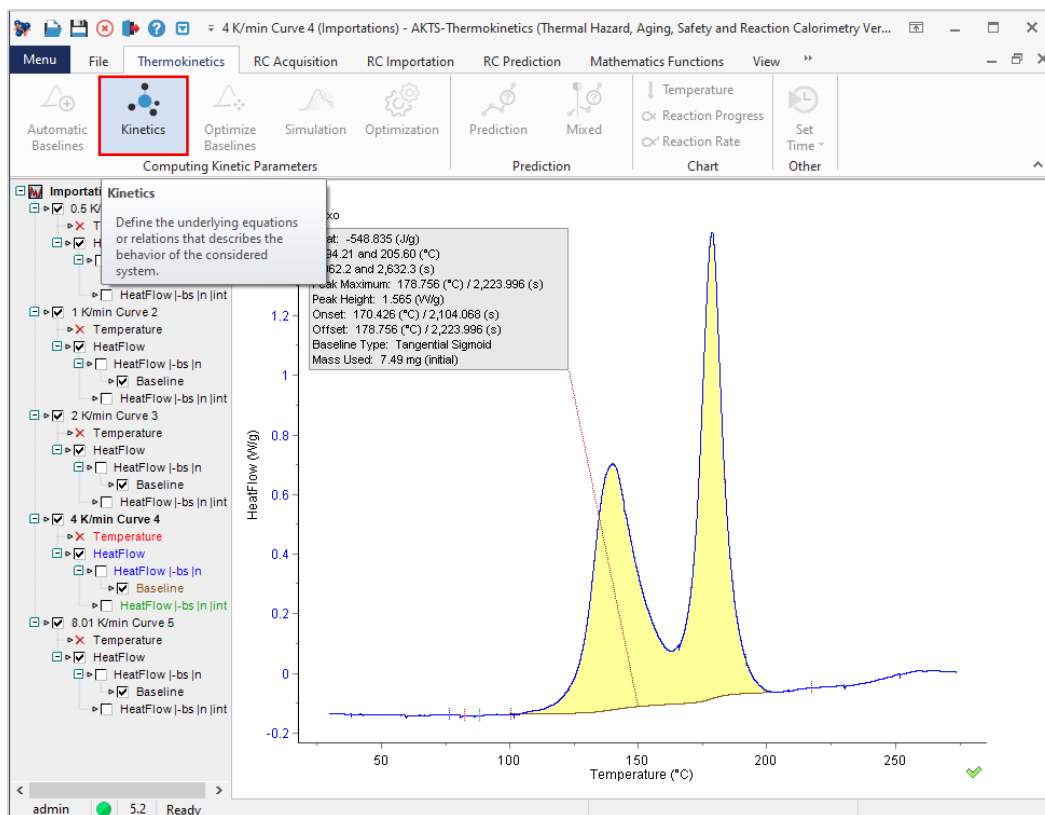


FIG. 1 - Start of the kinetic analysis.

After checking correctness of the baseline constructions, the user can begin the kinetic analysis of the recorded data. The differential isoconversional analysis starts after choosing the tool “Kinetics”, see red square marked above.

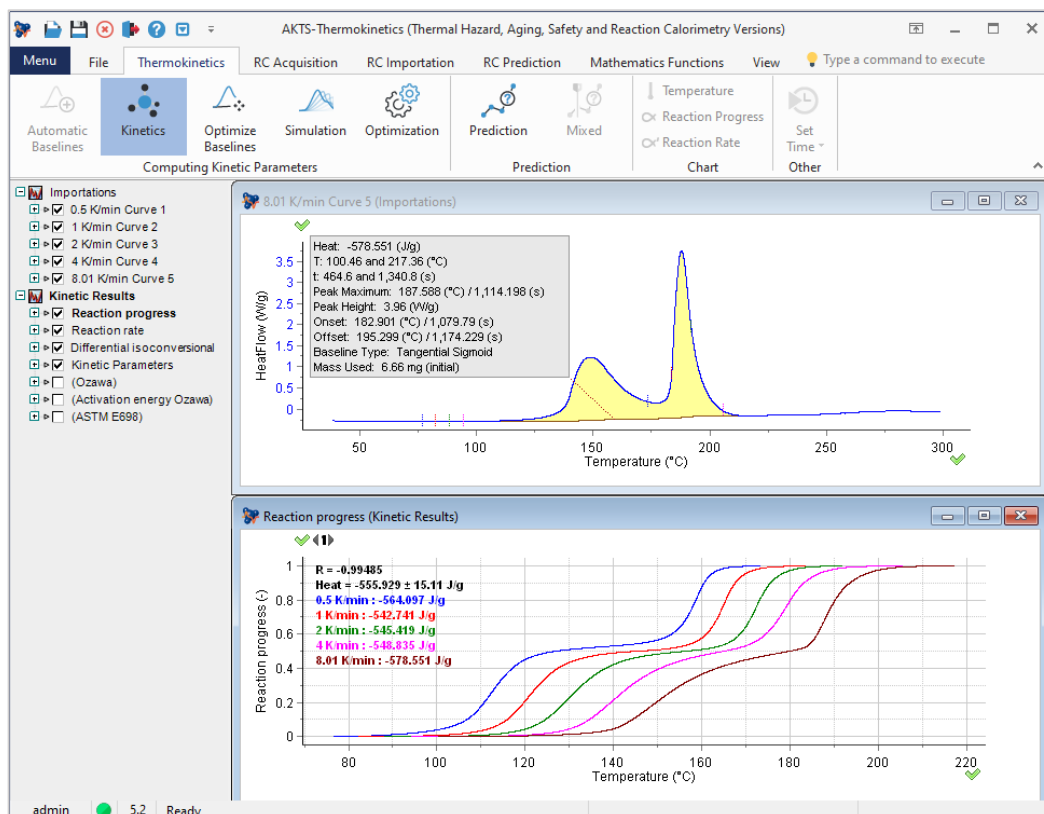


FIG. 2 - Reaction extent alpha as a function of temperature for all heating rates.

In the first stage the reaction extent vs temperature is calculated in the form of  $\alpha$ -T dependence (plot above).

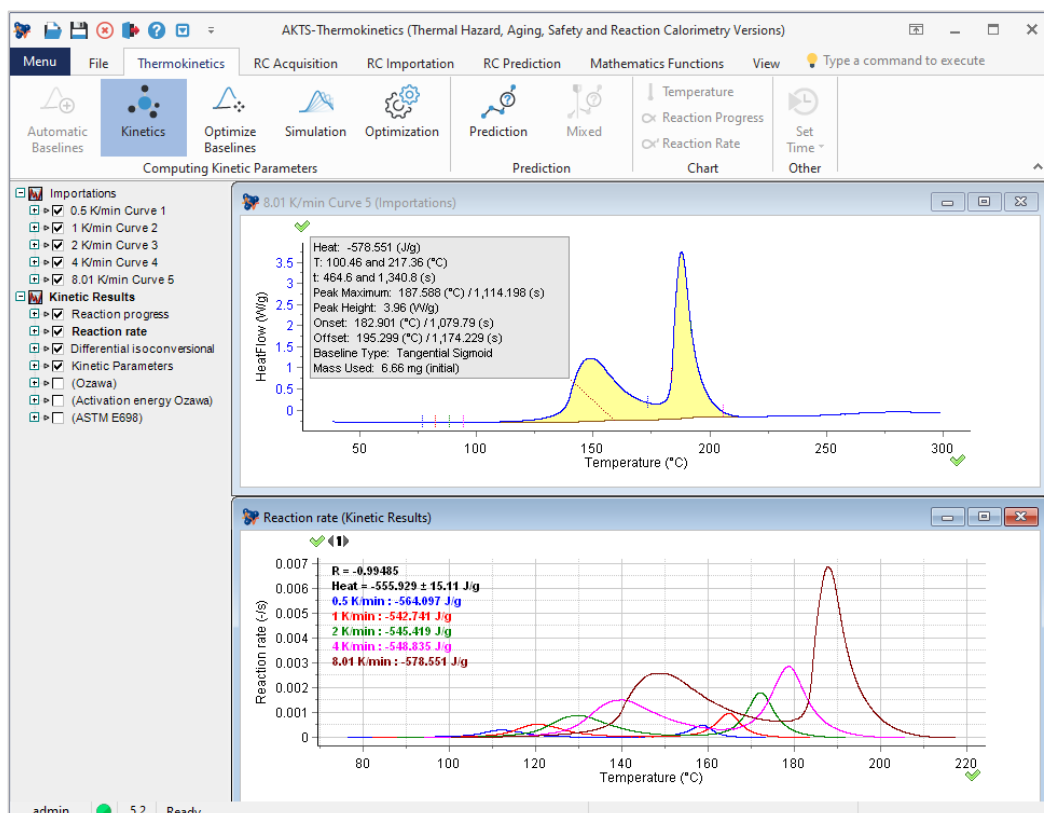


FIG. 3 - Reaction rates as a function of temperature for all heating rates.

In the second stage the plot showing the dependence of the reaction rate on temperature at all heating rates is created.

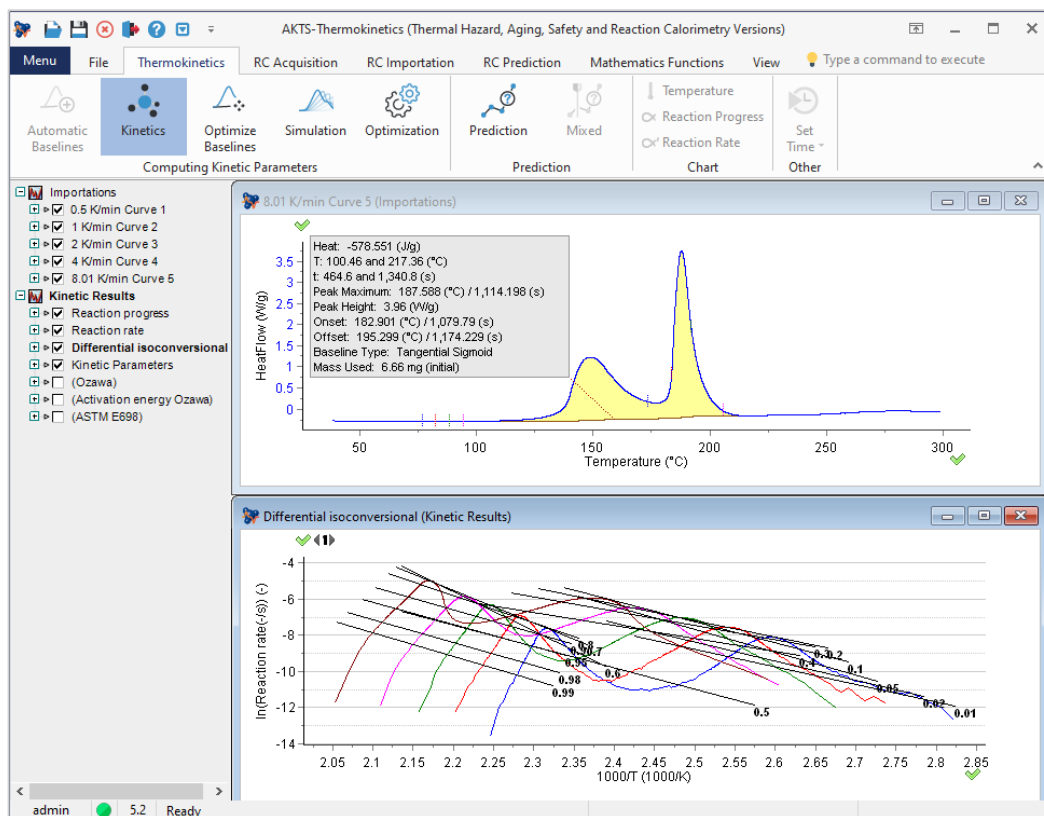


FIG. 4 - Differential isoconversional analysis.

In the third stage the logarithms of the reaction rates are presented as a function of the reciprocal temperature for the different heating rates.

In the differential isoconversional analysis, the slopes and intercepts of the lines drawn through the isoconversional points (points at which the values of the reaction extents 'alpha' are the same) at different heating rates enable the determination of:

- ▶ The activation energy  $E(\alpha)$ ,
- ▶ The term combining the pre-exponential factor  $A(\alpha)$  with the  $f(\alpha)$  i.e. the kinetic model in the form:
  - $\ln(A(\alpha) \cdot f(\alpha))$



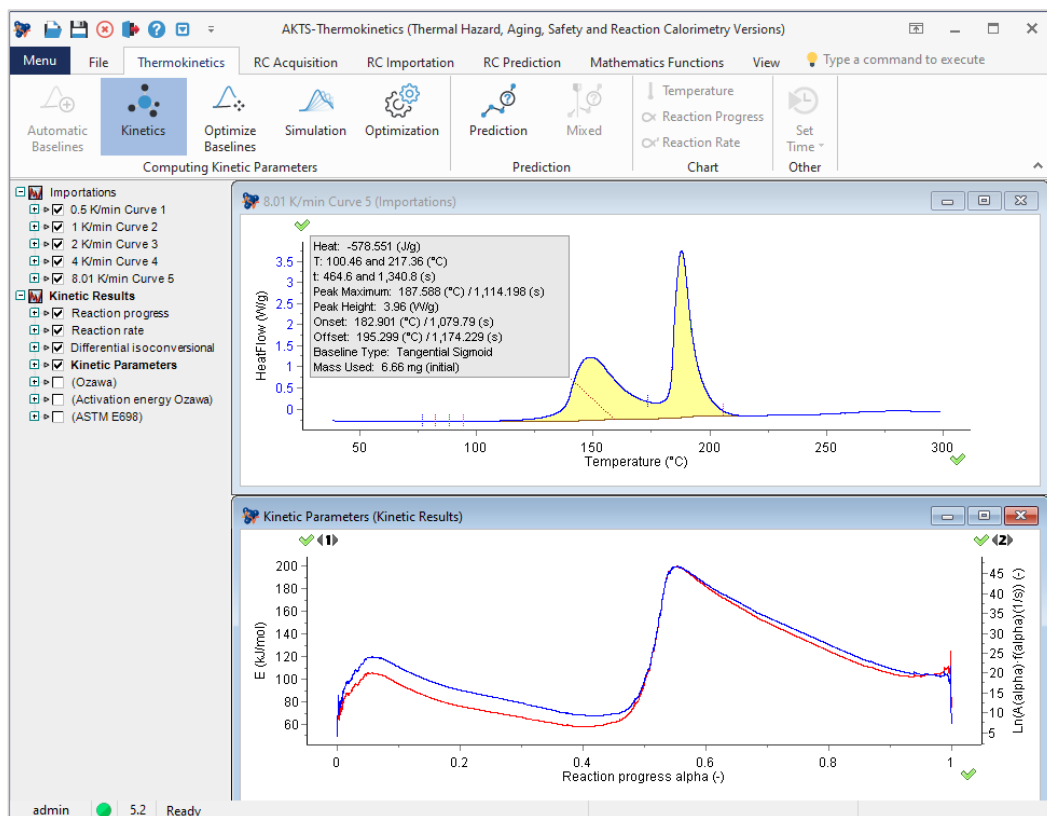


FIG. 5 – Dependence of the kinetic parameters on the reaction extent  $\alpha$ .

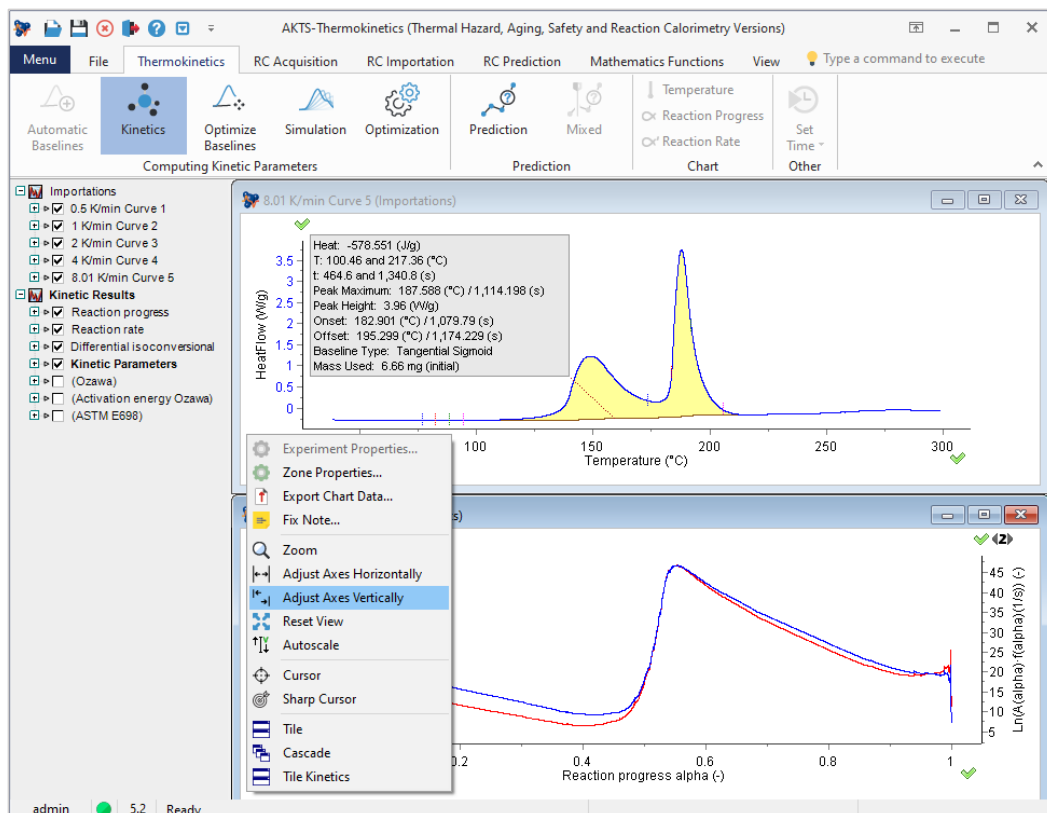
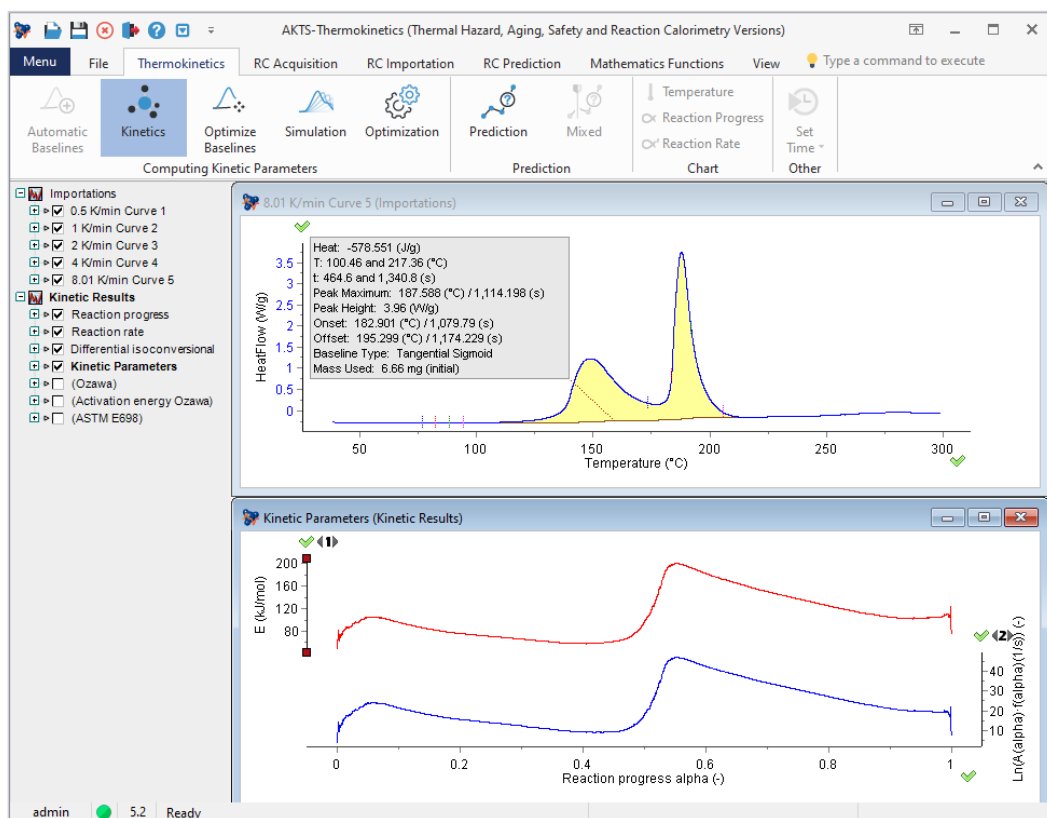
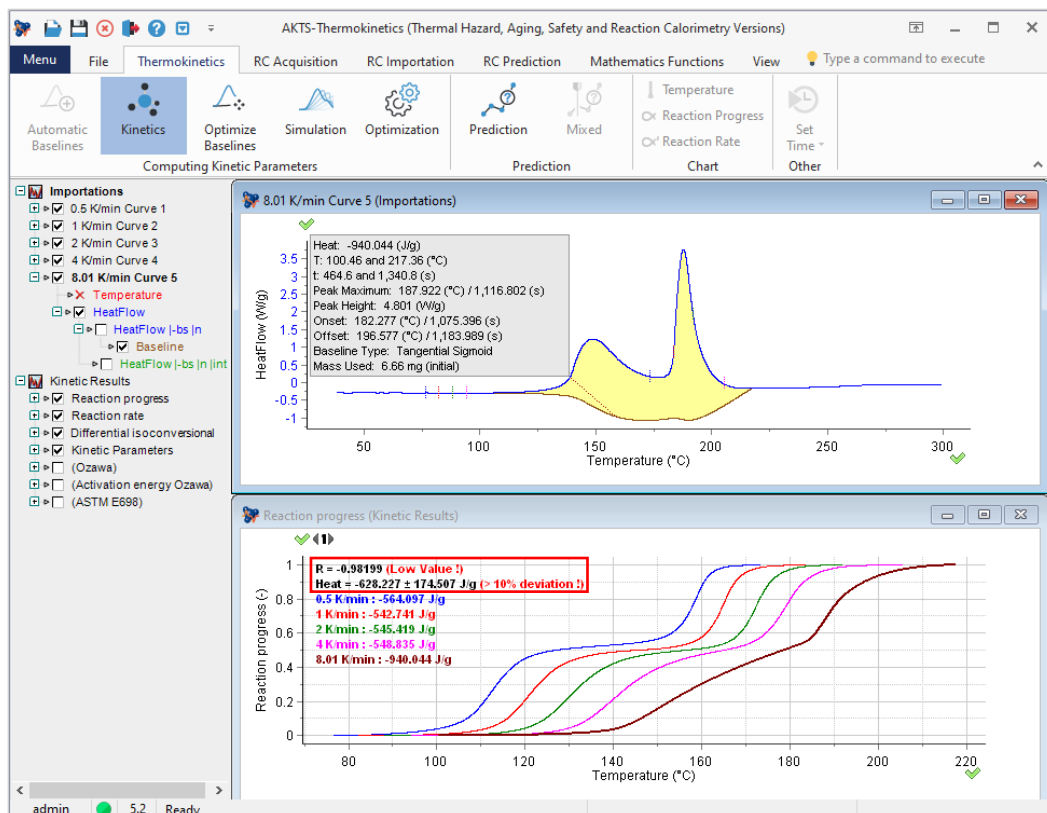


FIG. 6 - Option 'Adjust Axes Vertically'.

For a better presentation of the dependence of kinetic parameters on the reaction progress one can split both curves with the option 'Adjust Axes Vertically' by placing the cursor on the panel and right click.



**FIG. 7** - Display the dependence of the kinetic parameters on the reaction progress after action "Adjust Axes Vertically".



**FIG. 8** - Warnings indicating that the criteria of proper construction of the baseline are not fulfilled.

Improper construction of the baselines may significantly influence the results of the kinetic analysis. In AKTS TK Software two criteria have to be fulfilled in order to evaluate the meaningful kinetic parameters:

- ▶ **Criterion 1:** The average correlation coefficient R of all straight lines plotted in isoconversional coordinates should amount to at least -0.99
- ▶ **Criterion 2:** Standard deviation of the reaction heats determined at all heating rates should not exceed 10%

In TK Software, two methods for improving the baseline construction may be applied:

- ▶ Manual adjustment of the baselines
- ▶ Optional: 'OBsl' = Optimize Baselines = Automatic adjustment of all baselines

Remark: the user should always try manually to improve the baseline construction first before proceeding with option 2, because 'OBsl' can be used only for fine-tuning. In case of an incorrect, illogical baseline (see below), it makes no sense to start the automatic adjustment because the construction is too far away from the optimal ones. Figure 8 shows the case when both criteria are not fulfilled what is indicated by the warnings displayed in red.

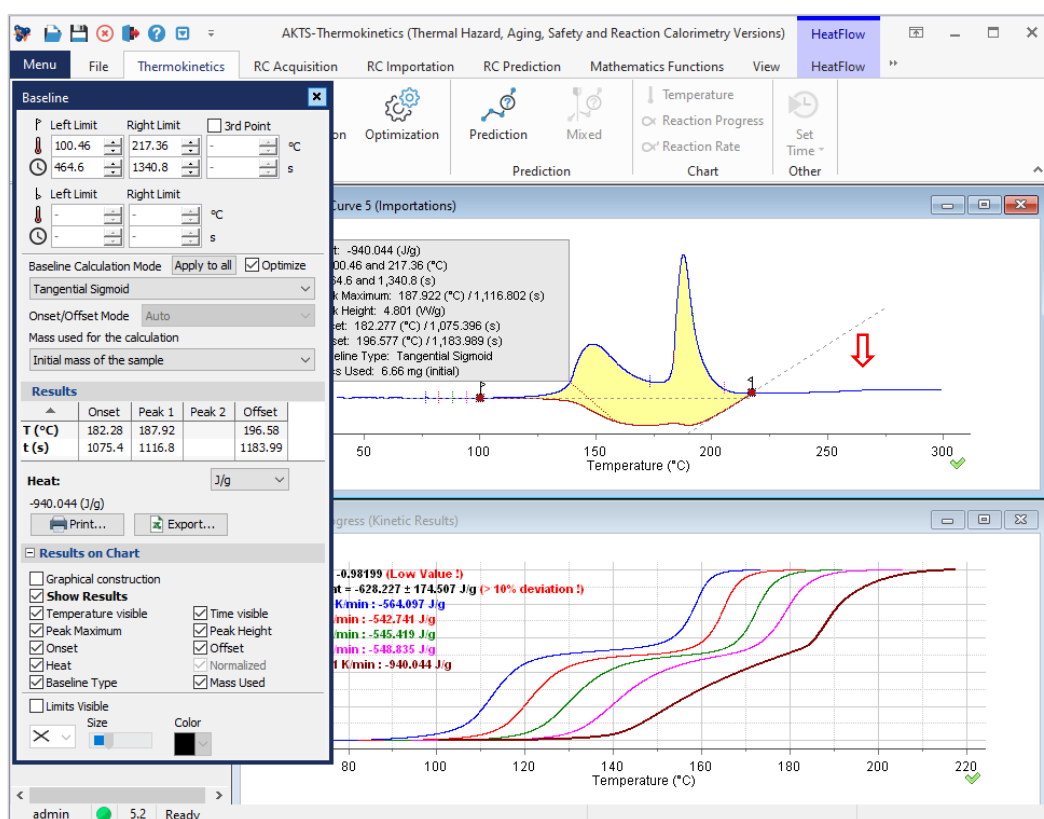


FIG. 9 - Improper baseline construction.

Improper baseline construction for the signal recorded at a certain heating rate which is not consistent with other baselines influences the course of  $\alpha$ -T dependence and results in improper kinetic data. Warnings Low Value! or deviation > 10% appear if criteria 1 or 2 are not fulfilled.

Optionally the user can try to improve and optimize the construction of the baselines by using the corresponding tool marked by red square below. This procedure is slightly changing the tangents at the left and right limits for the signals recorded at all heating rates in order to improve the criterion 1 (R-value) by achieving a value closer to -1. (Remark: If the R value after manual adjustment is already close to -1 the user can skip this option).

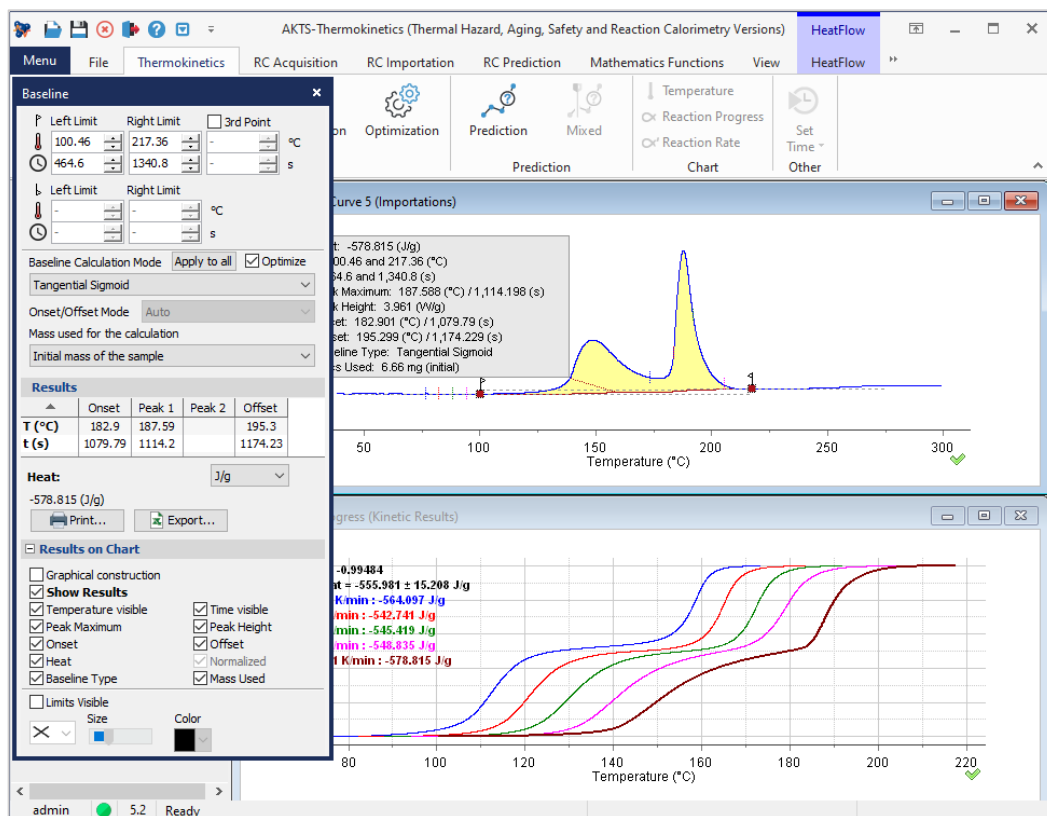


FIG. 10 - Corrected baseline.

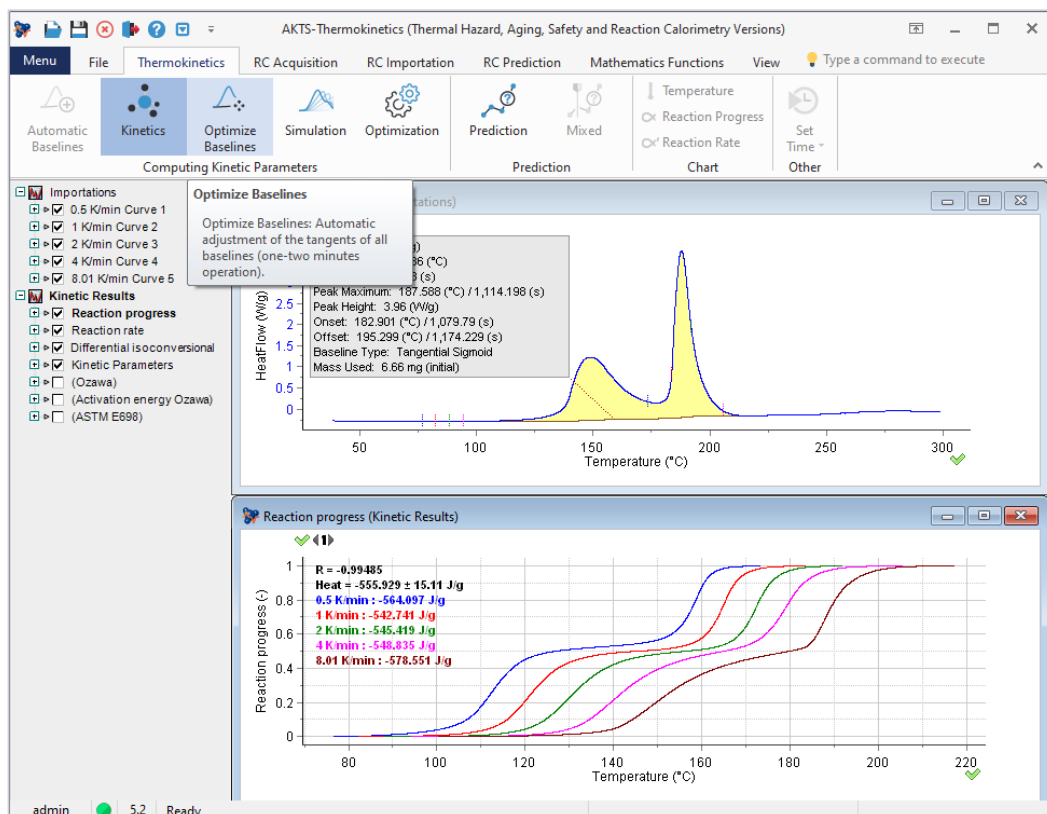
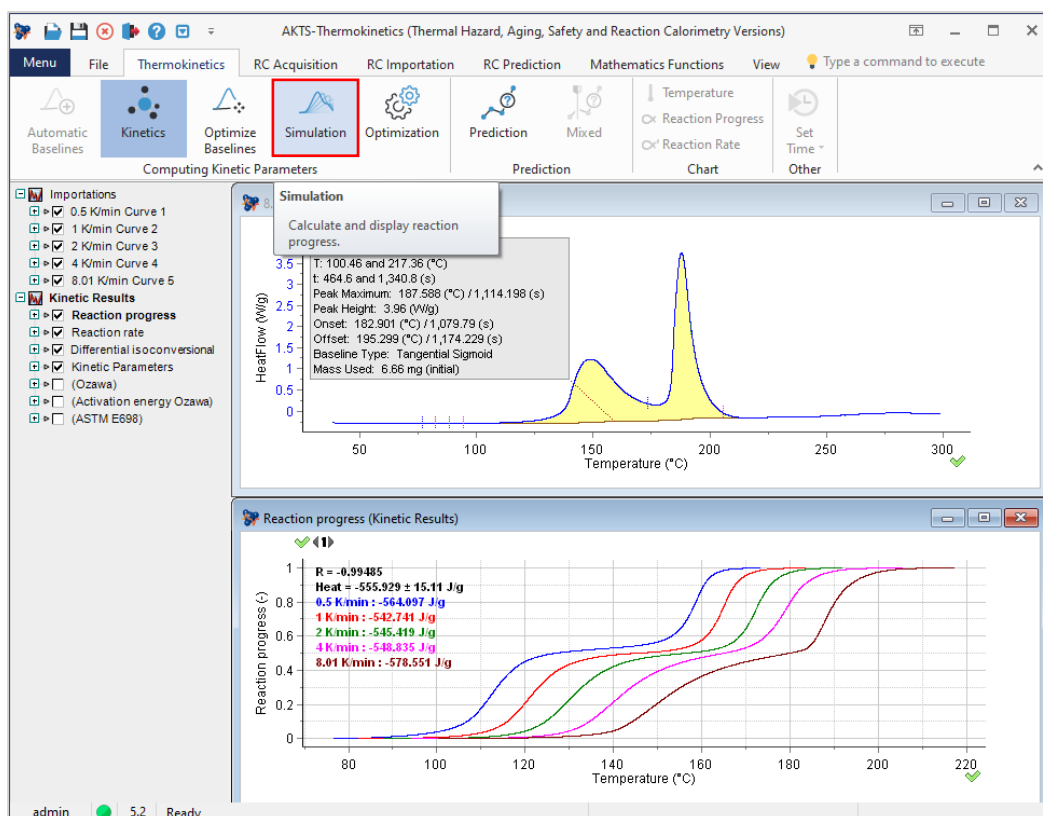
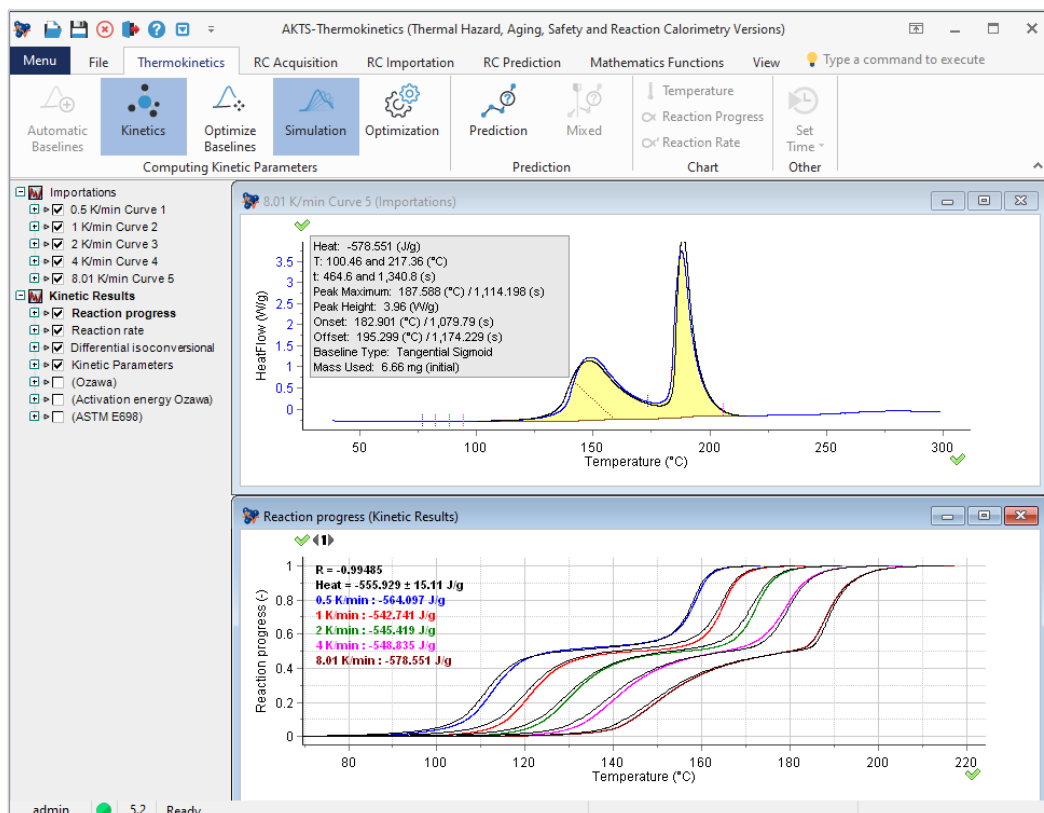


FIG. 11 - Optimization of the baselines (Fine-tuning).

After baseline adjustment the kinetic parameters are calculated and used to simulate and display the reaction progress for all measured heating rates. This procedure starts after choosing the tool 'Simulation', see below.



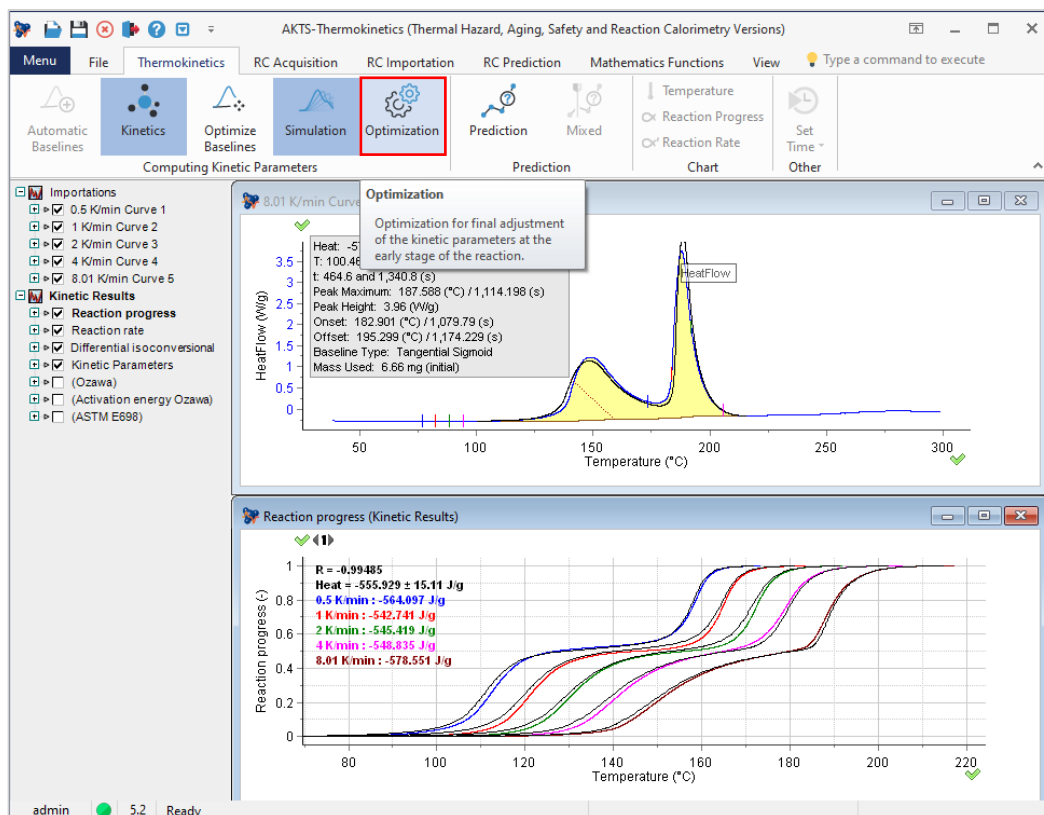
**FIG. 1** - Tool 'Simulation' applying the kinetic parameters for simulation the reaction course at different heating rates.



**FIG. 2** - Tool "Simulation" - Comparison of simulated (black) and experimental (coloured lines) reaction rate at 8K/min (top) and reaction courses at different heating rates (bottom).

The thermoanalytical peak (e.g. the signal of a heat flow rate as in a case of DSC) is placed between the points of departure from (left limit) and return to the baseline (right limit). The choice of such point significantly depends on the sensitivity of the thermoanalytical device and shape of the measured signal. The temperature of the reaction beginning, increases when the heating rate increases. Often the beginning and the end of the recorded signal are not well defined, therefore the reliable information concerning the reaction course are generally possible in the range of alpha between 0.01 and 0.99.

The better prediction can be achieved after further optimization of the kinetic parameters.



**FIG. 3** - Optimization for final adjustment of the kinetic parameters

The tool 'Optimization' (marked in red above) opens a popup window allowing optimization of the kinetic parameters.

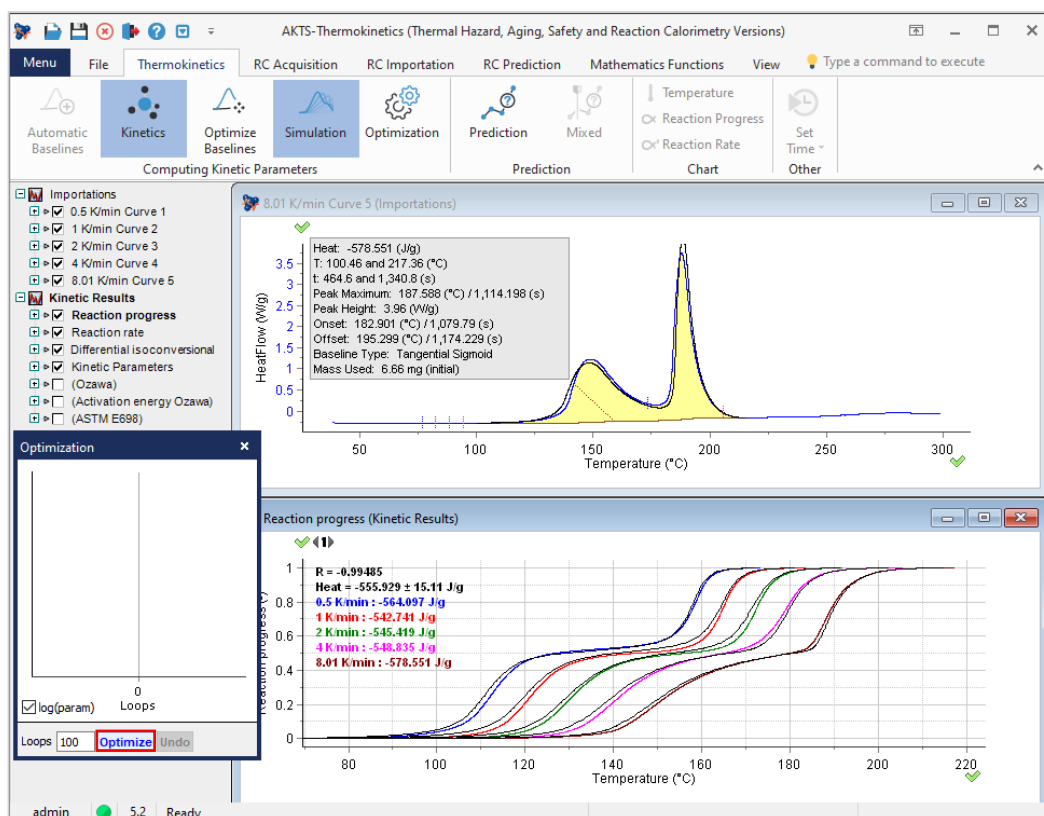


FIG. 4 - Start of the optimization procedure.

The optimizing procedure starts by choosing the “Optimize” Tool (marked in red, see above).

In general, 100 loops are enough to achieve a good fit between simulations (black) and measurements (coloured curves). In case of any doubts, the user can repeat the optimization procedure or undo it.

Remark: if both criteria (R value and standard deviation of the reaction heat) are fulfilled, the user can expect a good fit of experimental signals by simulated curves. If this is not the case, further optimization is needed, i.e. more optimization loops than 100 are necessary.

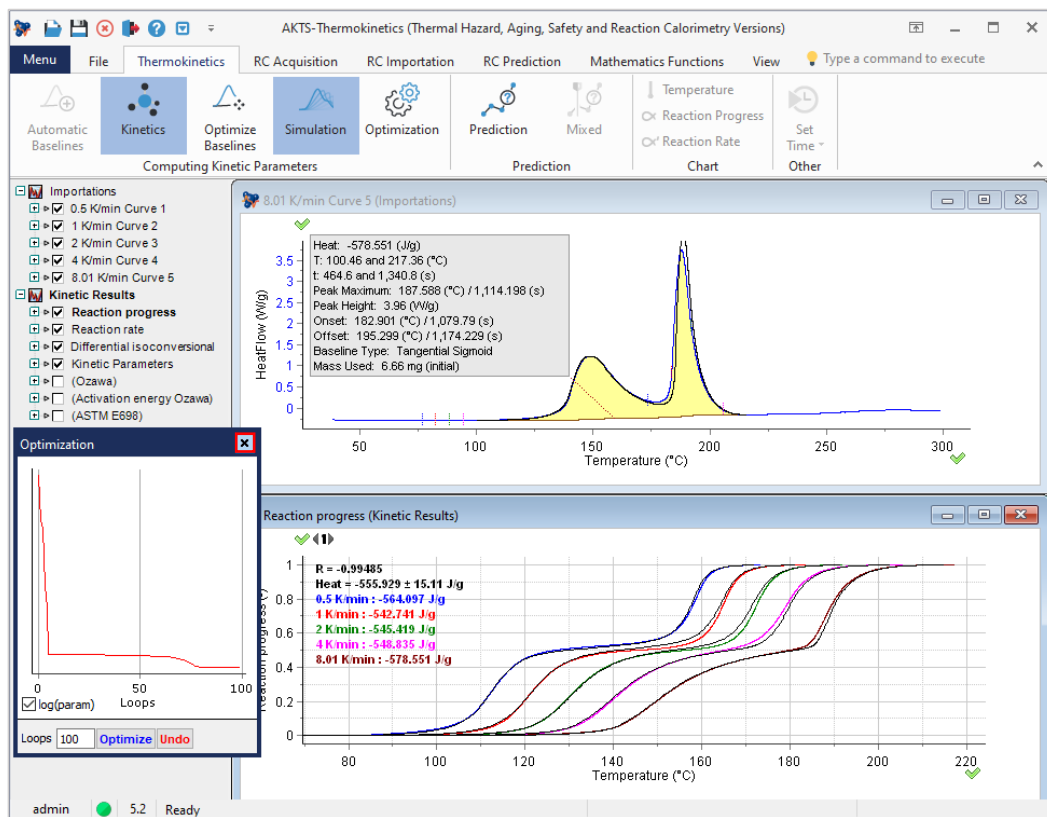


FIG. 5 - Optimization procedure finished.

After adjustment of the kinetic parameters the simulations (black curves) fit much better the experimental reaction course. The user can close the optimization window and continue with saving results of the kinetic analysis.



## SAVING THE 'KINETIC PROJECT FILE' (\*.KPF)

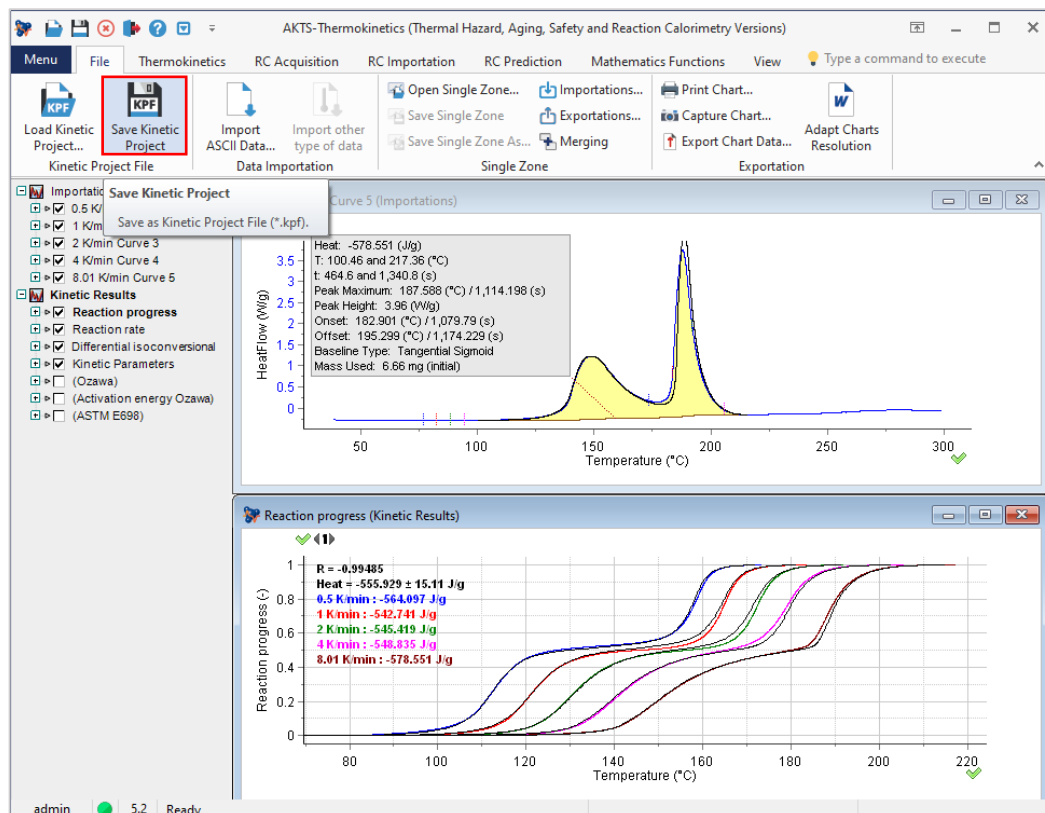


FIG. 1 - Saving the 'kinetic project file' (kinetic analysis data).

Before using the final results of the kinetic analysis for further predictions, one should save the kinetic analysis / kinetic project file (= \*.kpf file). The kinetic data can be saved using "Save Kinetic Project" Tool (marked in red).

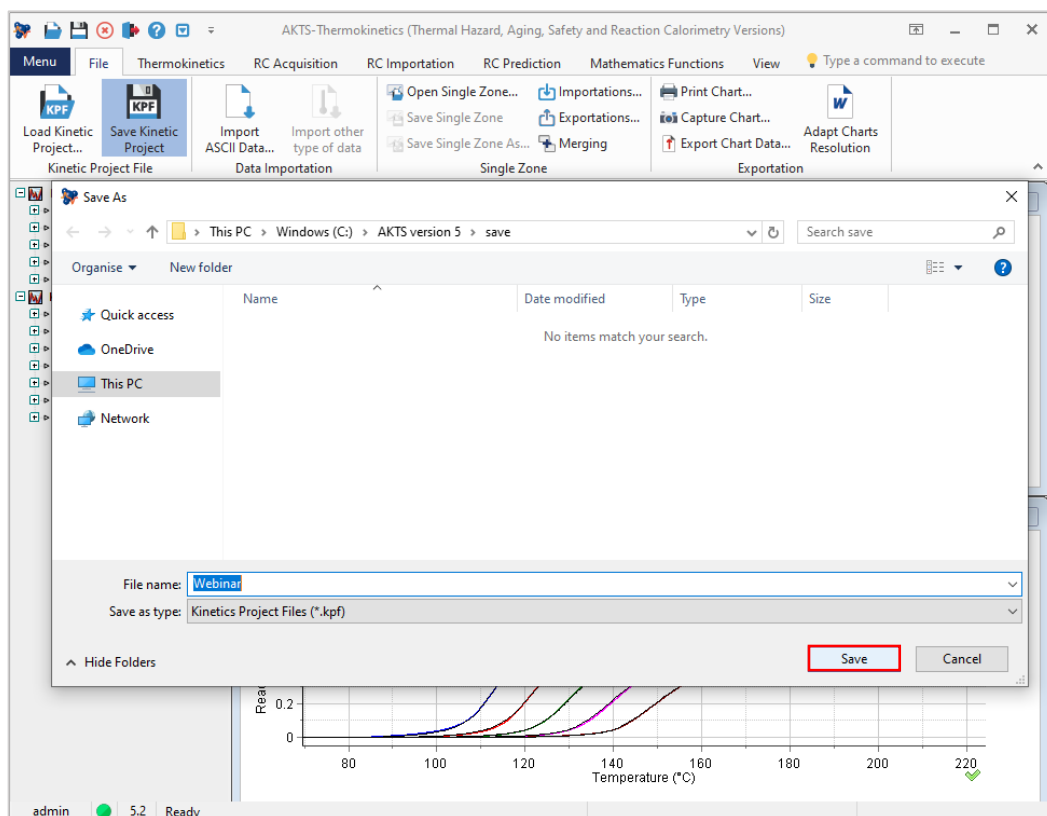


FIG. 2 - Saving the file.

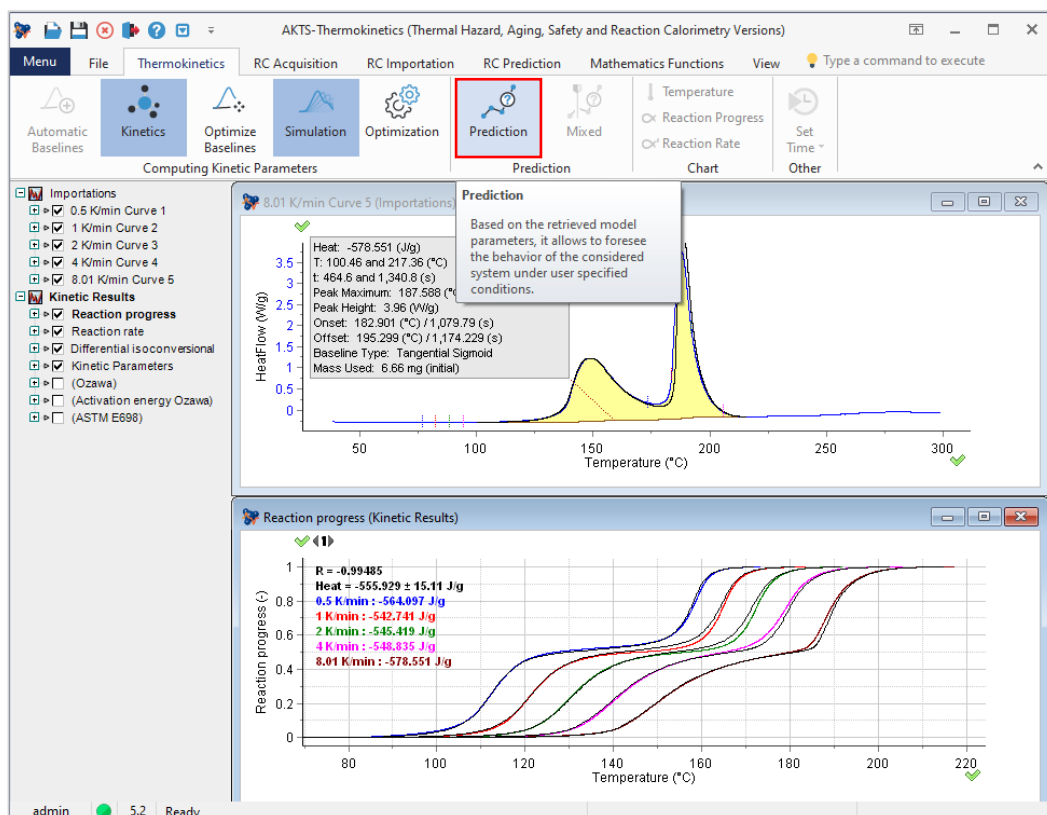


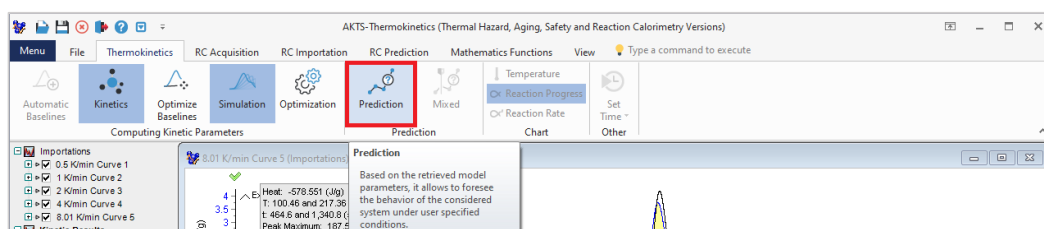
FIG. 3 - Prediction mode.

Finally, the user can start the prediction of the reaction rate and progress at any temperature profiles by using the tool 'Prediction' marked in red.

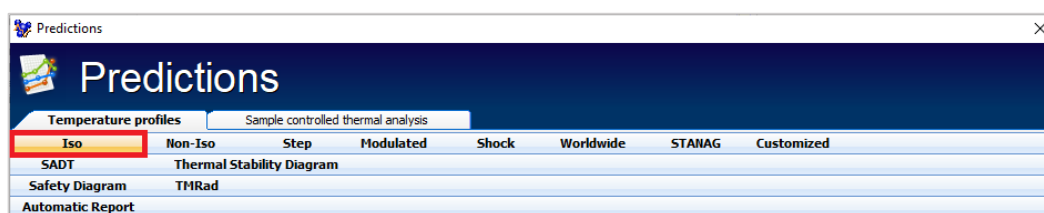
# AKTS E-LEARNING PREDICTIONS

## ISOTHERMAL

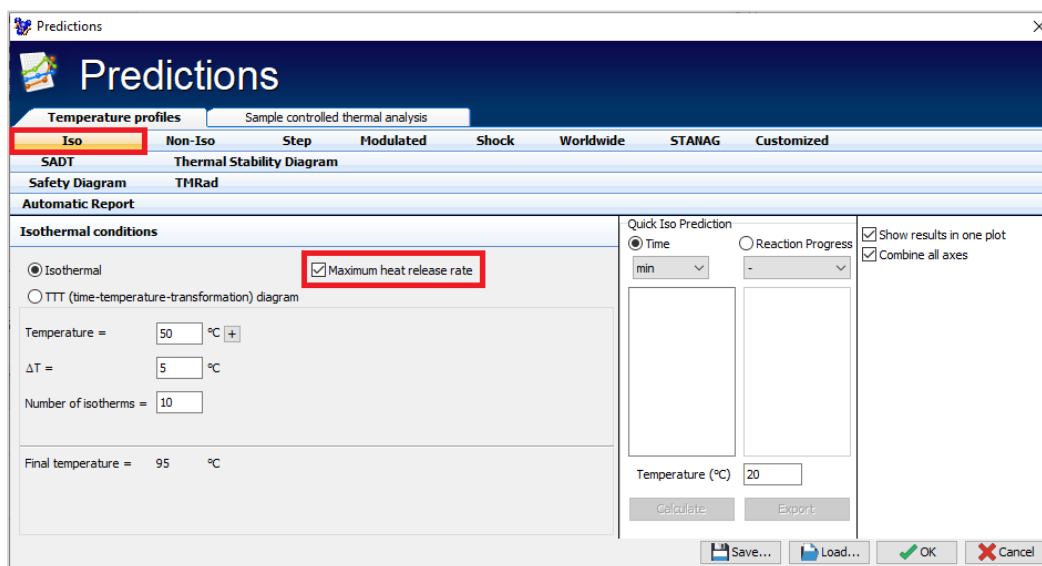
For the prediction of the reaction course at any temperature profile click the icon “Prediction”.



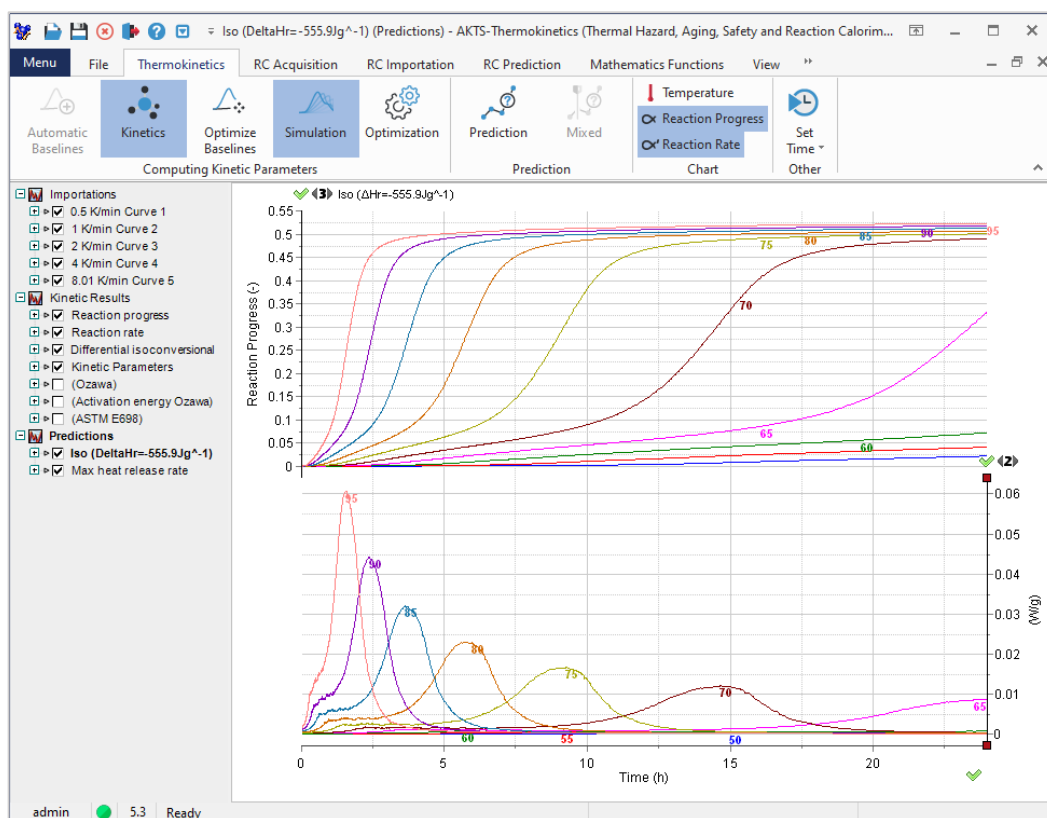
Below the predictions at different temperature profiles are presented.



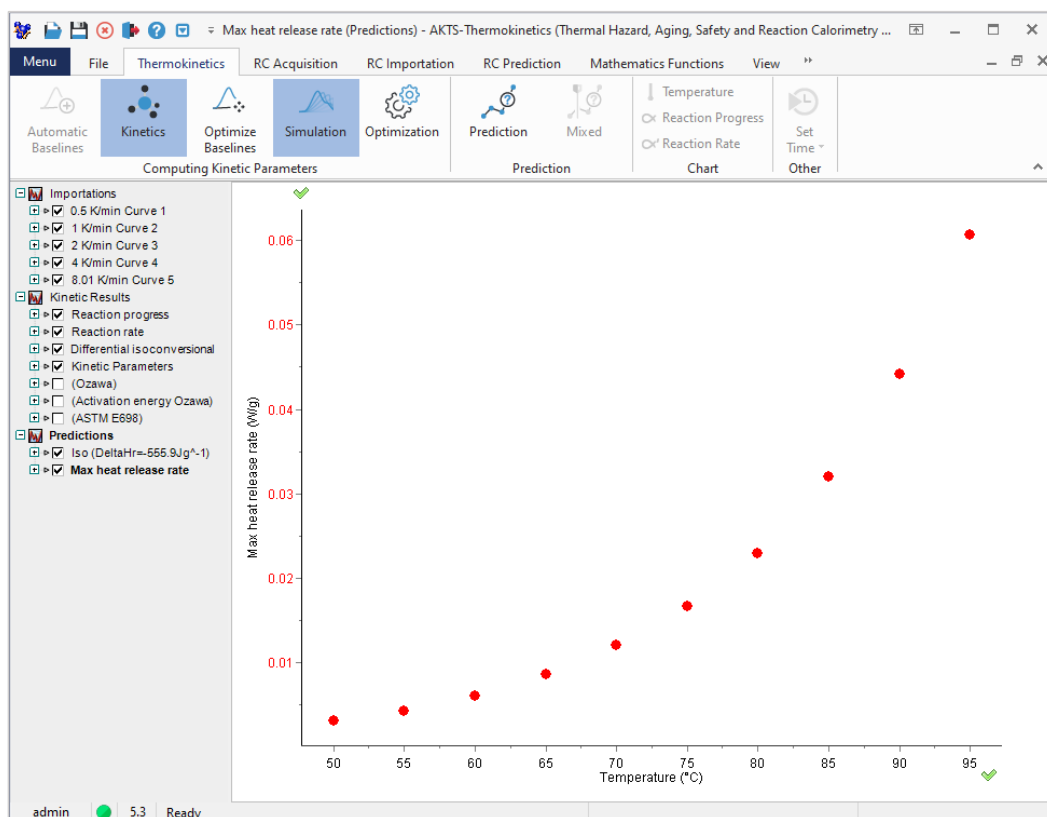
**FIG. 1** - For the prediction of the reaction course at isothermal conditions click bar “Iso”.



**FIG. 2** - Introduce the lowest required temperature (in presented example 50°C), the temperature difference between the isotherms (here 5°C) and specify the number of isotherms (here 10). It is also possible to calculate the maximal heat release rate.

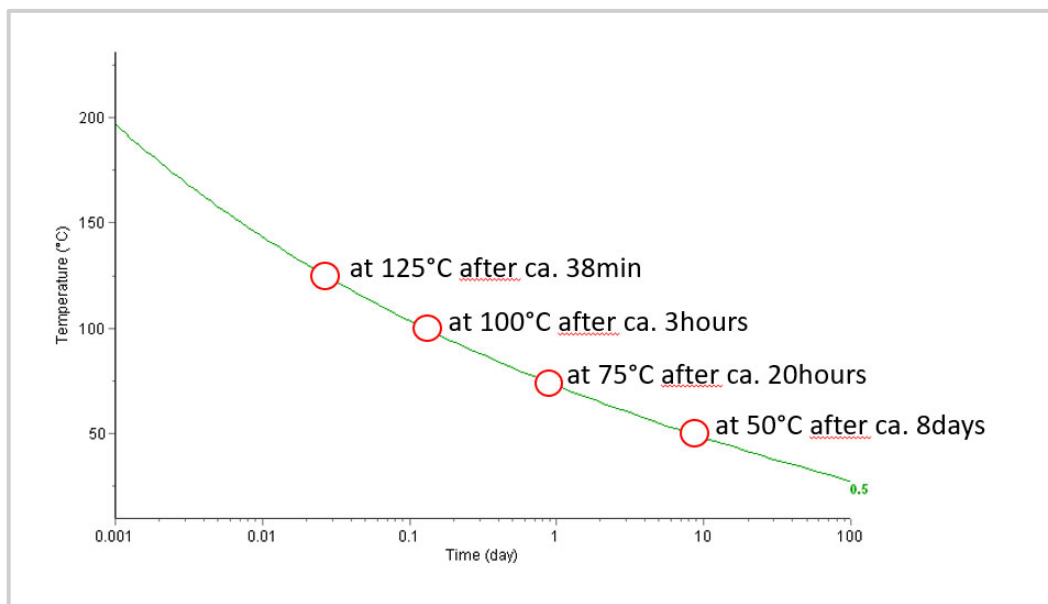


**FIG. 3** - Calculated reaction rates (bottom graph) and progresses (normalized signals) as a function of time under isothermal conditions. The values of the temperature in °C are marked on the curves.

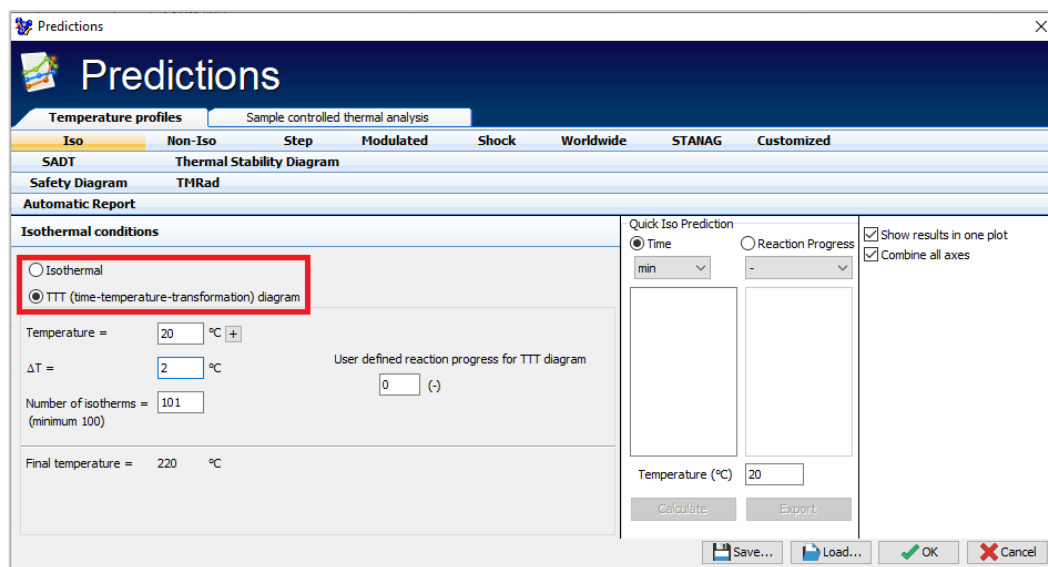


**FIG. 4** - Dependence on the maximal heat release rate on temperature.

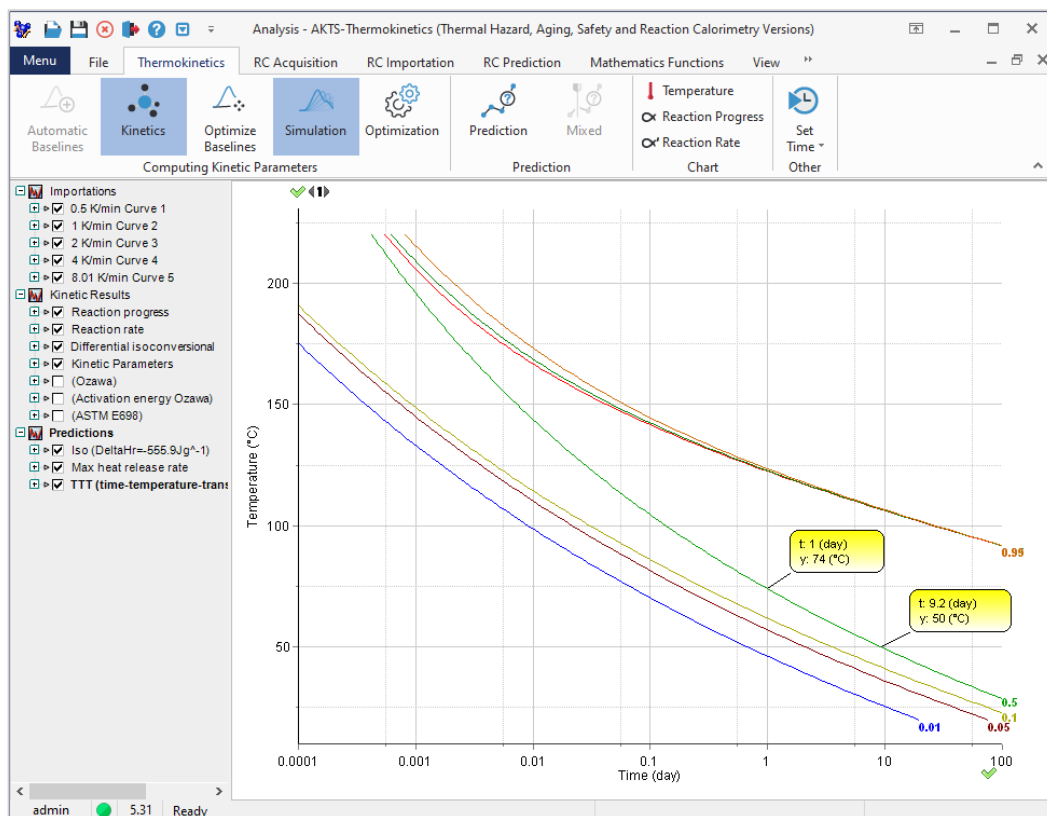
TK Software allows determination of Temperature-Time-Transformation (TTT) diagram which displays the equivalent time temperature points for which the arbitrarily chosen reaction progress is the same.



**FIG. 5** - The plot presents the general idea of TTT diagram for the one-stage reaction with arbitrarily chosen kinetic parameters. The reaction extent of 50% is reached after 38 min at 125°C and after ca. 8 days at 50°C.



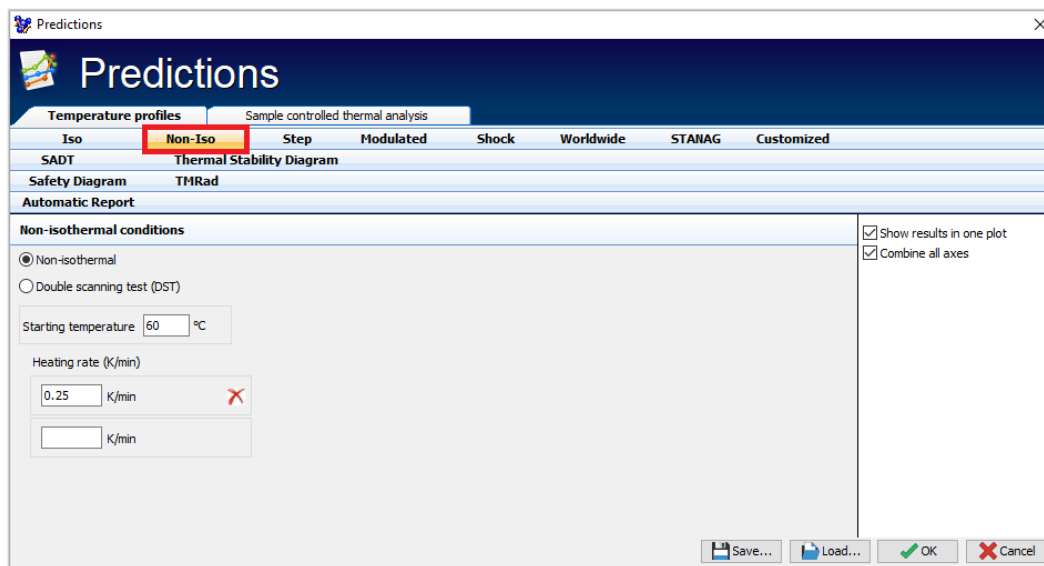
**FIG. 6** - For building the TTT diagram uncheck the option “isothermal” and check the option “TTT”.



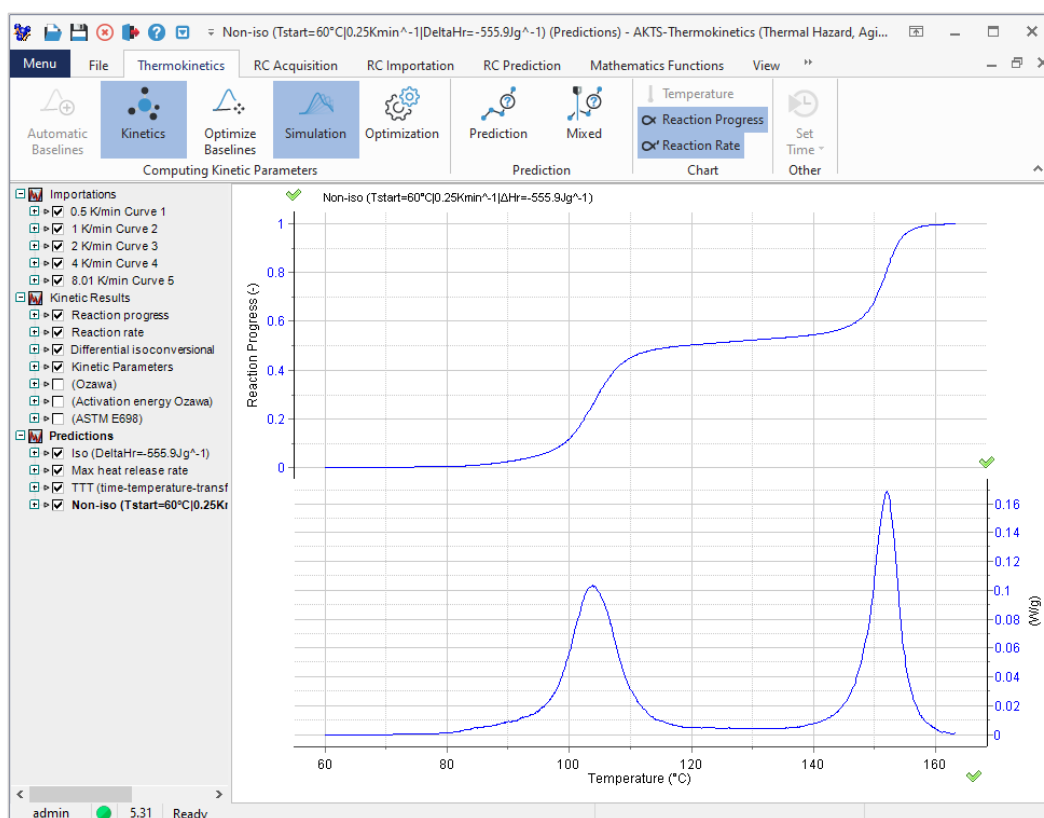
**FIG. 7** - Temperature-Time-Transformation (TTT) diagram.

The TTT diagram for the reaction having the same kinetic parameters as those used for the isothermal predictions displayed in Fig.3. Note logarithmic time-scale on the plot. Half of the material (reaction extent of 50%) is decomposed in 1 day at 74°C and after 9,2 days at 50°C.

## NON-ISOTHERMAL

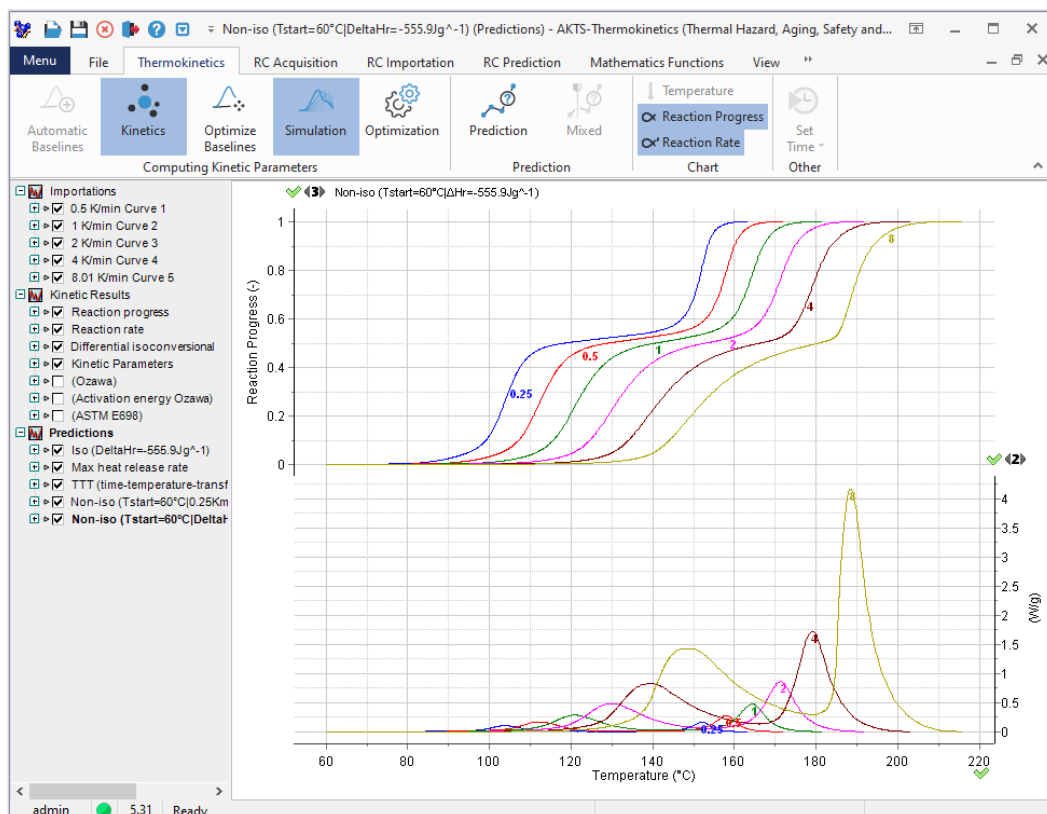
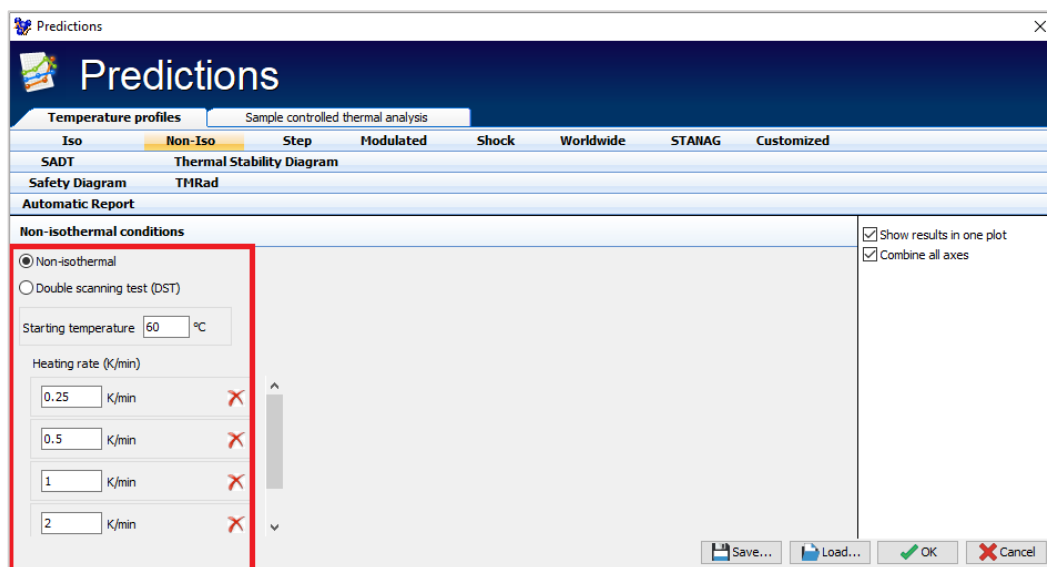


**FIG. 1** - For the prediction of the reaction course under non-isothermal conditions choose “Non-Iso” and specify the starting temperature and the heating rate (here 60°C and 0.25 K/min, respectively)



**FIG. 2** - Calculated reaction rate (bottom graph) and progress (normalized signals) as a function of temperature under non-isothermal conditions (heating rate of 0.25 K/min).

To display a set of non-isothermal curves at different heating rates introduce the required values as shown below.



**FIG. 3** - Calculated reaction rates (bottom graph) and progresses (normalized signals) as a function of temperature under non-isothermal conditions. The values of the heating rates in K/min are marked on the curves.



## STEP-WISE TEMPERATURE MODE

The 'Predictions' window displays the 'Step' tab under 'Sample controlled thermal analysis'. The 'Stepwise conditions' section contains a table for defining temperature zones. The table has columns for 'From temp (°C)', 'To temp (°C)', 'Heating rate (K/min)', and 'Time (min)'. The input data is as follows:

From temp (°C)	To temp (°C)	Heating rate (K/min)	Time (min)
30	100	5	14
100	100	0	360
100	20	-5	16
20	20	0	60
20	200	1	180

Additional parameters include: Time unit: min, Time max: 630 min, Number of cycles: 1. Checkboxes for 'Show results in one plot' and 'Combine all axes' are also present.

FIG. 1 - Input of the parameters for chosen temperature zones.

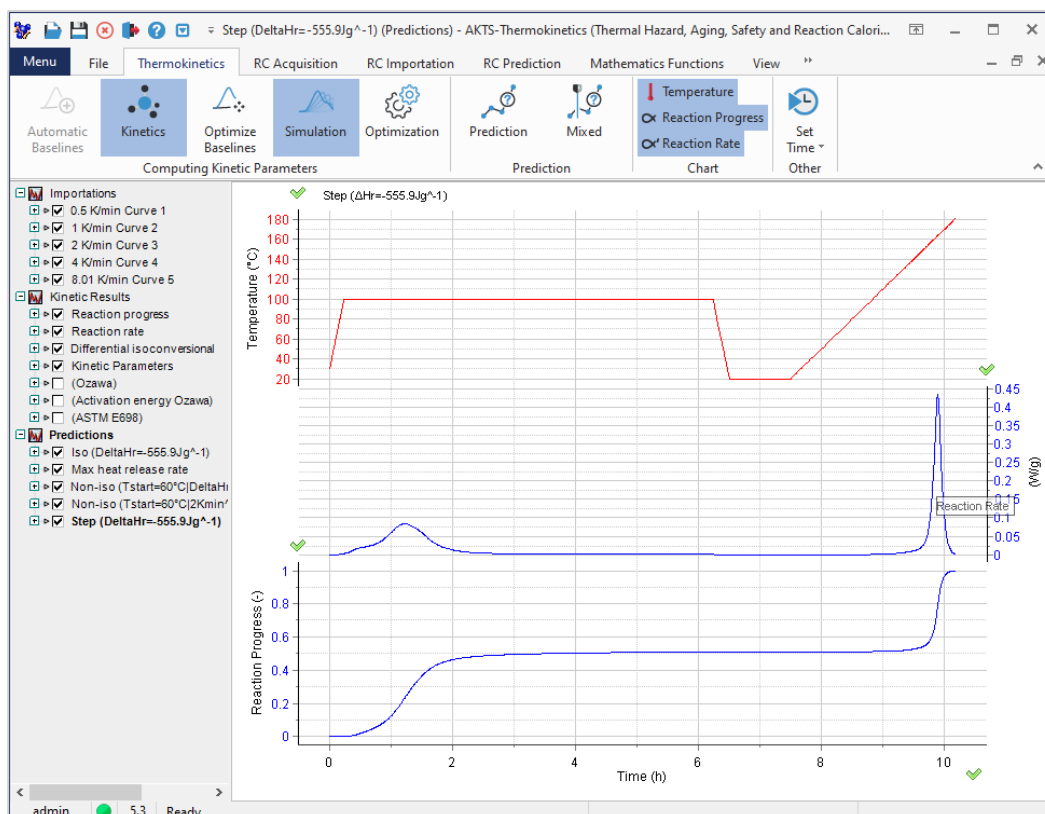


FIG. 2 - Step-wise mode. Reaction rate (top blue curve) and progress  $\alpha$  (normalized signals) as a function of time at subsequent isothermal and non-isothermal temperature zones.

## MODULATED TEMPERATURE MODE

**Predictions**

Temperature profiles | Sample controlled thermal analysis

Iso | Non-Iso | Step | **Modulated** | Shock | Worldwide | STANAG | Customized

SADT | Thermal Stability Diagram

Safety Diagram | TMRad

Automatic Report

**Modulated or periodic temperature variations**

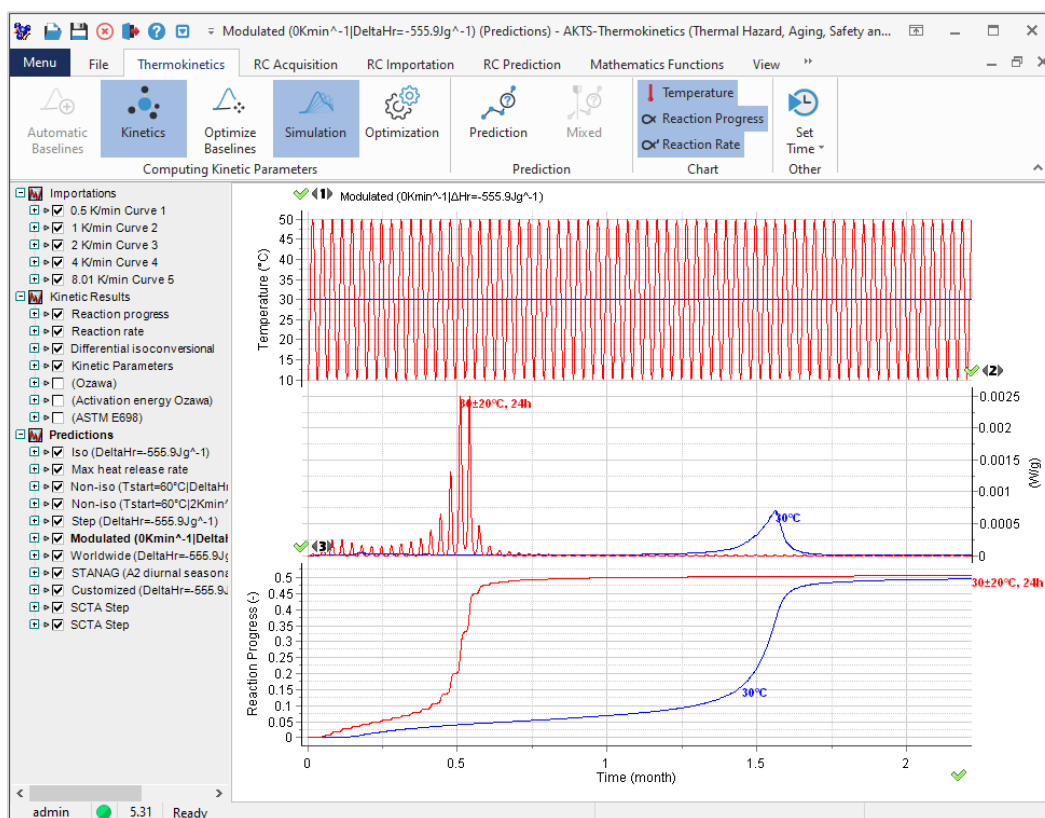
Time max: 1 year

Underlying temperature	Amplitude/2	Frequency	Units	Underlying heating rate	Nbr of oscillations
30	± 0	0	hour	0 K/min	0 (Iso-mode)
30	± 20	24	hour	0 K/min	3.7E02
	±		hour	0 K/min	Not applicable

☒ Show results in one plot  
☒ Combine all axes

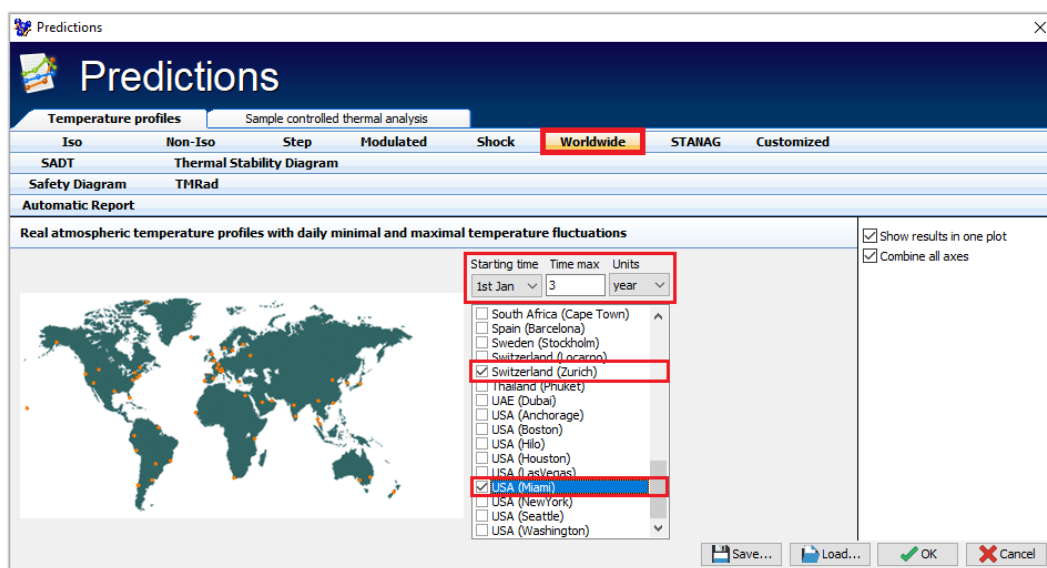
Save... Load... OK Cancel

**FIG. 1** - Input of parameters of isothermal (30°C) and modulated experiment (temperature of 30°C fluctuating with amplitude of 20°C and frequency of 24 hrs).

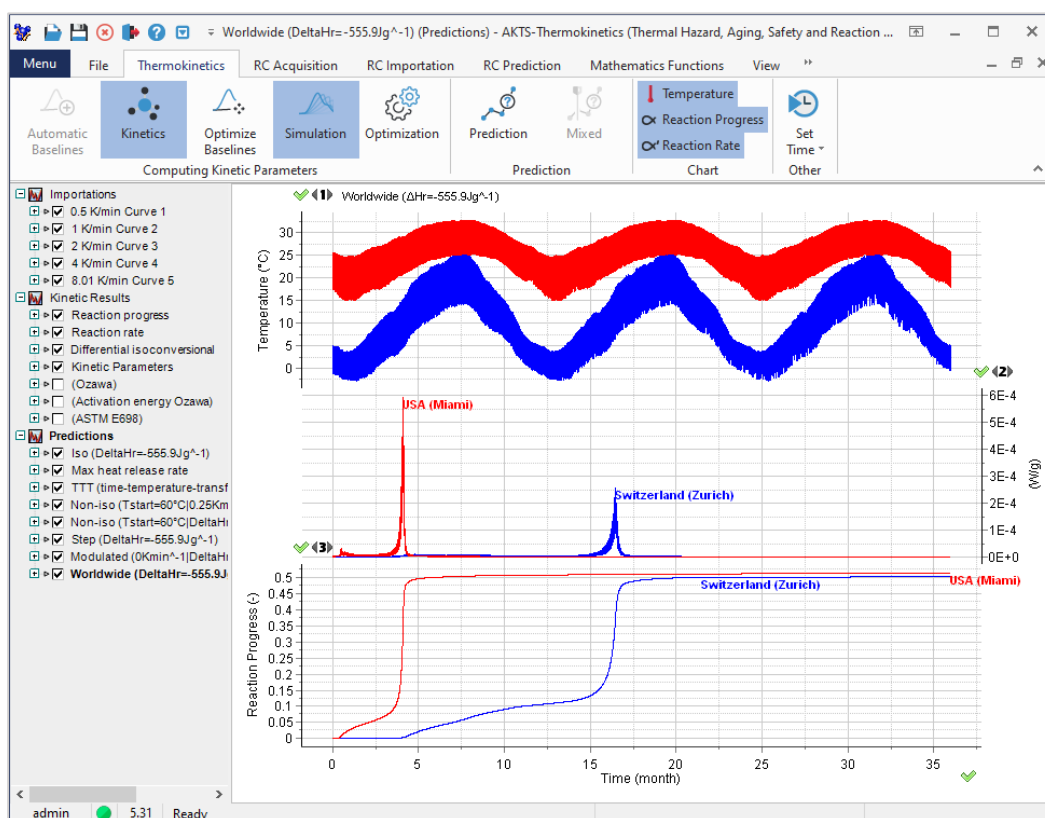


**FIG. 2** - Reaction rate (middle) and reaction progress (bottom, normalized signals) as a function of time under isothermal (blue curves, 30°C) and modulated temperature conditions (red curves, 30°C with amplitude of ±20°C and frequency 24 h).

## — WORLDWIDE REAL ATMOSPHERIC TEMPERATURE PROFILES —

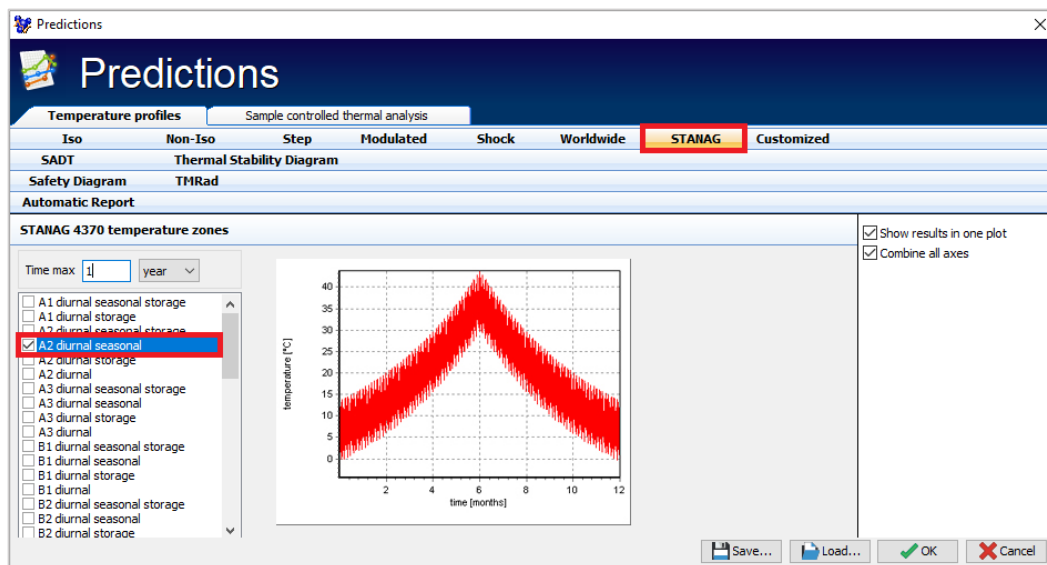


**FIG. 1** - Prediction of the influence of the real atmospheric temperature profiles on the reaction course. The user can choose the location from the scrolling list, the date of the beginning of the experiment and its duration.

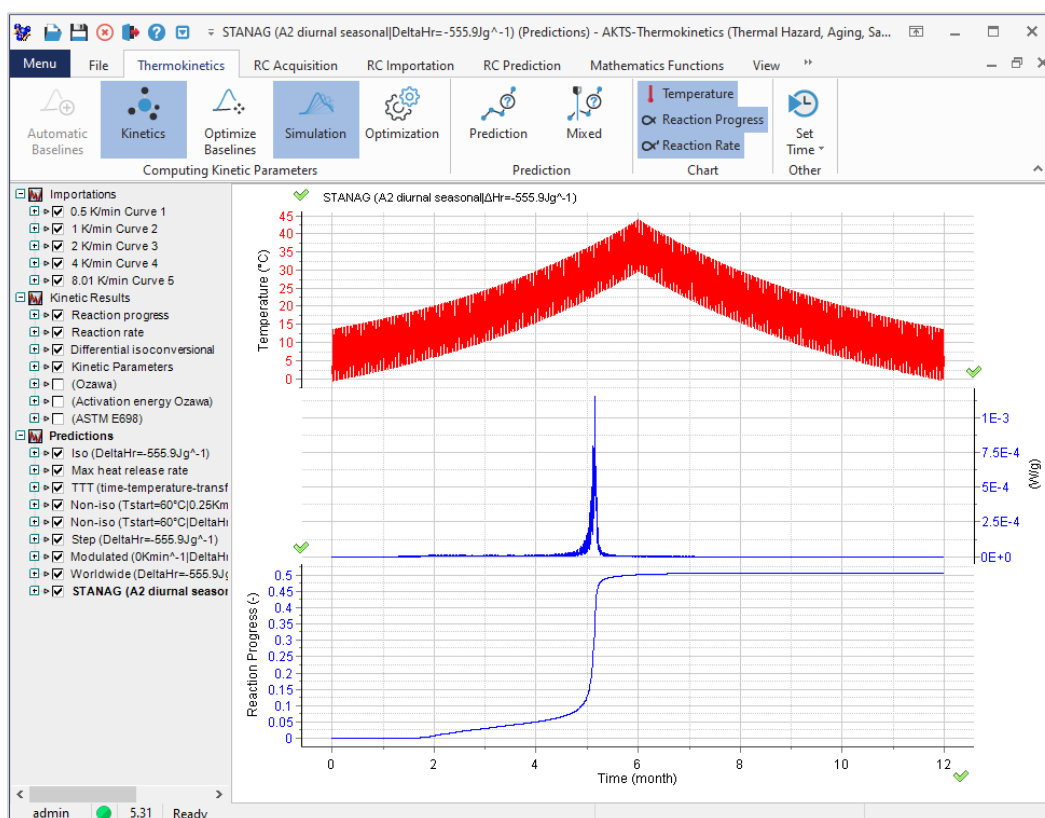


**FIG. 2** - Top: Average daily minimal and maximal temperatures recorded between 1961 and 1990 in Zurich (blue) and Miami, USA, (red); Reaction rate (middle section) and reaction progresses (normalized signals) as a function of time for the Zurich and Miami temperature profiles.

## STANAG CLIMATIC CATEGORIES

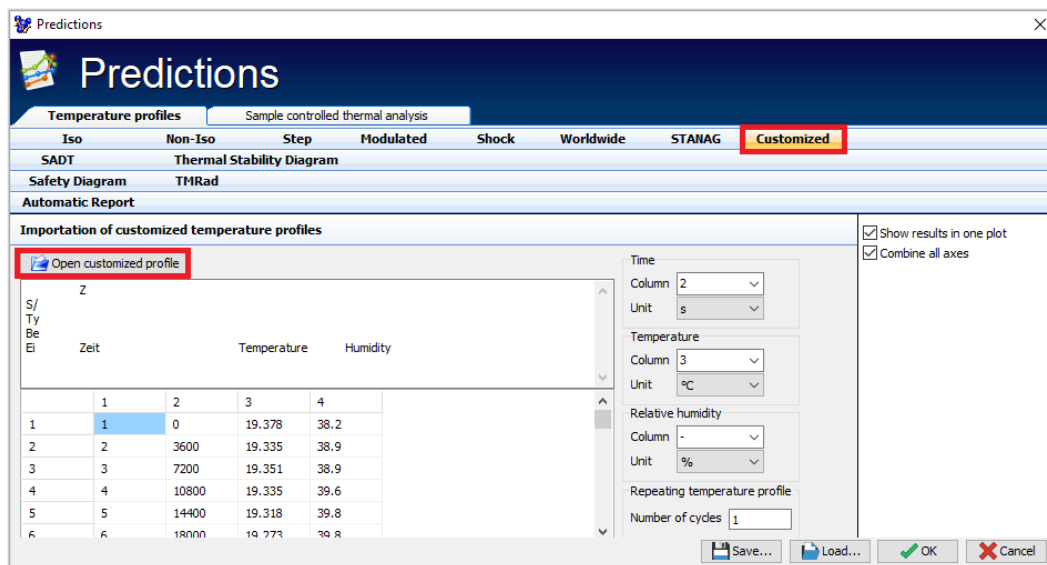


**FIG. 1** - The climate categories defined by STANAG can be chosen from the scrolling list.

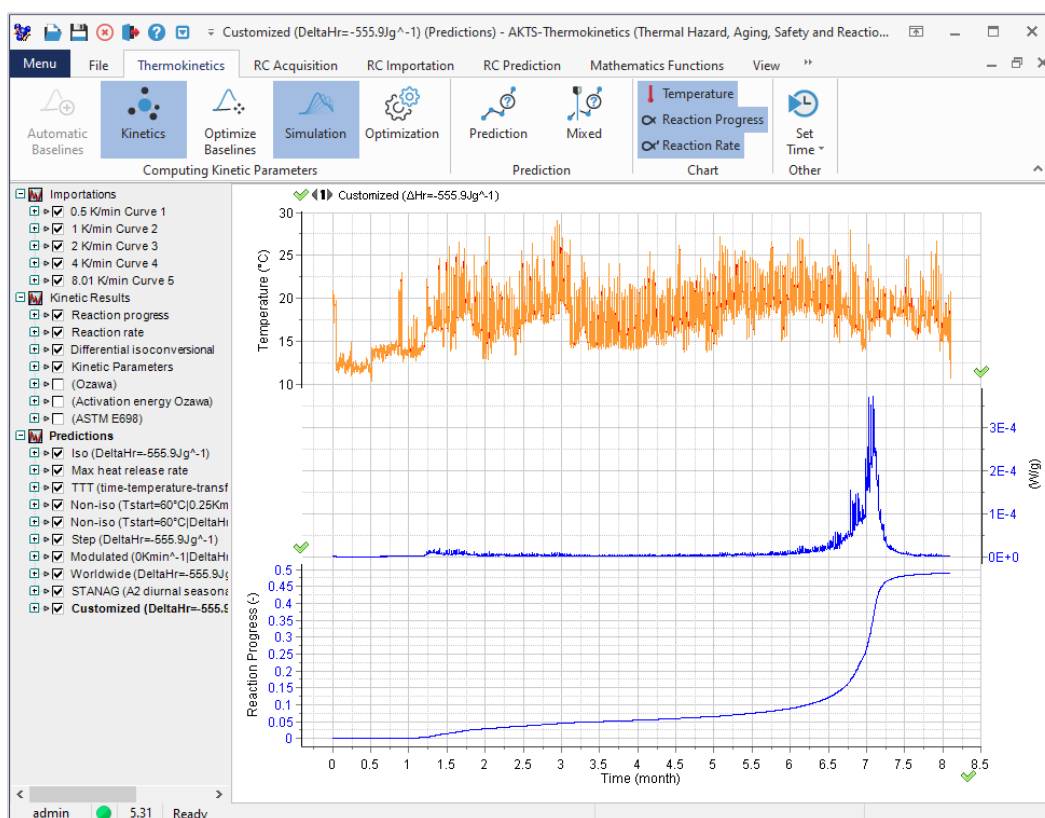


**FIG. 2** - Top: Average daily temperature fluctuations in STANAG A2 zone. Reaction rate (middle section) and reaction progress (normalized signals) as a function of time.

## USER CUSTOMIZED TEMPERATURE MODE

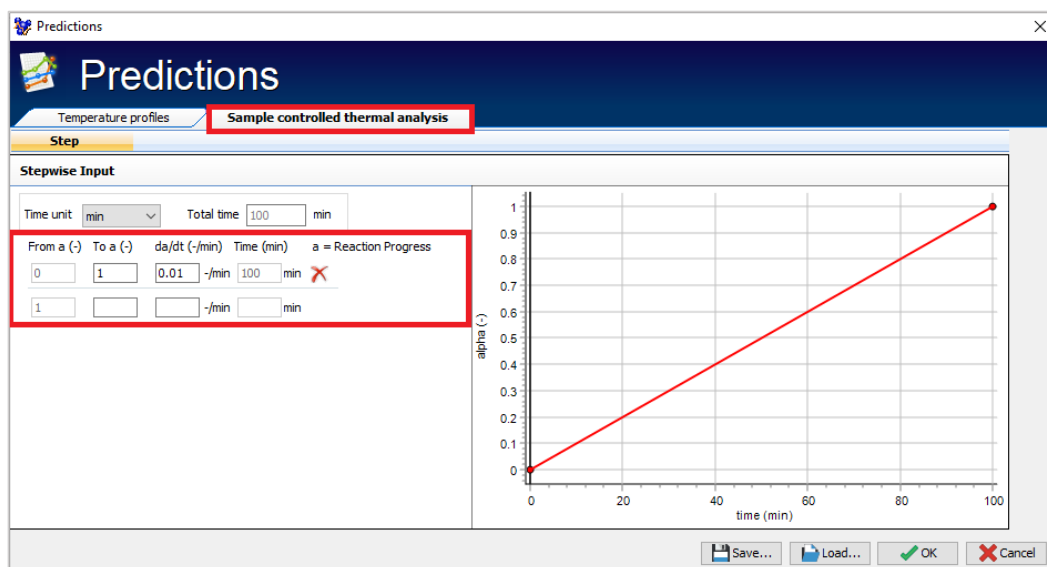


**FIG. 1** – Prediction of the reaction course for any set of temperature-time data as e.g. for the real temperature profiles recorded by temperature trackers.

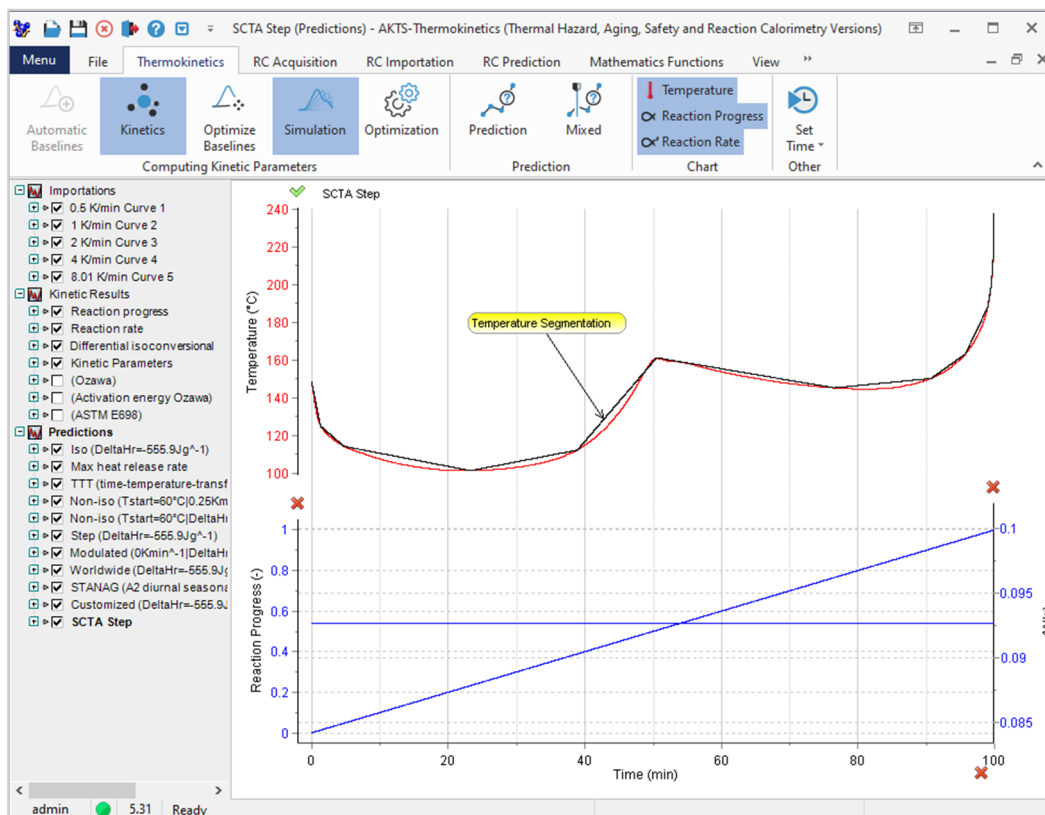


**FIG. 2** - Prediction of the reaction rate (middle-) and reaction progress (bottom curve) during temperature variations recorded by the temperature tracker (top).

## SAMPLE CONTROLLED THERMAL ANALYSIS

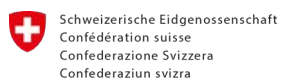


**FIG. 1** - TK Software allows the prediction of the reaction course for the temperature mode which is required to obtain the chosen, set by user, constant reaction rate. This specific technique is known as Sample Controlled Thermal Analysis or Controlled Rate Thermal analysis (CRTA). In presented example the reaction rate from the beginning to the end is set as 1% of reaction progress per minute: the reaction from the beginning to the end proceeds in 100 min with the constant rate.



**FIG. 2** - Prediction of rate-controlled reaction course in Sample Controlled Thermal Analysis mode: the dependences temperature vs time (top), reaction rate and reaction extent vs time (bottom).

FOR FURTHER INFORMATION VISIT:  
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