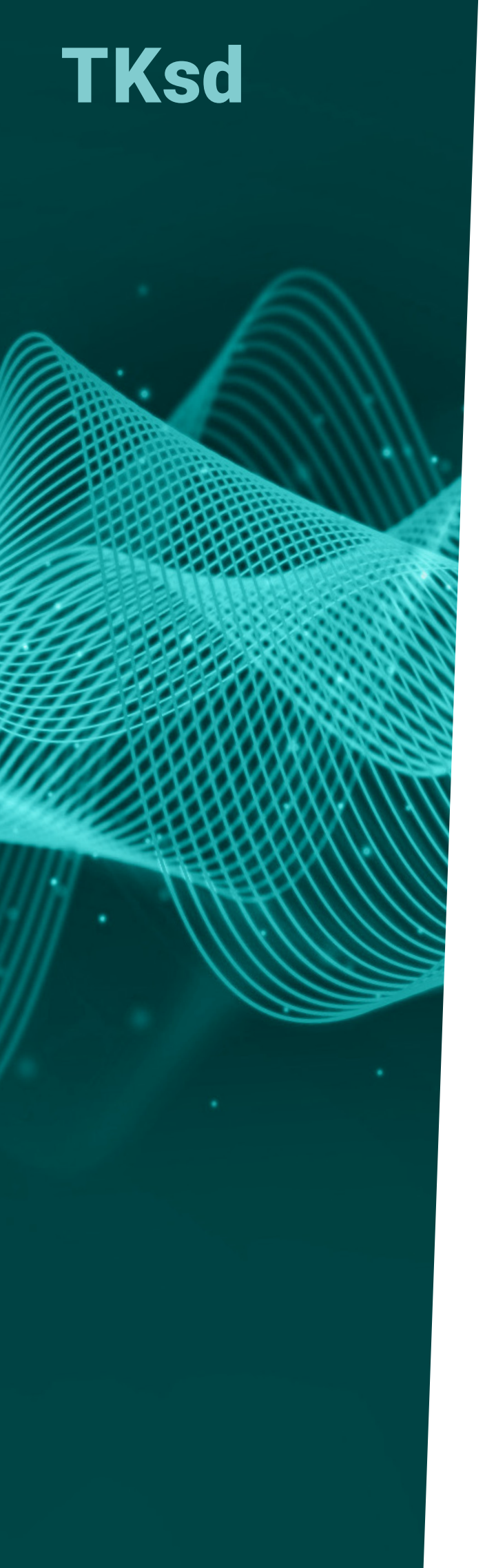
TKsd



THERMOKINETICS Sparse Data Software (TKsd)

Evaluation of Kinetic Parameters from Sparse, Discontinuously Collected Thermoanalytical Data

CONTENT

AKTS E-Learning

www.akts.com/tksd/e-learning

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THERMOKINETICS SPARSE DATA SOFTWARE (TKSD) BASED ON ADVANCED KINETIC AND STATISTICAL MODEL SELECTION APPROACHES (AIC&BIC)

PREDICTIONS

AKTS E-LEARNING

THERMOKINETICS SPARSE DATA SOFTWARE (TKsd) BASED ON ADVANCED KINETIC AND STATISTICAL MODEL SELECTION APPROACHES (AIC&BIC)

TKsd Software allows, among others:

- Life-time prediction from small amount of experimental points
- Determination of the prediction bands
- Simulation of the reaction course under any temperature mode
- Verification of the predictions by additional experimental data

DATA COLLECTION AND IMPORTATION

At least 20-30 experimental points have to be collected at a minimum of three temperatures. Additional experiments at different temperatures or additional time-points increase the accuracy of the kinetic analysis. In our case study the experiments used for kinetic analysis were performed at 45, 37, 25 and 5°C.

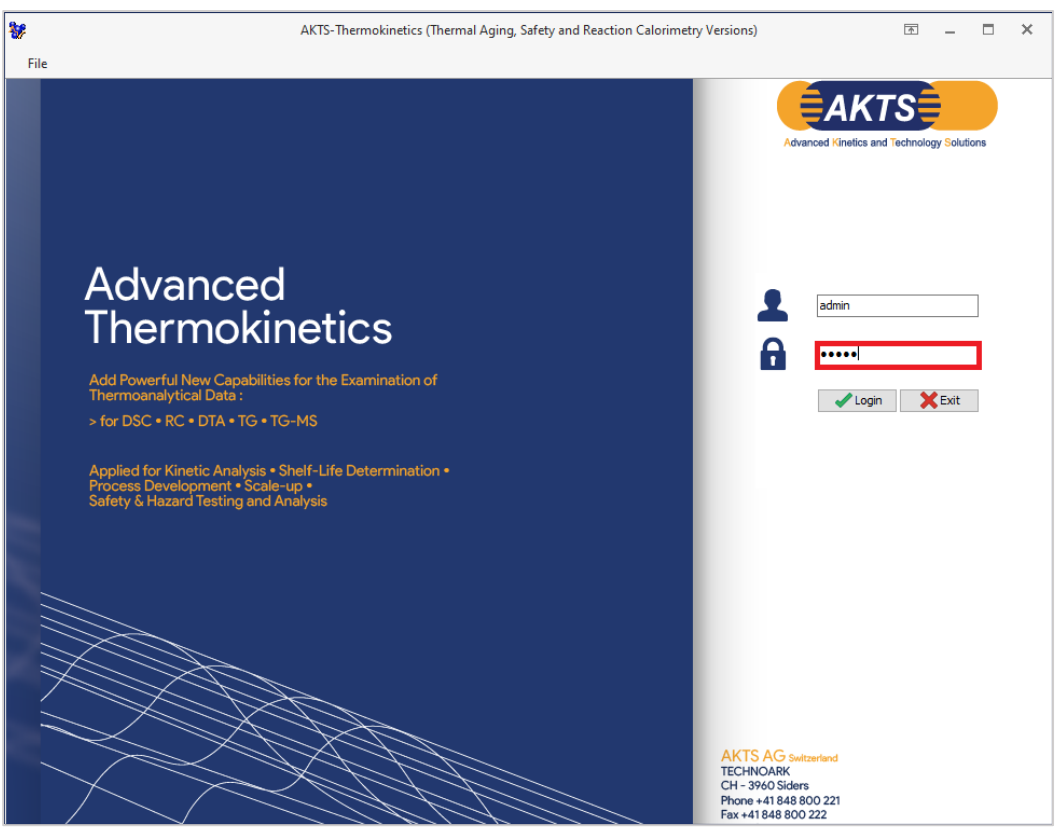

FIG. 1 - Introducing password to start the AKTS-Thermokinetics software (TKsd).

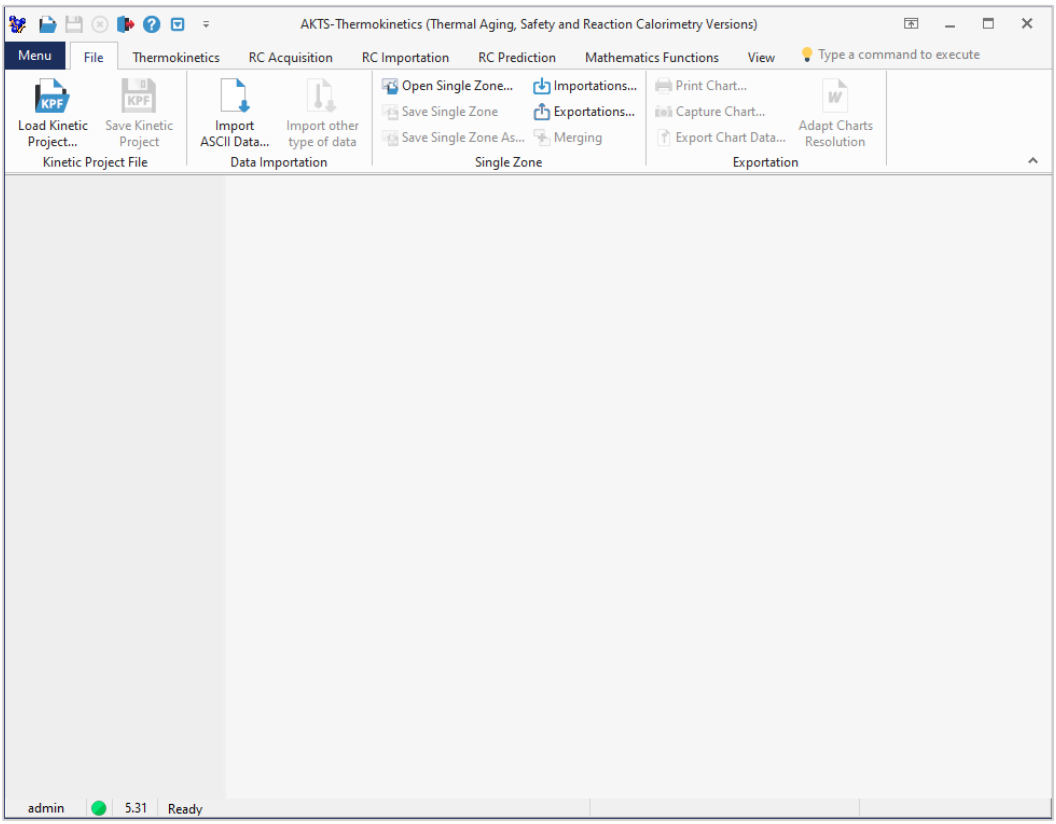

FIG. 2 - Opening screen of TKsd

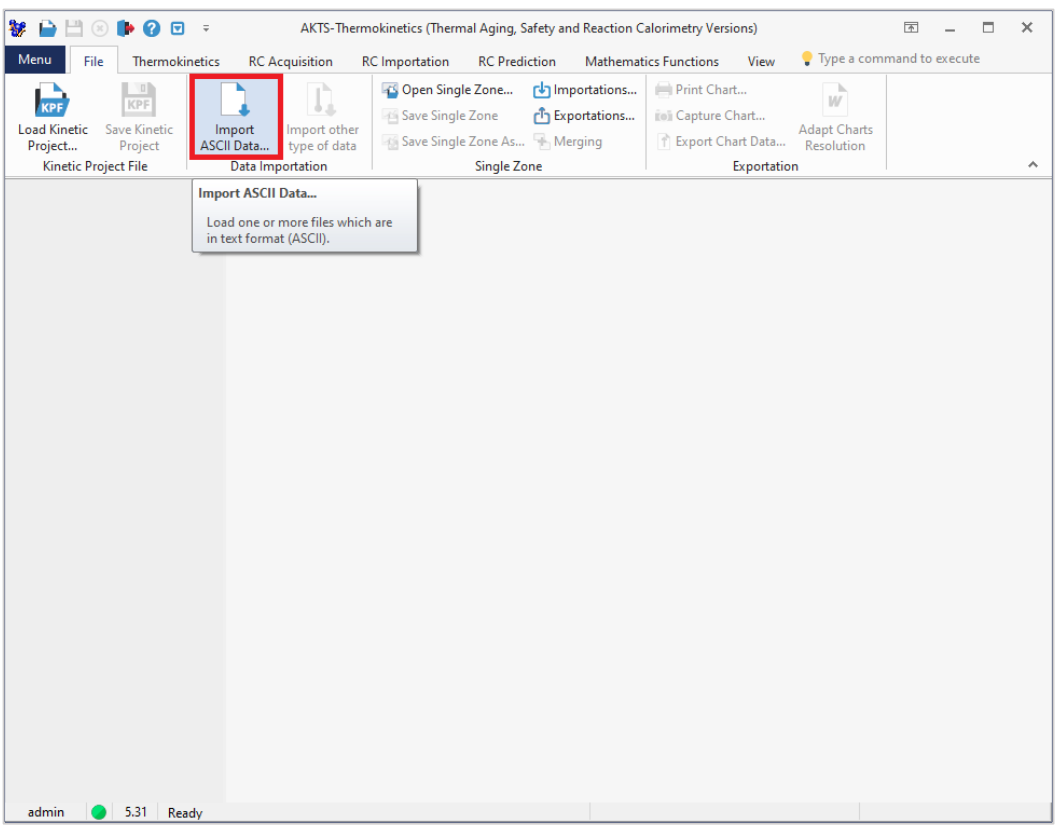

FIG. 3 - Importation of ASCII-data (.txt).

The user can import any data in ASCII-format (.txt-files) independent of its source containing information about:

- Time
- Temperature
- Measured quantity changing as a function of time and/or temperature and/or relative humidity as e.g. the sample mass, heat flow, concentration of active component, amount of degradation product etc.

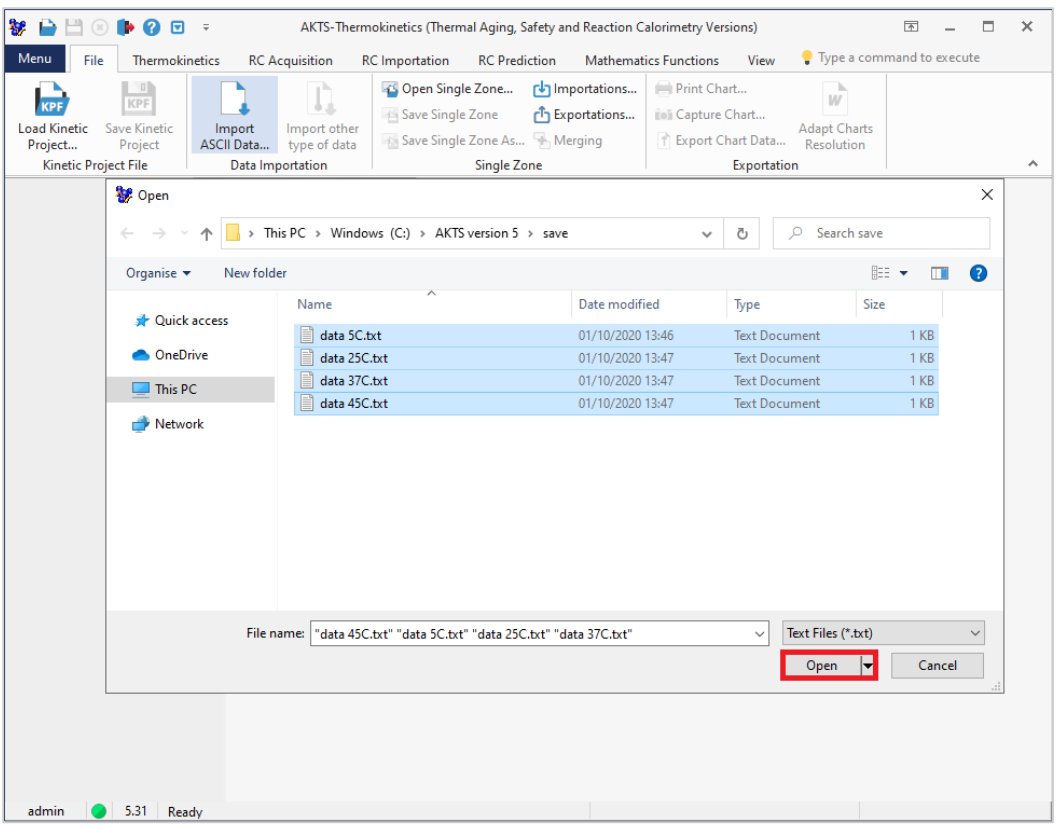

FIG. 4 - Selection of the requested data files.

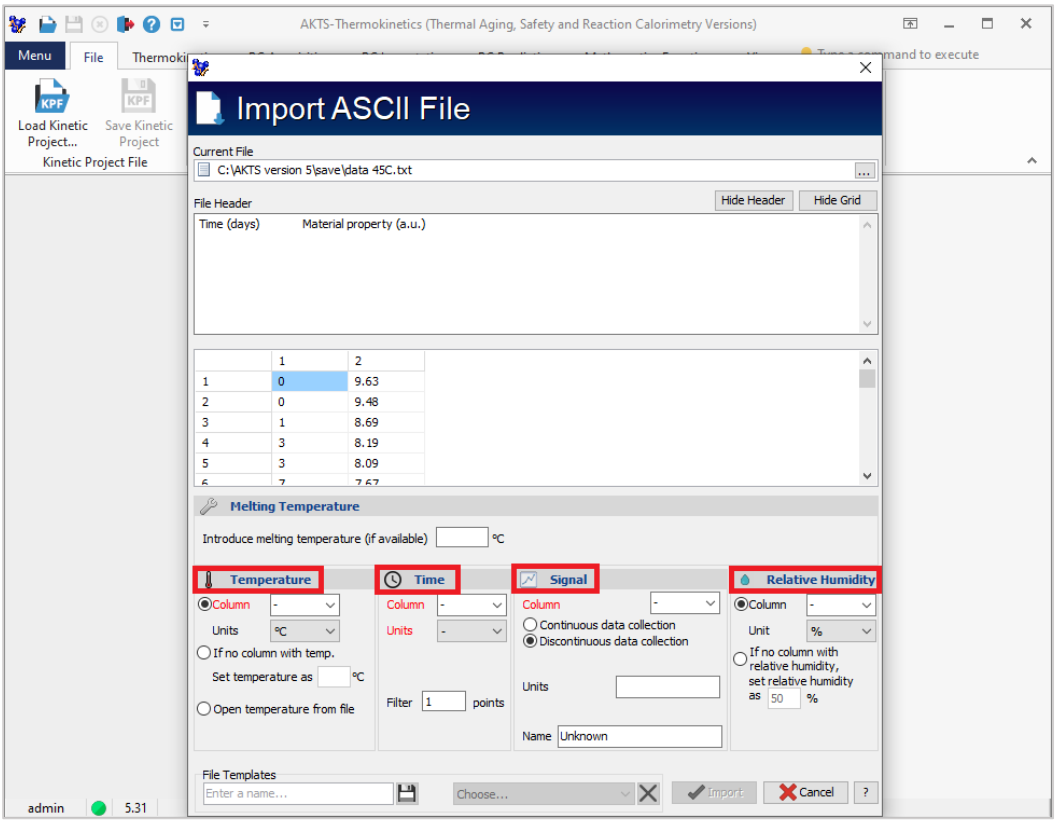

FIG. 5 - Selection of temperature, time, measured quantity (signal) and relative humidity.

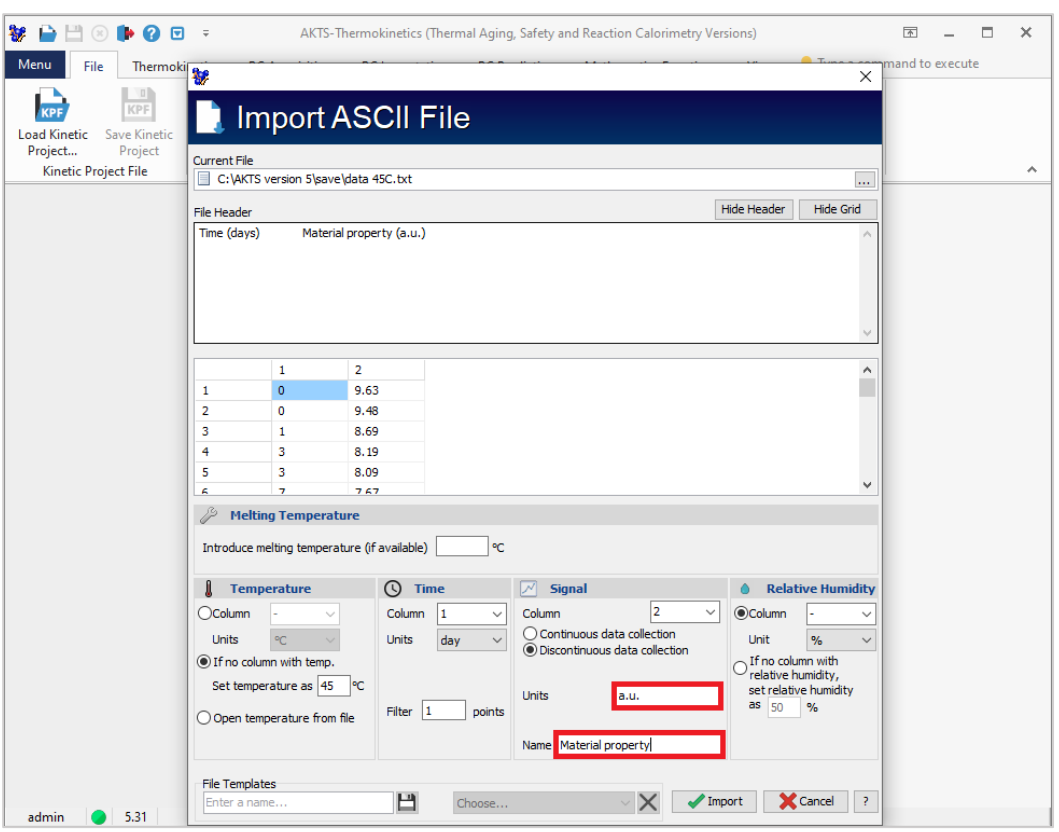

FIG. 6 - Defining the name and units of the measured quantity.

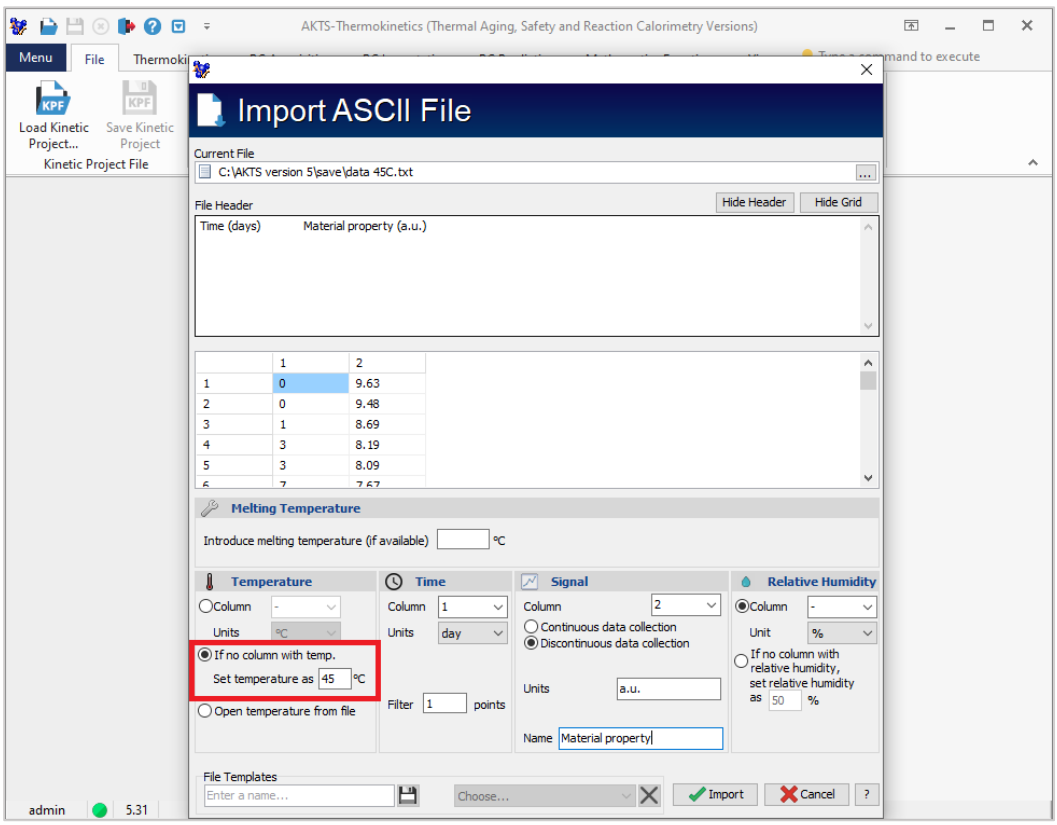

FIG. 7 - Specifying temperature (here 45°C) if the temperature column is not included in the ASCII data files.

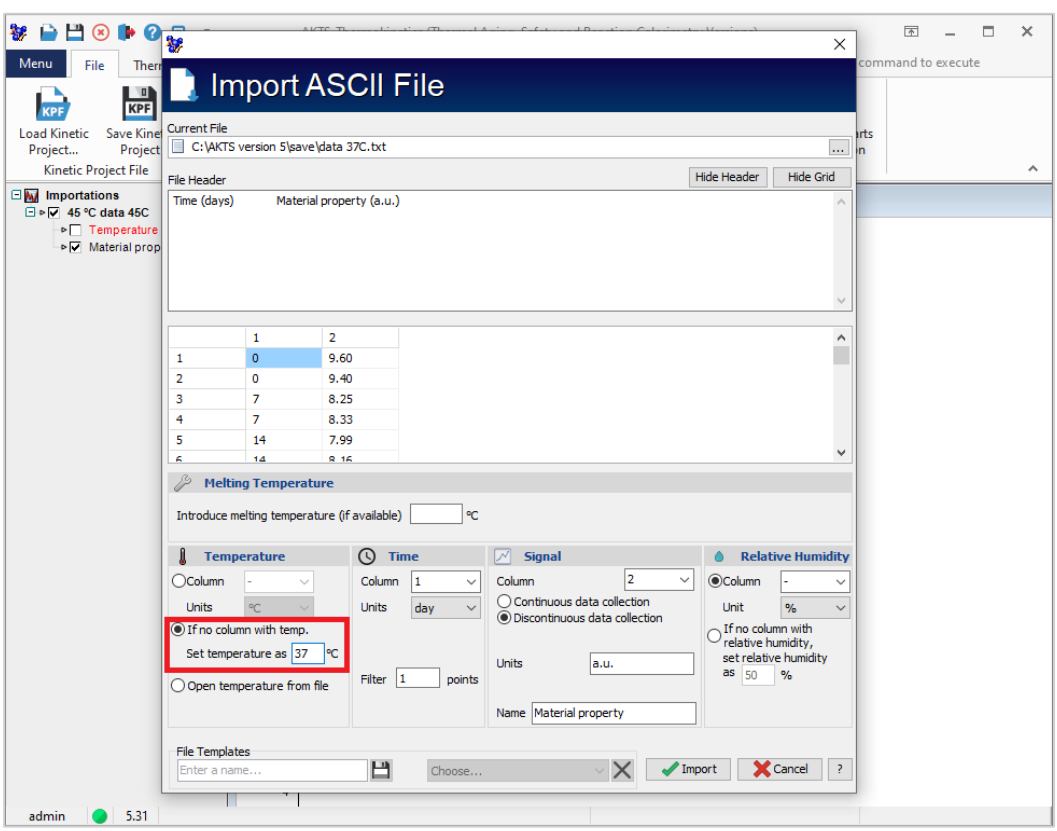

FIG. 8 - Introducing data set recorded at 37°C.

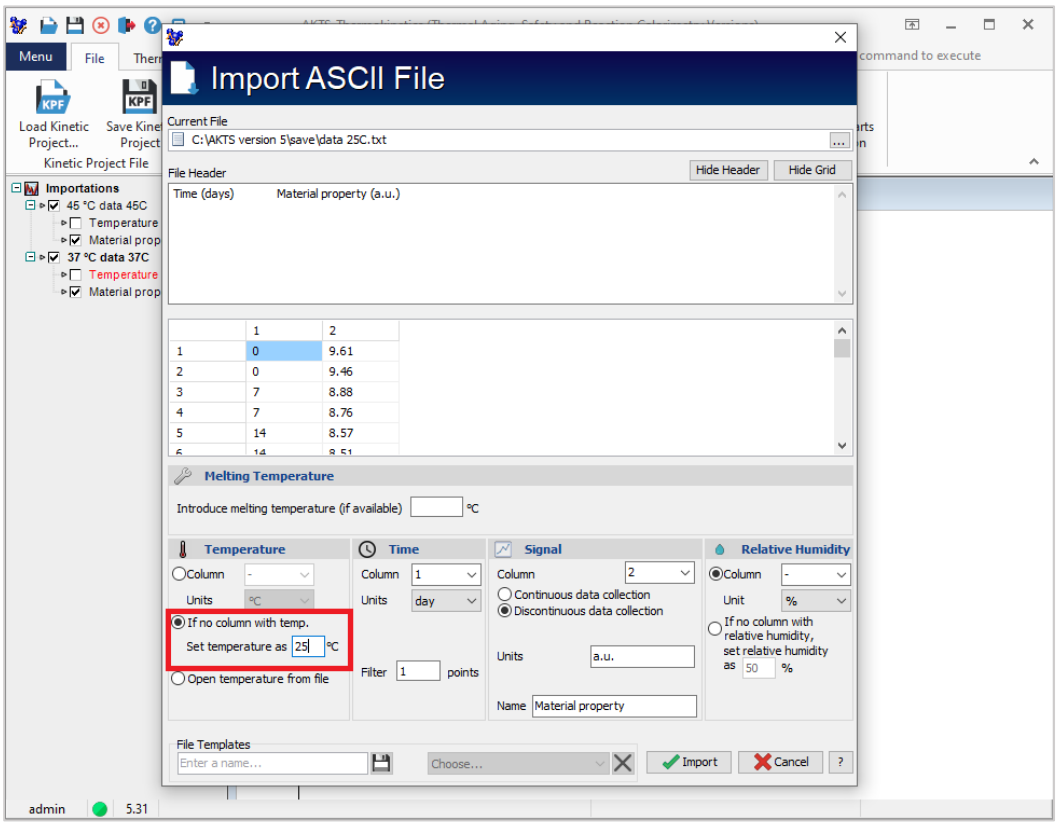

FIG. 9 - Introducing data set recorded at 25°C.

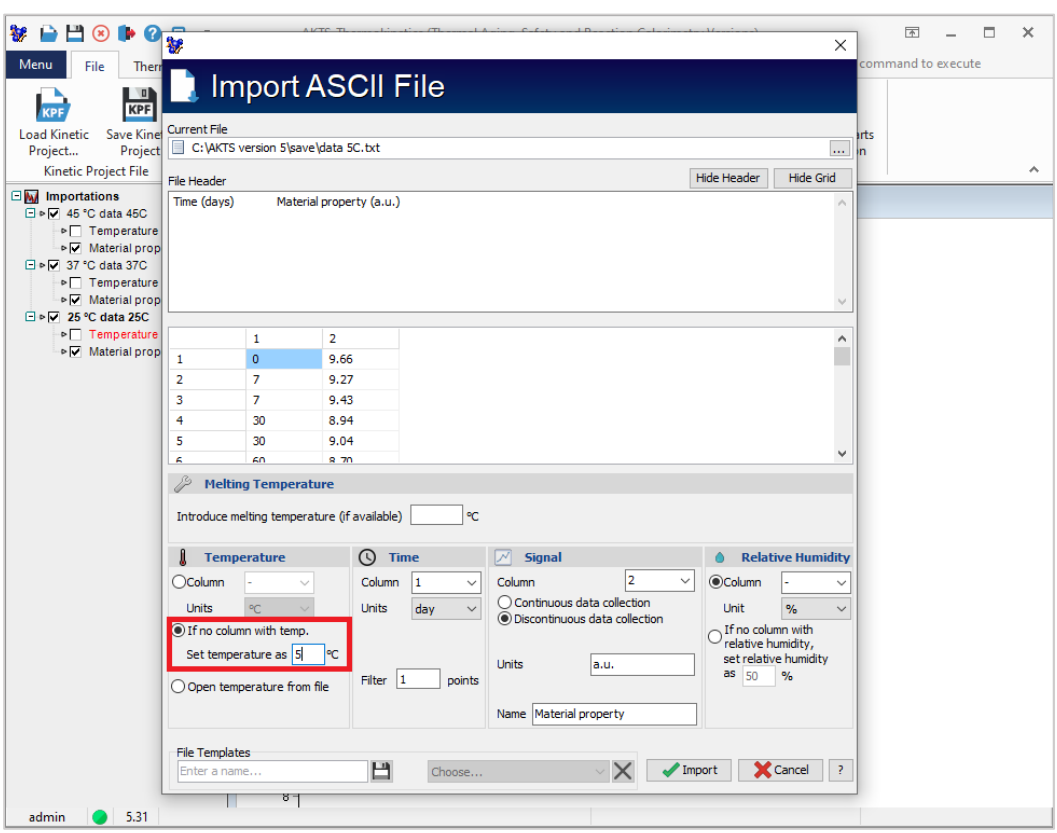

FIG. 10 - Introducing data set recorded at 5°C.

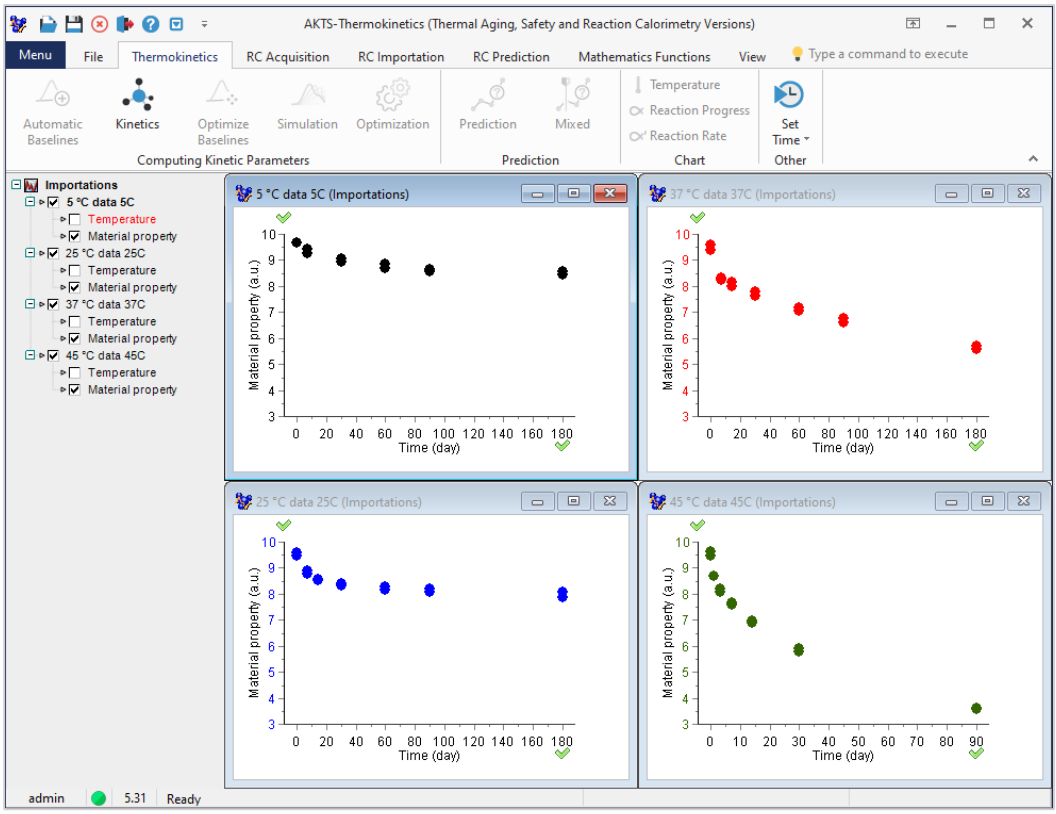

FIG. 11 – Graphical presentation of the imported sparse data collected at 5, 25, 37 and 45°C.

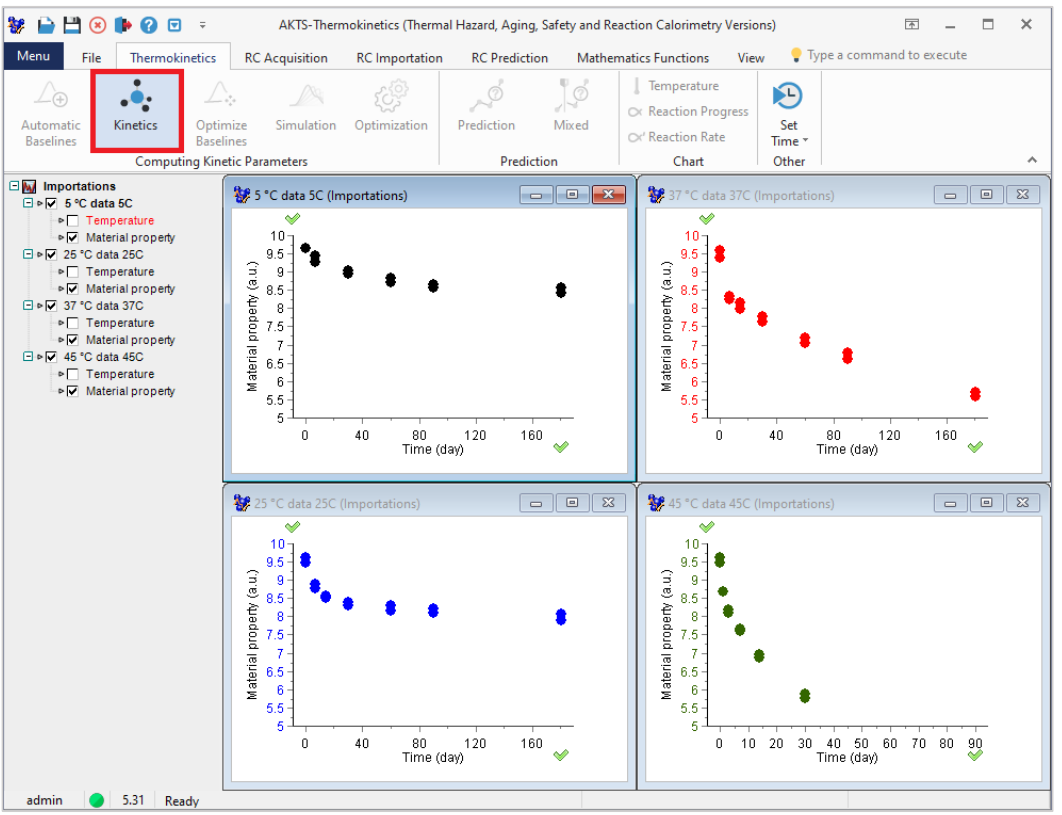

FIG. 1 – Choose the "Kinetics" tool; data collected at 45, 37, 25 and 5°C will be used in the kinetic analysis.

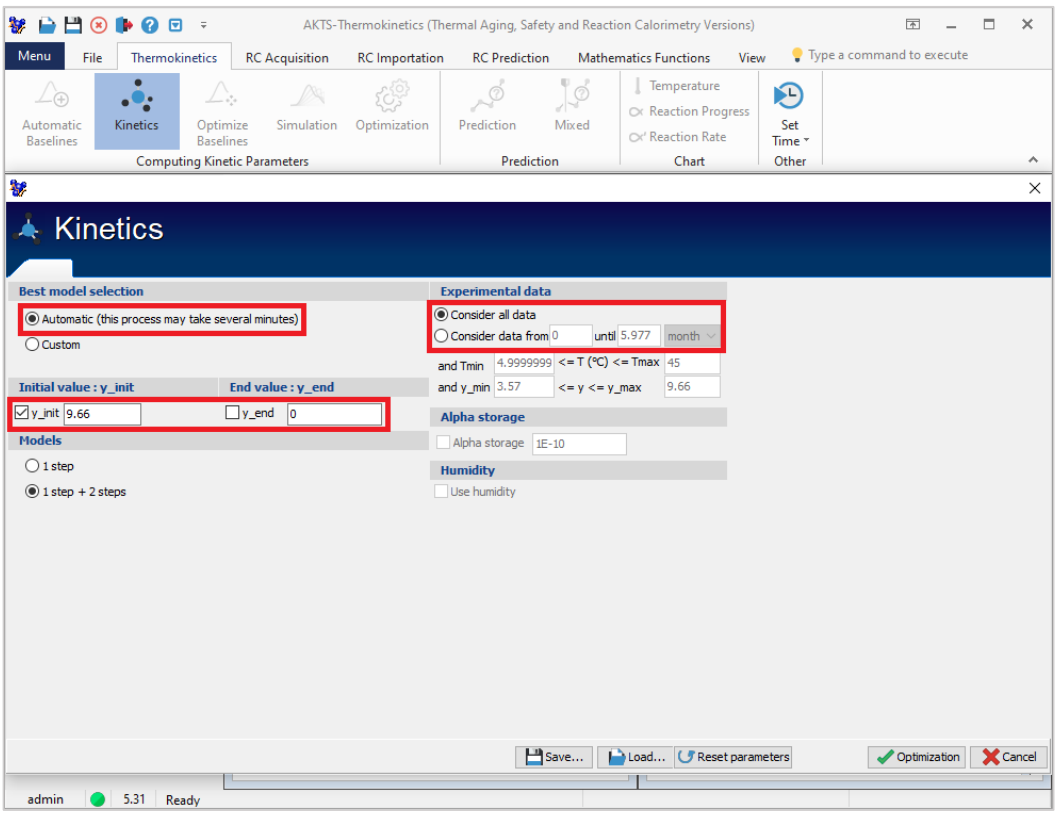

FIG. 1 - Evaluation of Kinetic Models and parameters. In this example: (i) For the best model selection ("1 step & 2 steps") the **Automatic mode** is chosen (ii) The "y-init"-value is checked, therefore it will be optimized during calculations. (iii) The y-end value is unchecked and set to zero, therefore during calculations the final y-end value is forced to be zero. (iv) All data are considered in the kinetic analysis.

Best model selection:
For the best model selection one can choose between the **Automatic** (recommended) or the **Custom** mode which is more advanced and requires manual introduction of the kinetic equations. User can choose between:

- "1 step" (for one-stage reaction)

or

- "1 step & 2 steps" (for two-stages reaction)

Successive models are consecutively checked to find the best fit of the experimental data. During fitting procedure all kinetic models present in the software library (for one- and two-stages reactions) are considered.

Input of "Initial" and "End" values ("y-init" and "y-end"):
The "Initial" and "End" values are generally picked up from the experimental data points however the user has the possibility to fix or optimize these values during calculations.

- If the box is checked, the y-init, y-end or both values are optimized during calculations.
- If the box remains unchecked, y-init, y-end or both values are forced to the entered values accordingly.

Experimental data:
During the determination of the best kinetic model one can change the range of data used in the kinetic analysis – see the red-marked top-right rectangle

RANKING OF KINETIC MODELS ACCORDING TO STATISTICAL CRITERIA AIC & BIC

The selection of the best kinetic models describing the reaction course is based on Akaike and Bayesian Information criteria (AIC&BIC). The application of both criteria helps balance between the goodness of the fit of the experimental results by the prediction curves, the number of required models and the number of parameters used.

- During selection of the best model not only the quality of fit (such as the sum of residual squares), but also the number of data points and model parameters are considered.
- Applied procedure indicates not only which model is more likely to be correct but also quantifies how much more likely by application of the AIC and BIC weights “w”.

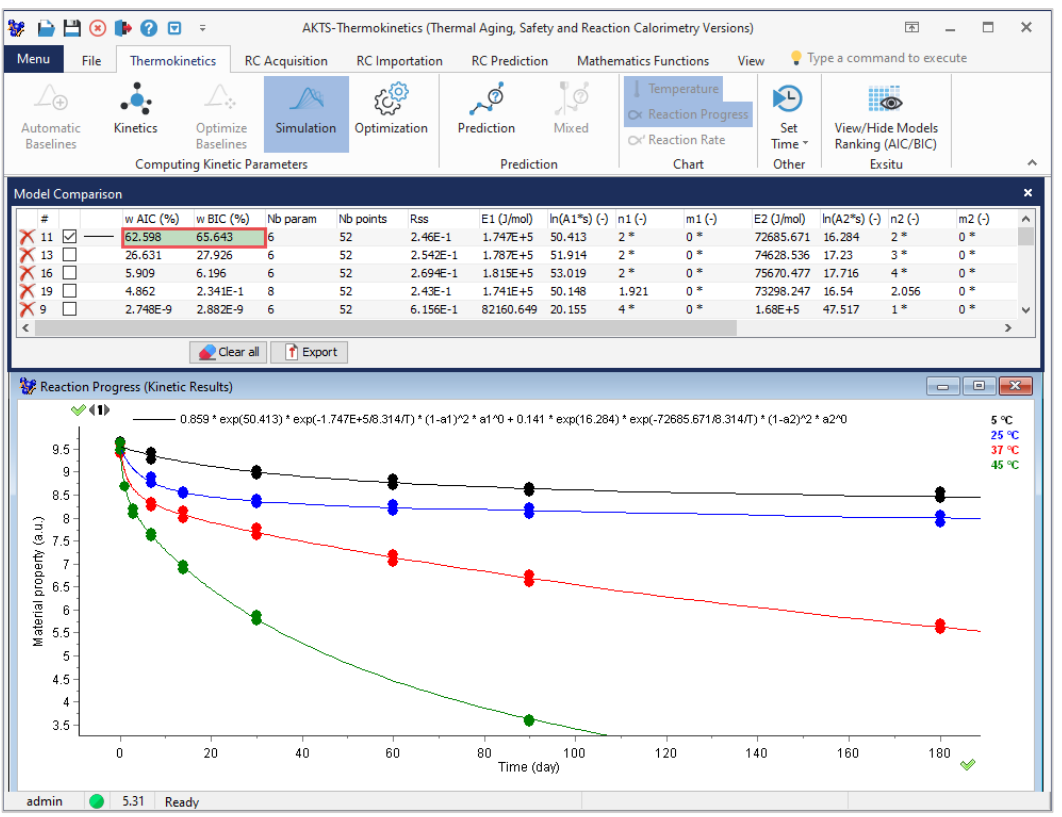

FIG. 1 - Kinetic parameters determined for all considered models and fit of experimental points (solid circles) by the best model. The best model has the highest weights (wAIC=ca.63% and wBIC=ca.66%).

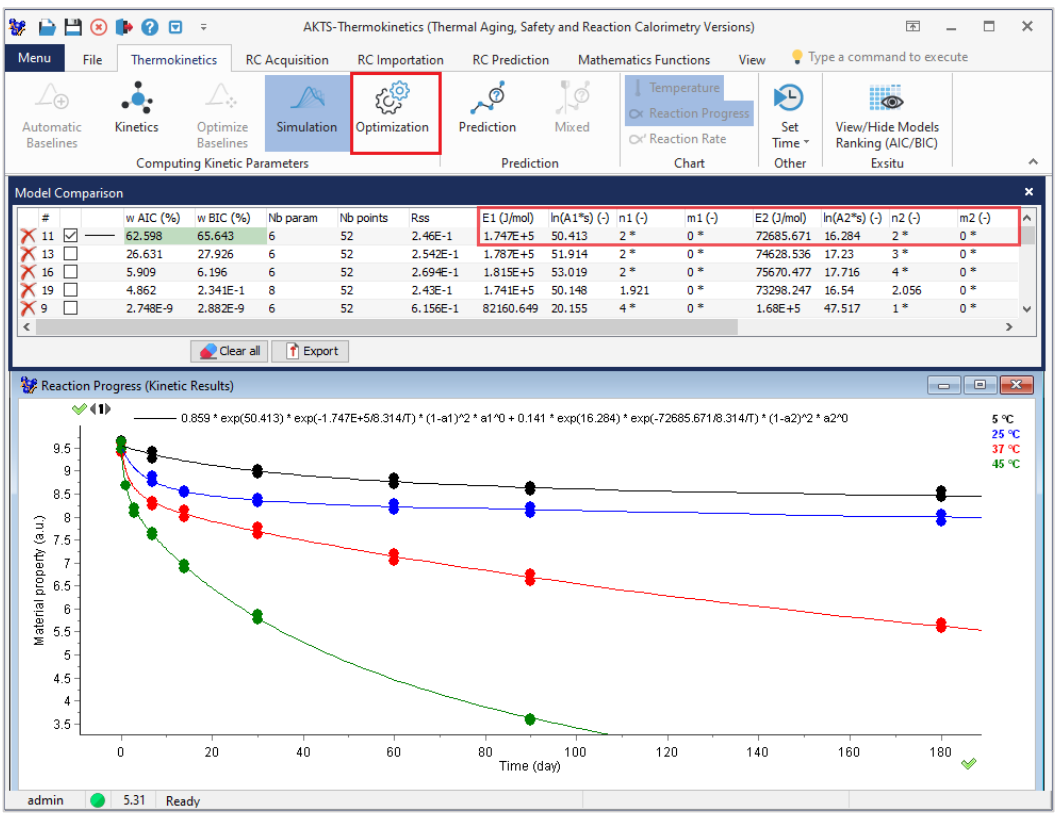

FIG. 2 - Kinetic parameters of the best model after optimization. Parameters with fixed value (denoted by *) were not optimized.

The parameters of the best kinetic models can be additionally optimized after selection of the tool **«Optimization».**

The software has already chosen which model is the best, but one can additionally select the other models (0-th order in Fig. 3 and 1-st order in Fig. 4) for comparison.

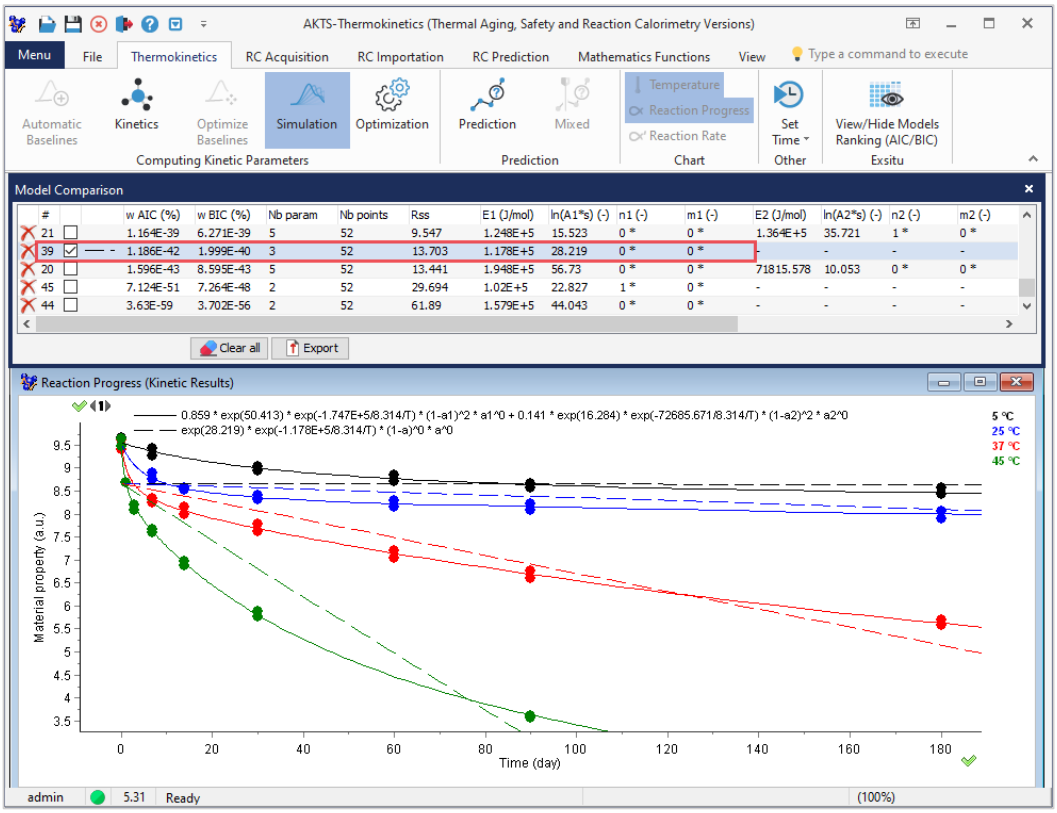

FIG. 3 - Fit of experimental data (solid circles) by the best model (solid lines) chosen according to Akaike and Bayesian criteria and by commonly applied 0-th order kinetic model (dashed lines).

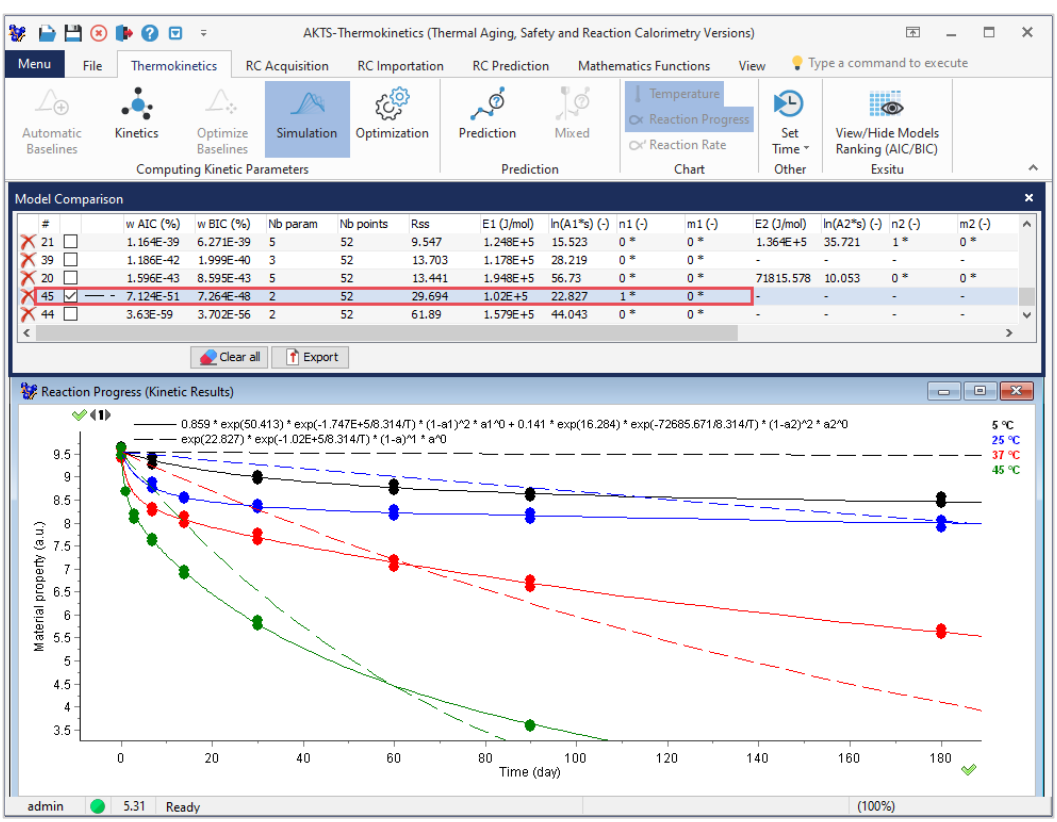

FIG. 4 - Fit of experimental data (solid circles) by the best model (solid lines) chosen according to Akaike and Bayesian criteria and by commonly applied first order kinetic model (dashed lines).

ISOTHERMAL TEMPERATURE MODE, TIME-TEMPERATURE-TRANSFORMATION (TTT) DIAGRAM

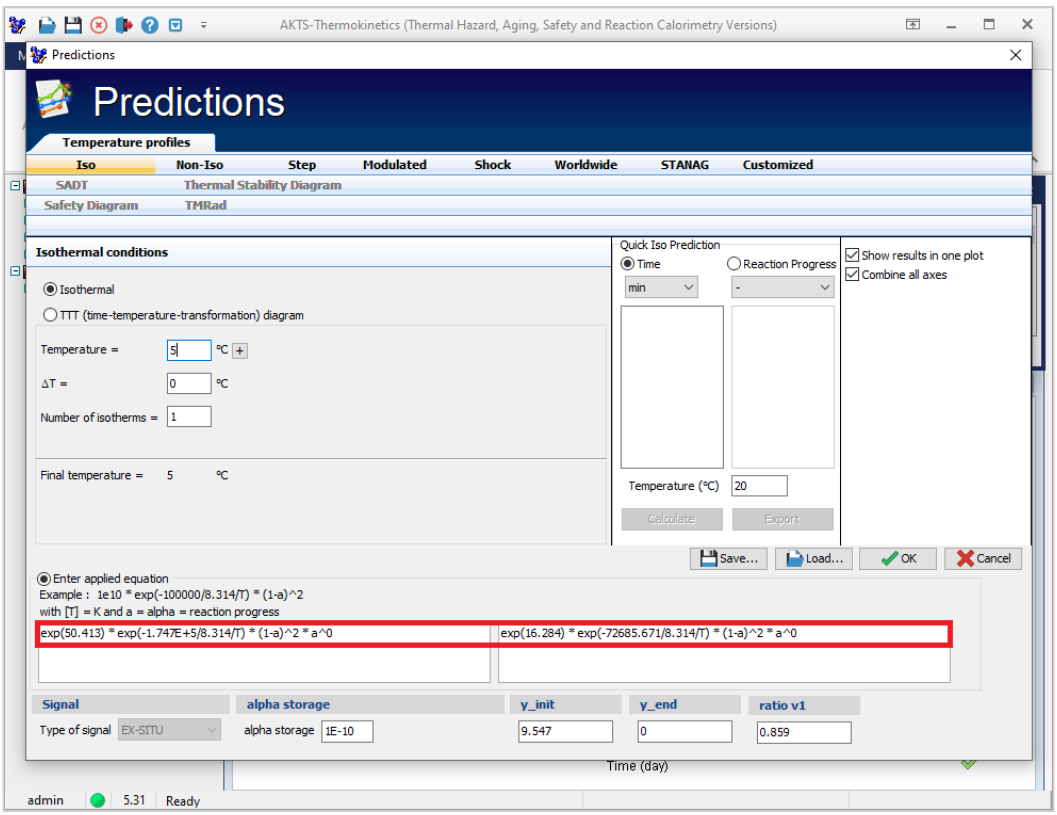

FIG. 1 - In an automatic mode the best ranked kinetic model is automatically introduced and used for the predictions.

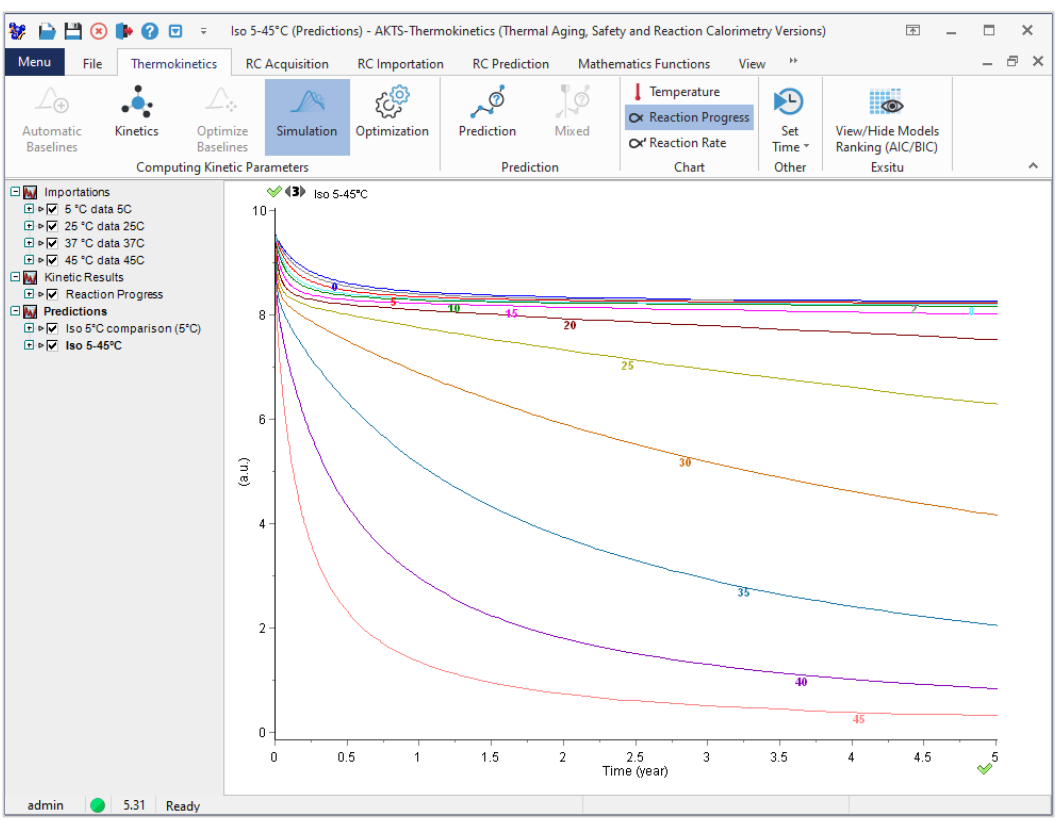

FIG. 2 - Prediction of the reaction course at chosen temperatures (isothermal temperature mode).

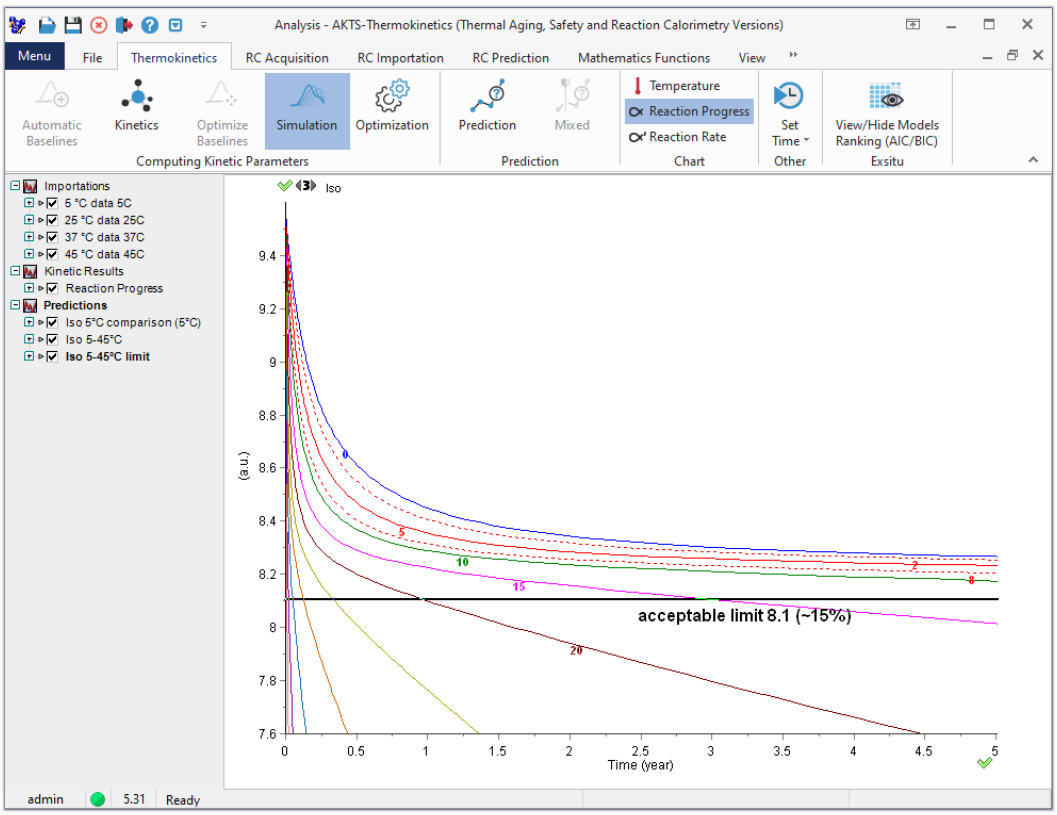

FIG. 3 - The arbitrarily chosen acceptable limit of the change of the measured quantity is set as 8.1 a.u. what corresponds to the ca. 15% deterioration extent (reaction progress). At 15°C this limit is reached after about 3 years.

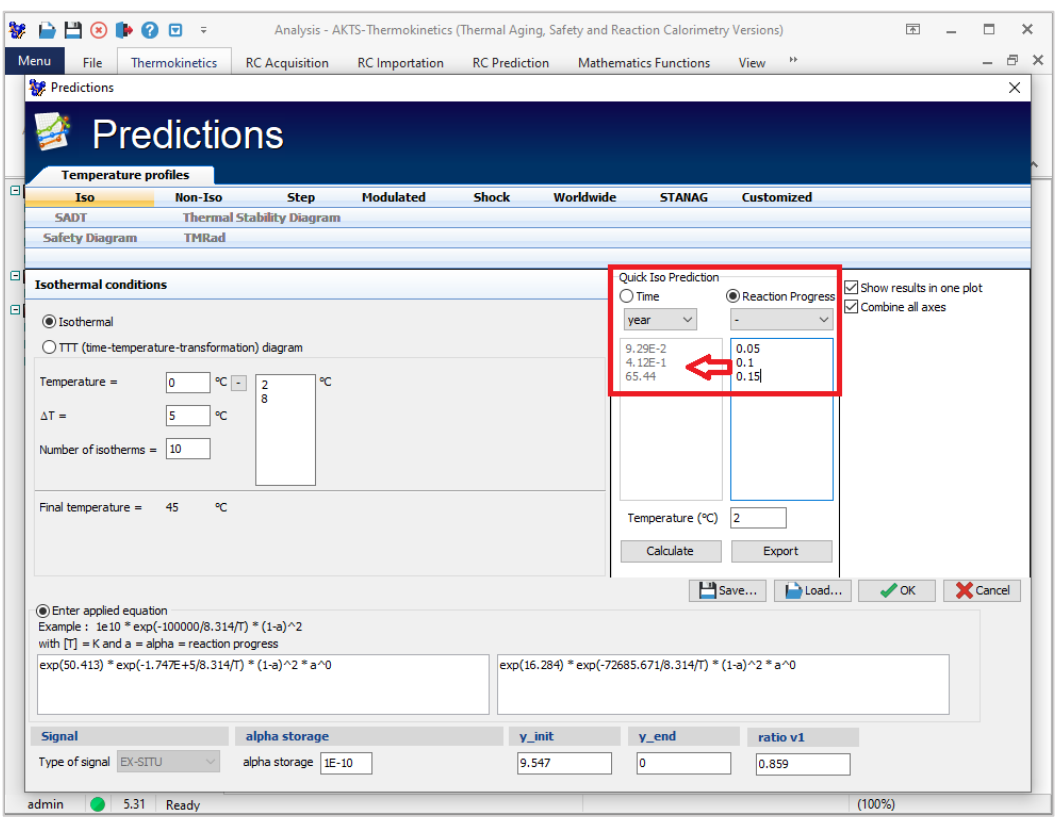

FIG. 4 - Quick isothermal prediction: reaction progresses of 0.05, 0.1 and 0.15 (15%) are reached at 2°C after ca. 34 days, ca. 150 days and ca. 65 years, respectively.

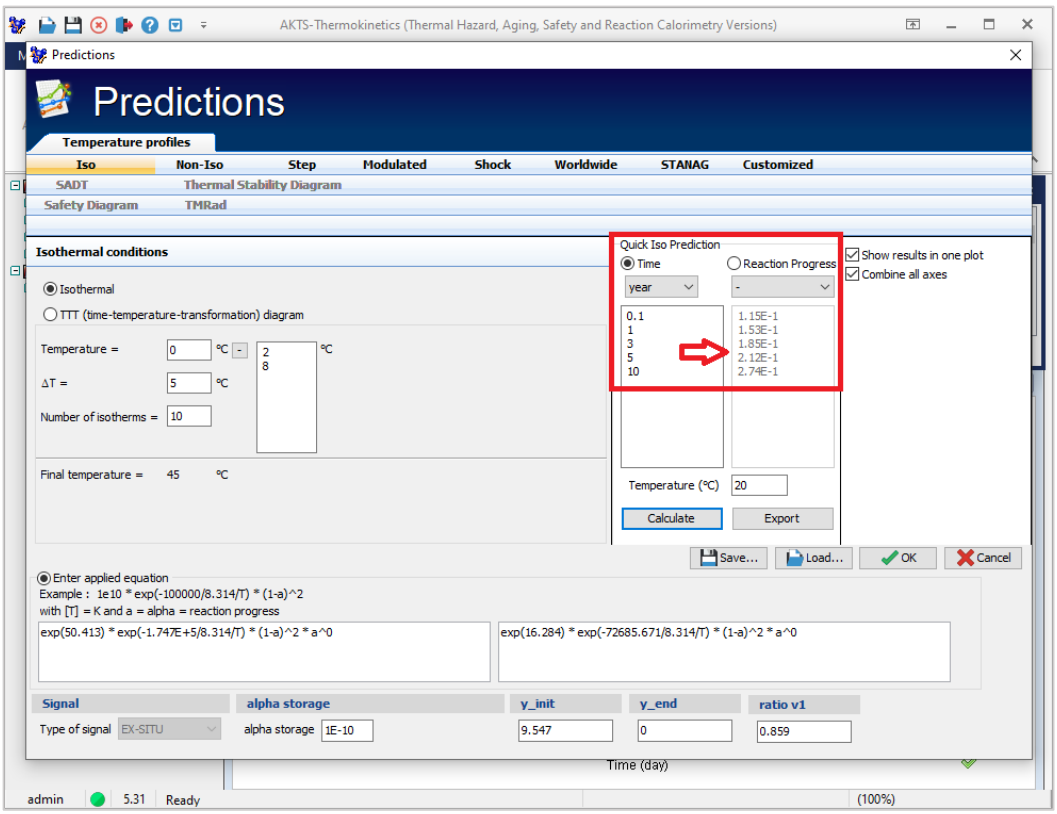

FIG. 5 - Quick isothermal prediction: the predicted reaction progress after 0.1, 1, 3, 5 and 10 years amounts at 20°C to ca. 11, 15, 18, 21 and 27%, respectively.

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

TTT plot can be used to determine immediately the time at which the required reaction extent is reached at chosen temperature.

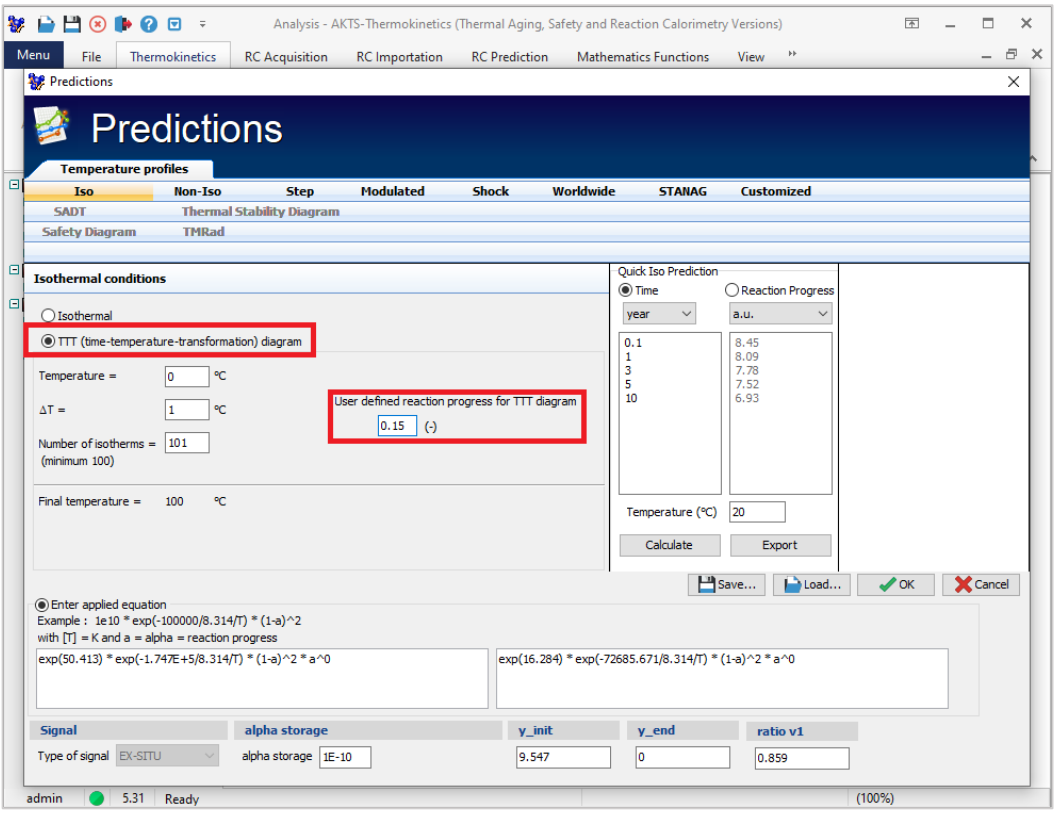

FIG. 6 - Calculating "TTT" diagram for different reaction progresses ranging from 0.01 to 0.99. User defined reaction progress 0.15 corresponds to the arbitrarily set shelf life limit (acceptable limit of the change of the measured quantity).

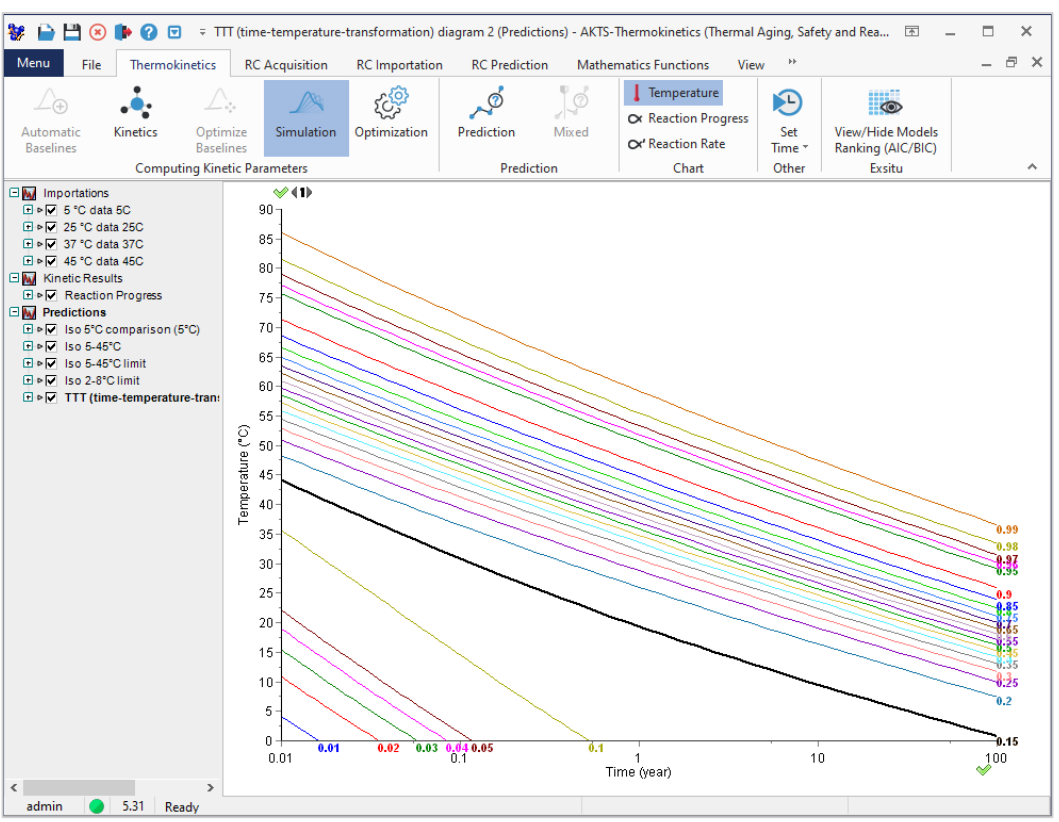

FIG. 7 – "TTT" diagram for the reaction progresses ranging from 0.01 to 0.99 and for user-defined acceptable limit of the change of the measured quantity (shelf-life criterion) set at 0.15 (bold black line).

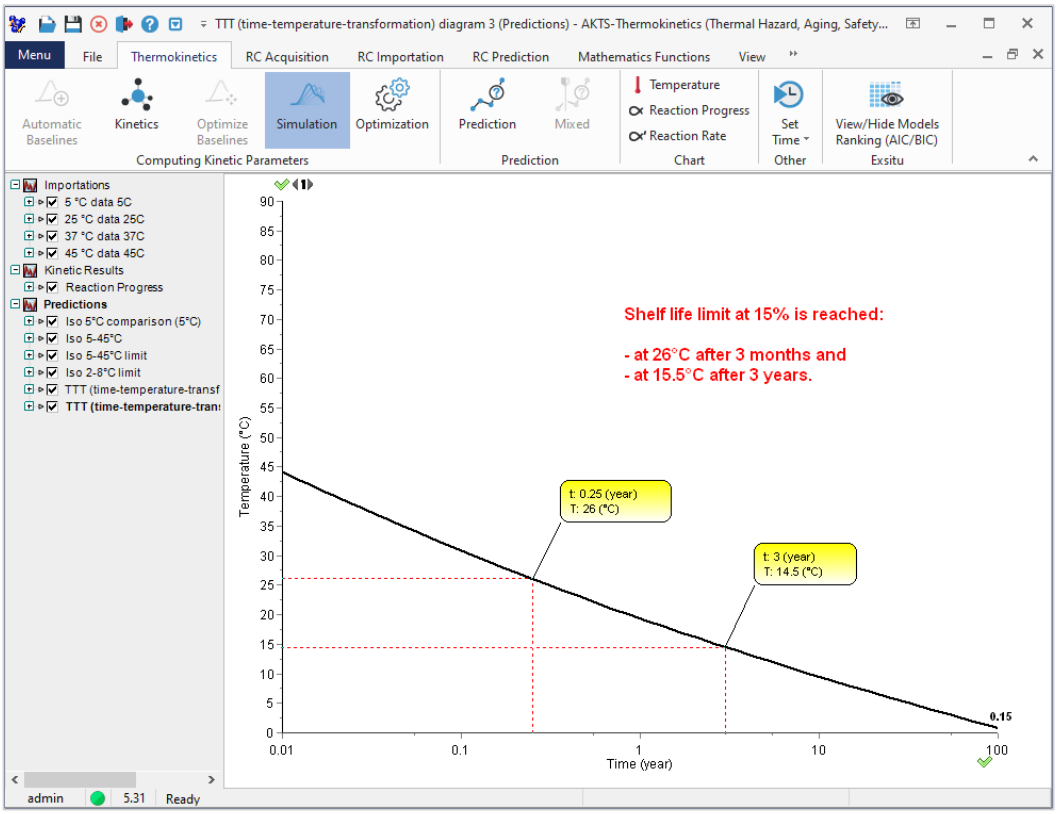

FIG. 8 – Prediction of "TTT" diagram for reaction progress at 0.15 (shelf life limit). The limit of the change of the measured quantity (15%) is reached at 26°C after 3 months and at 14.5°C after 3 years.

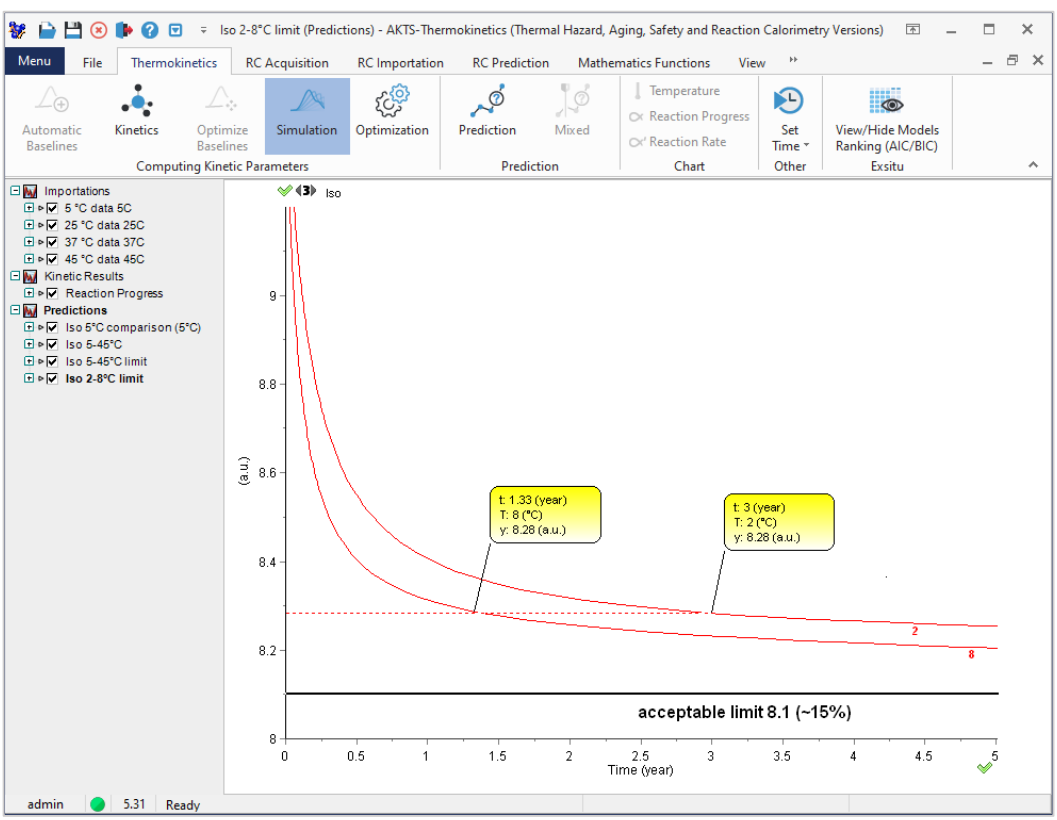

FIG. 9 – Simulation of the long-term prediction of the change of the material property at temperatures of 2 and 8°C (marked on the curves) during a cold chain storage. Note the severe change of the time of reaching arbitrary chosen drop of measured quantity to 8.28 a.u. from 1.33 to 3 years for 8 and 2°C, respectively. Both temperatures fulfill the cold chain criterion (2°C < T < 8°C).

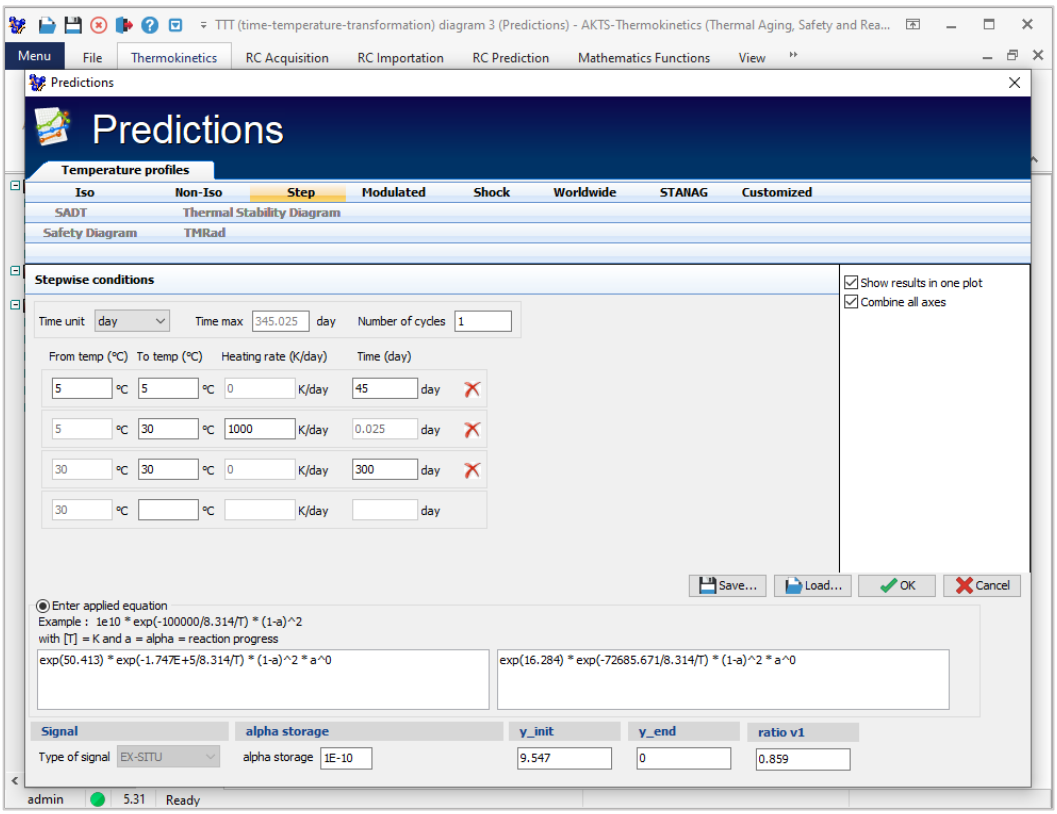

FIG. 1 - The input of parameters for calculation of the reaction extent for the following temperature profile: 45 days at 5°C followed by exposition to 30°C for 300 days.

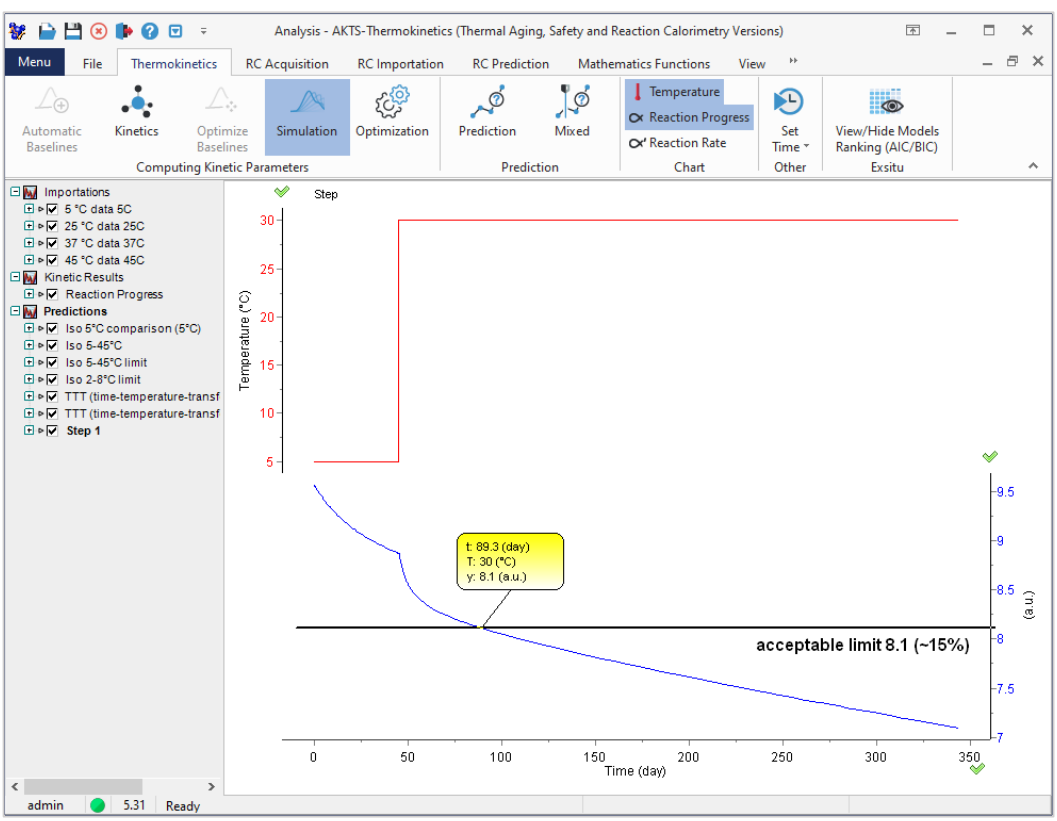

FIG. 2 - The reaction extent for the following temperature profile: 45 days at 5°C followed by exposition to 30°C for 300 days.

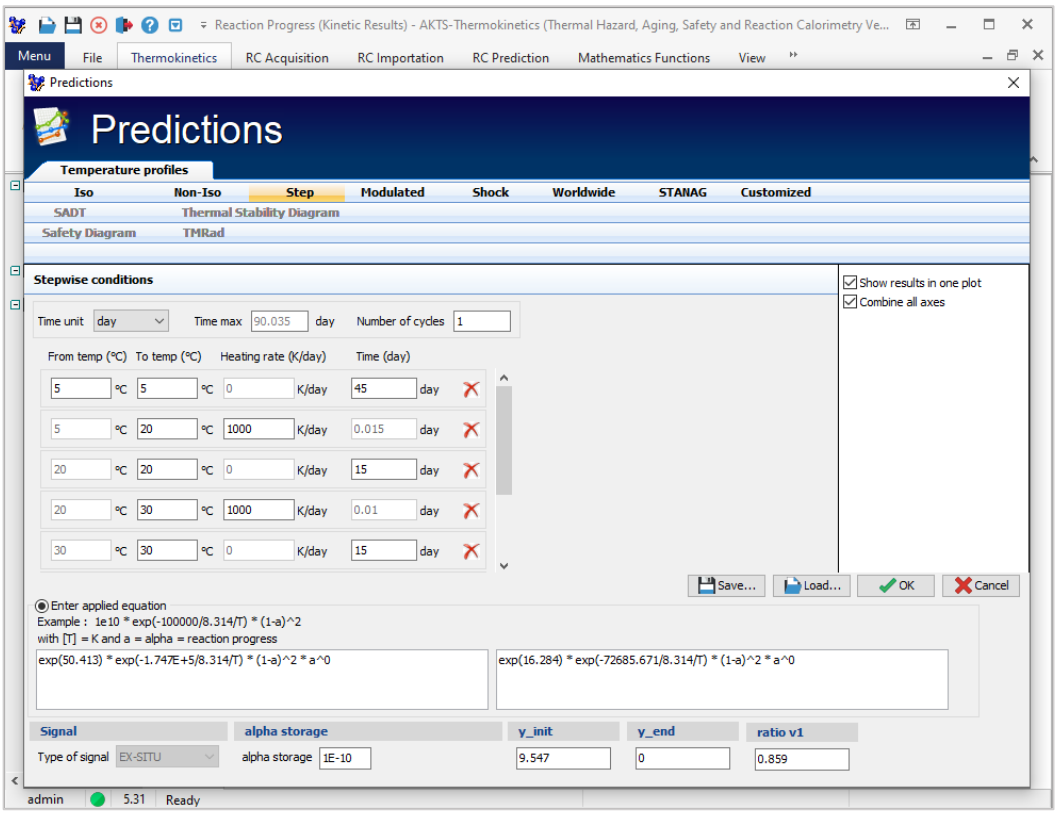

FIG. 3 - The input of parameters for the prediction of the reaction extent for the following step-wise temperature profile: 45 days at 5°C, 15 days at 20°C, 15 days at 30°C, 15 days at 40°C.

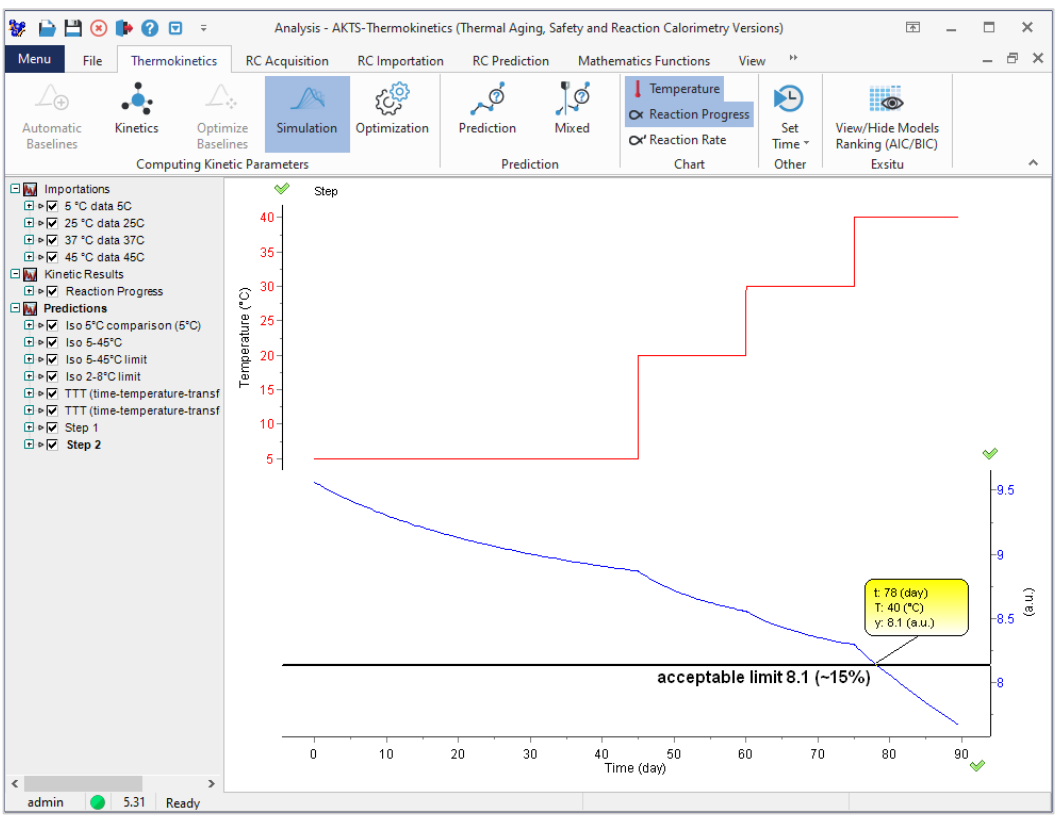

FIG. 4 - Simulation of the prediction of the deterioration course during: 45 days at 5°C, 15 days at 20°C, 15 days at 30°C, 15 days at 40°C. The value of 15% corresponding to the acceptable limit (8.1 a.u.) is reached after 78 days.

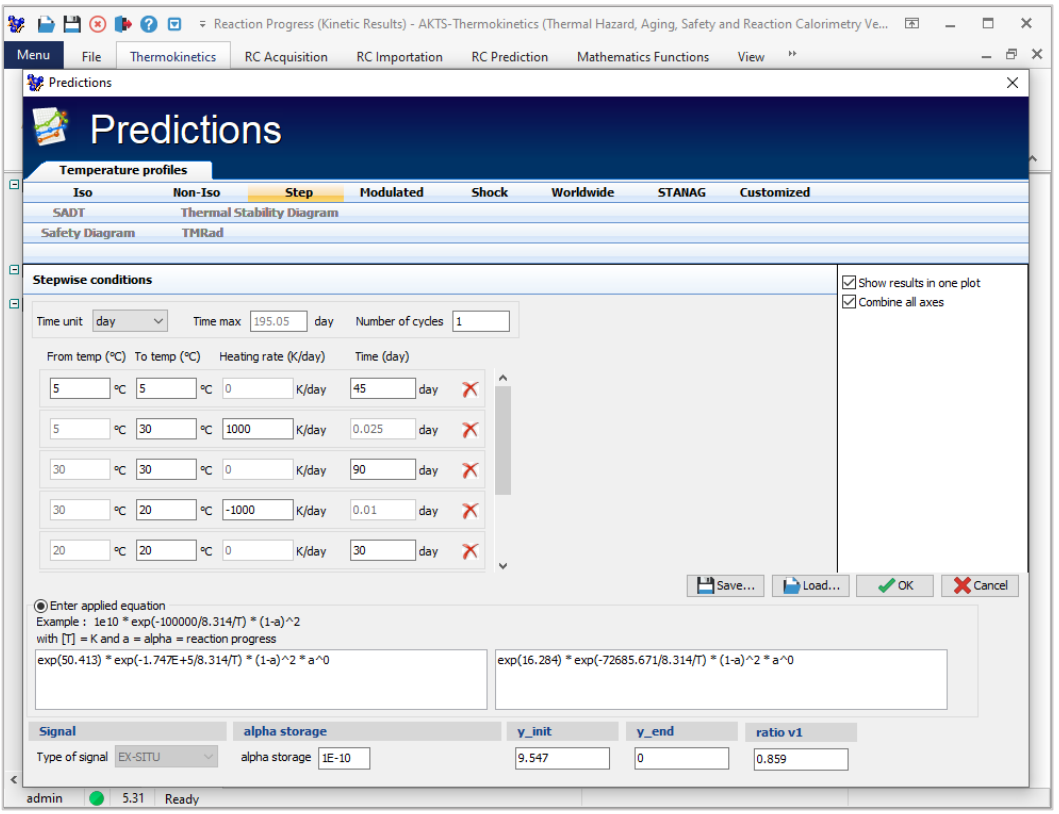

FIG. 5 - The input of parameters for the prediction of the deterioration course for the following temperature profile: 45 days at 5°C, 90 days at 30°C, 30 days at 20°C, 30 days at 5°C.

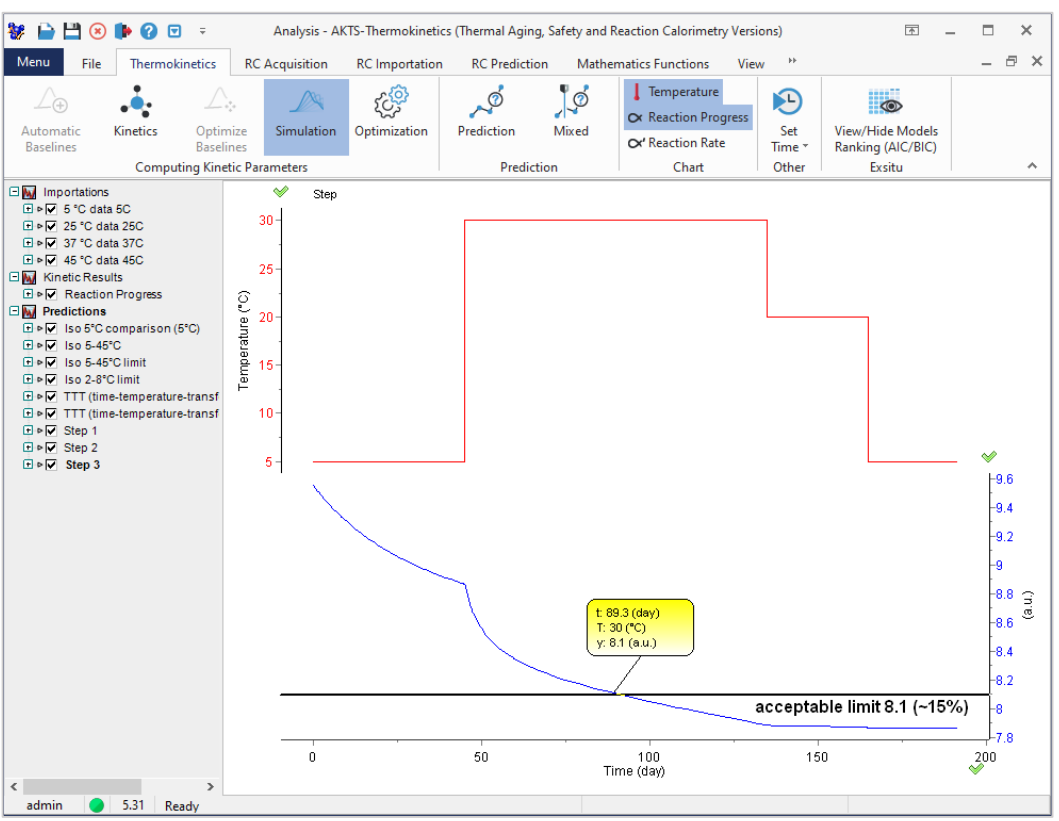

FIG. 6 - Simulation of the prediction of the change of the measured quantity during: 45 days at 5°C, 90 days at 30°C, 30 days at 20°C, 30 days at 5°C. The value of 15% corresponding to the acceptable limit (8.1 a.u.) is reached after 89.3 days.

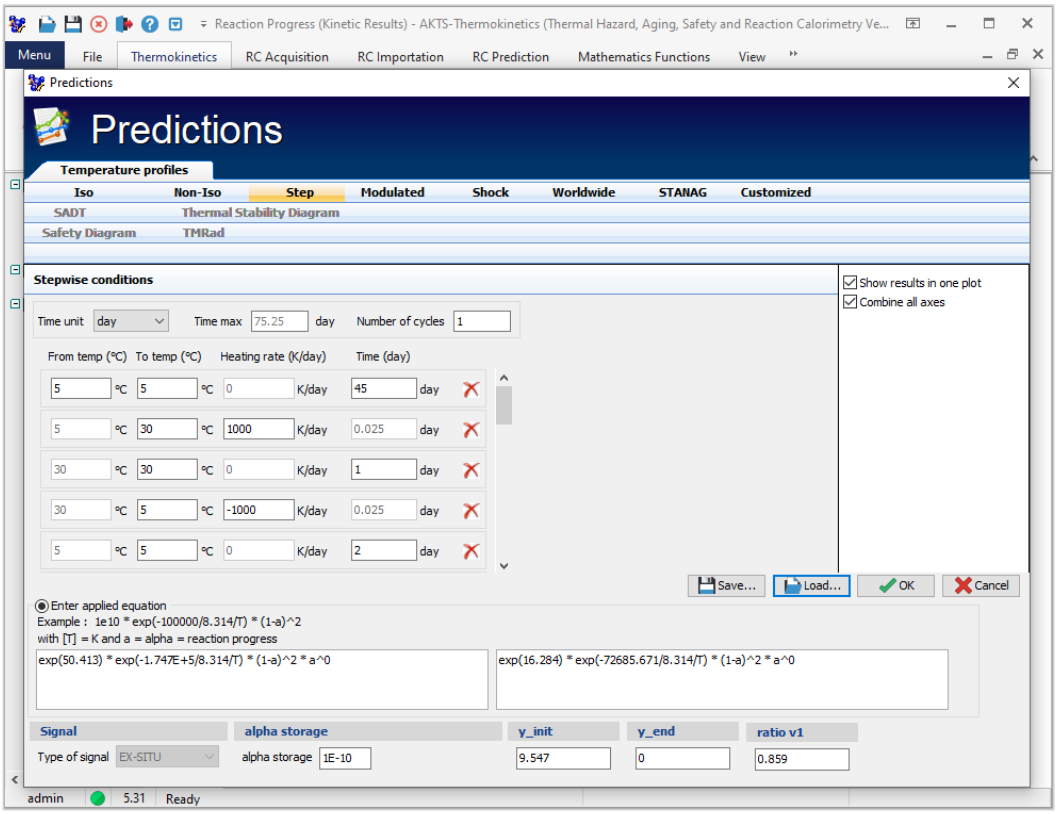

FIG. 7 - The input of parameters for calculation of the reaction extent for the following temperature profile: 5°C for 45 days, 30°C for 1 day followed by 2 days at 5°C, 30°C for 1 day followed by 2 days at 5°C, 30°C for 1 day followed by 2 days at 5°C, 30°C for 1 day followed by 2 days at 5°C, 30°C for 1 day followed by 2 days at 5°C, 5°C for 15 days.

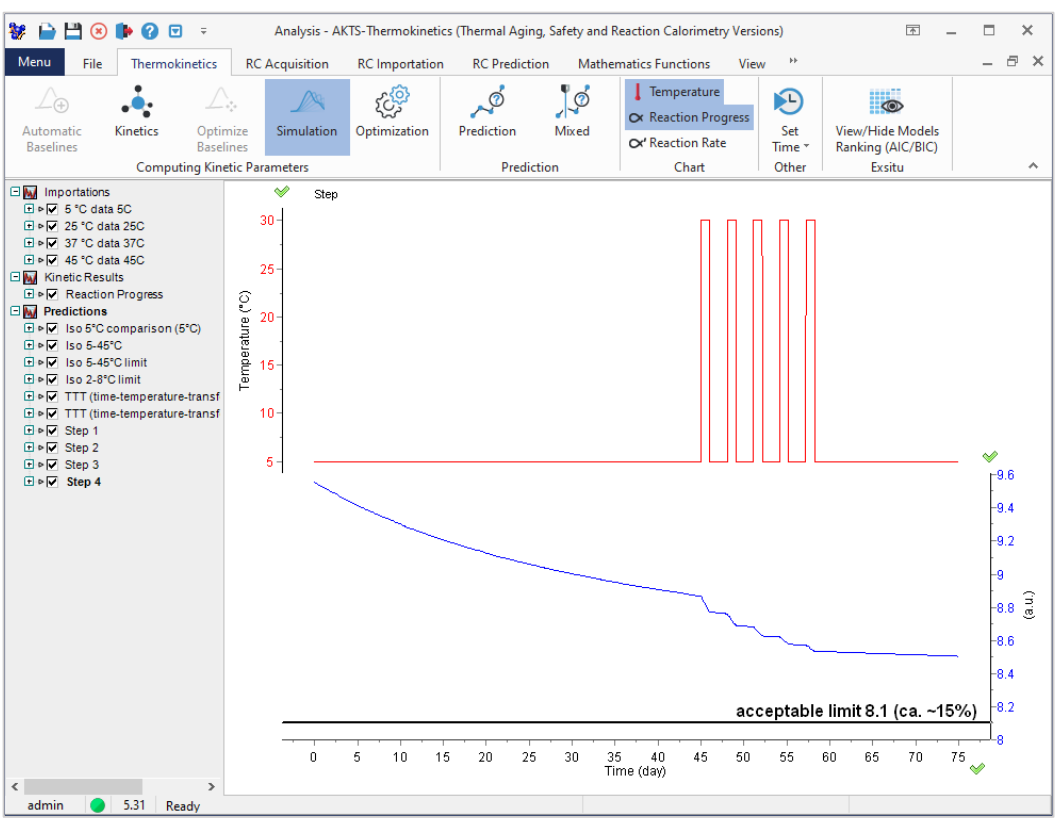

FIG. 8 - Simulation of the prediction of the change of the measured quantity at temperature profile specified in Fig 7. The value of 15% corresponding to the acceptable limit (8.1 a.u.) is not reached during the temperature cycling.

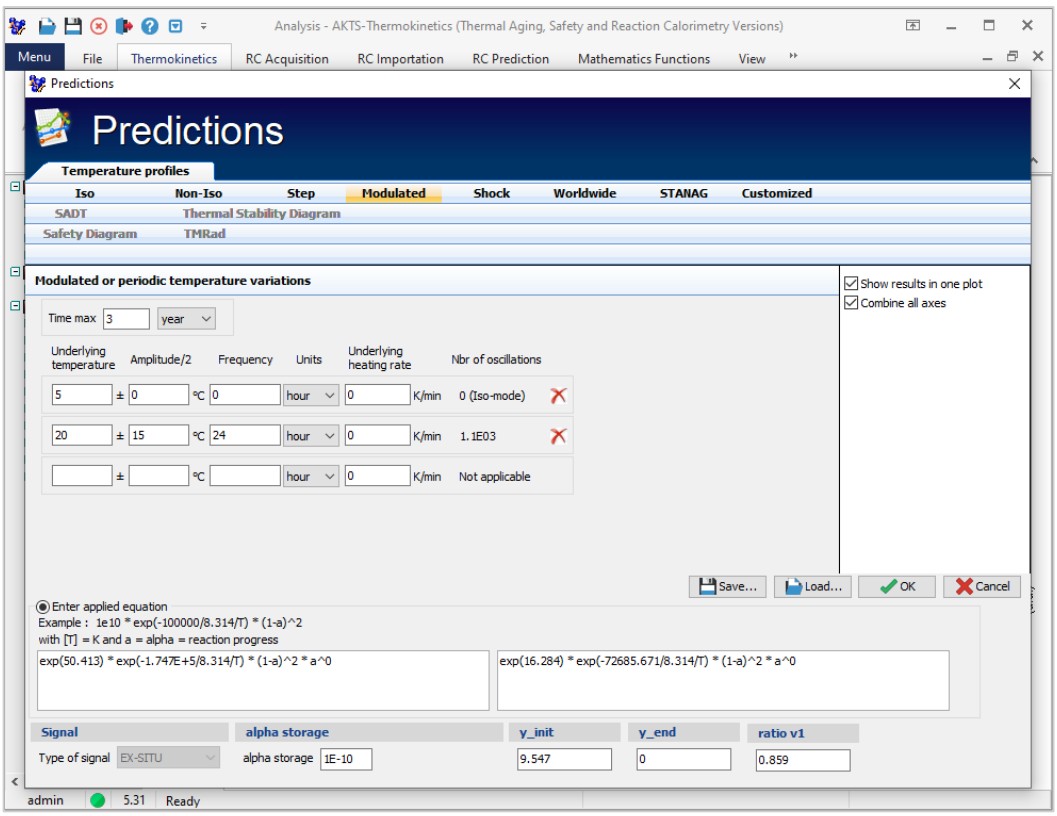

FIG. 1 - The option **'Modulated'** allows to predict the reaction extent at two temperature modes (i) storage in a cold chain at 5°C (i.e. isothermal mode) and (ii) storage at ambient conditions of 20°C with daily temperature fluctuations of ±15°C.

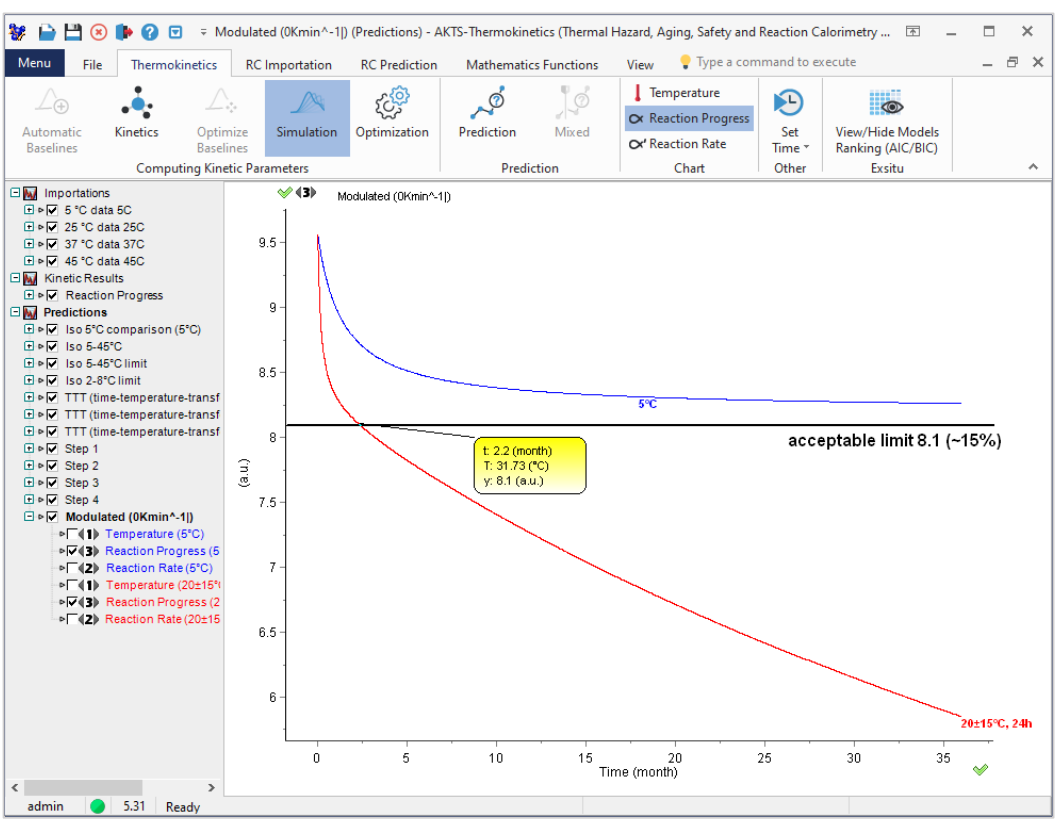

FIG. 2 - The value of 15% corresponding to the acceptable limit (8.1 a.u.) is reached after 2.2 months under ambient temperature conditions (i.e. 20°C) with daily fluctuations of ±15K (red curve). In the cold chain (blue line) the limit is not reached during 3 years.

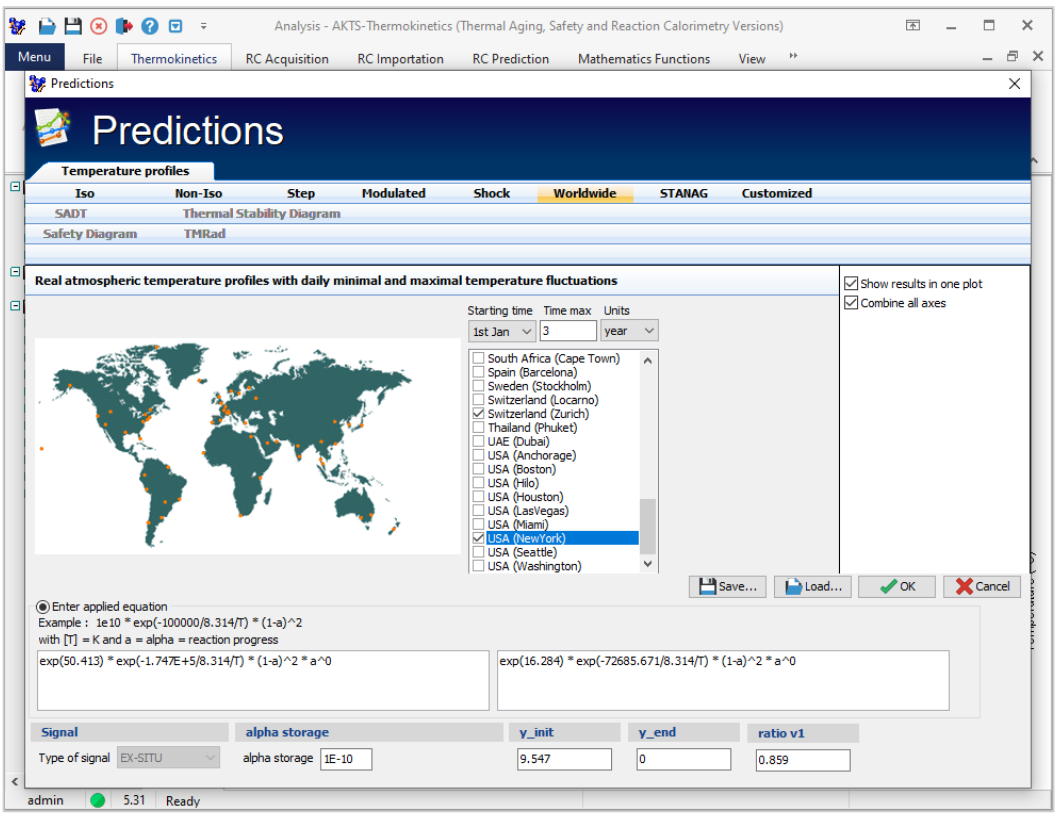

FIG. 1 - The option « Worldwide » allows for the prediction of the reaction extent at real atmospheric temperature mode, i.e. for the yearly temperature profiles with daily minimal and maximal fluctuations.

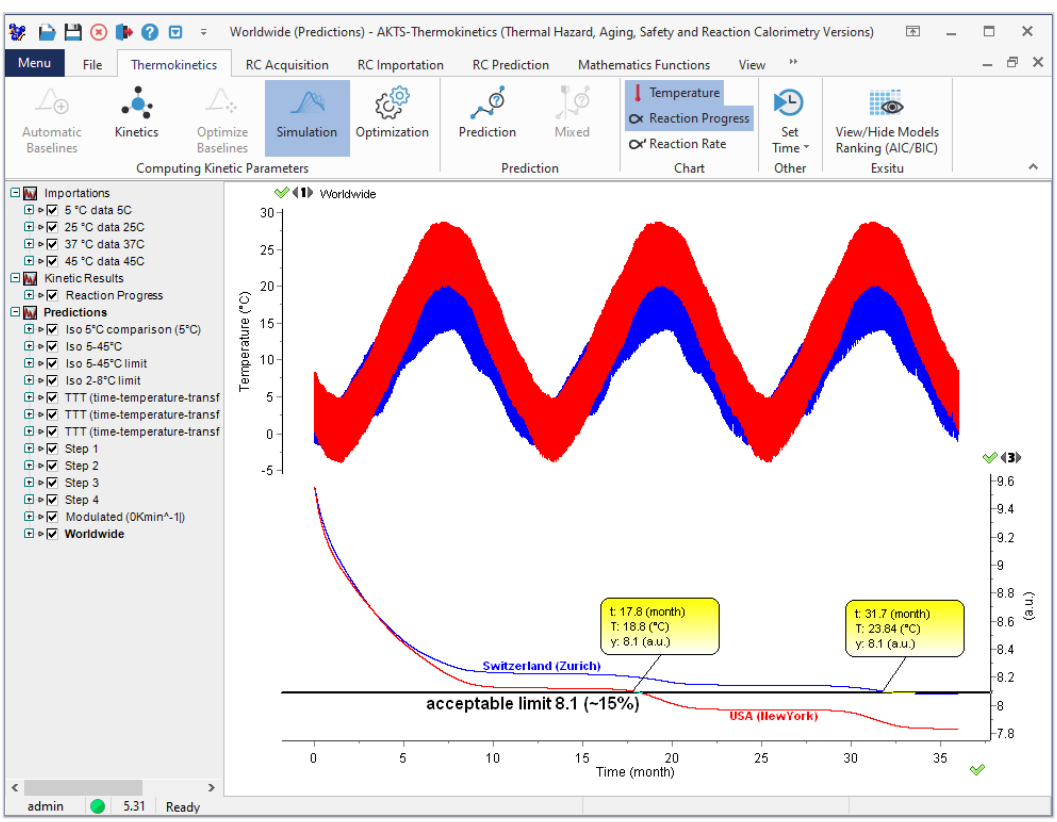

FIG. 2 - The value of 15% corresponding to the acceptable limit (8.1 a.u.) is reached after 17.8 months in New York (red lines) and 31.7 months in Zurich (blue lines), respectively.

STANAG CLIMATIC CATEGORIES

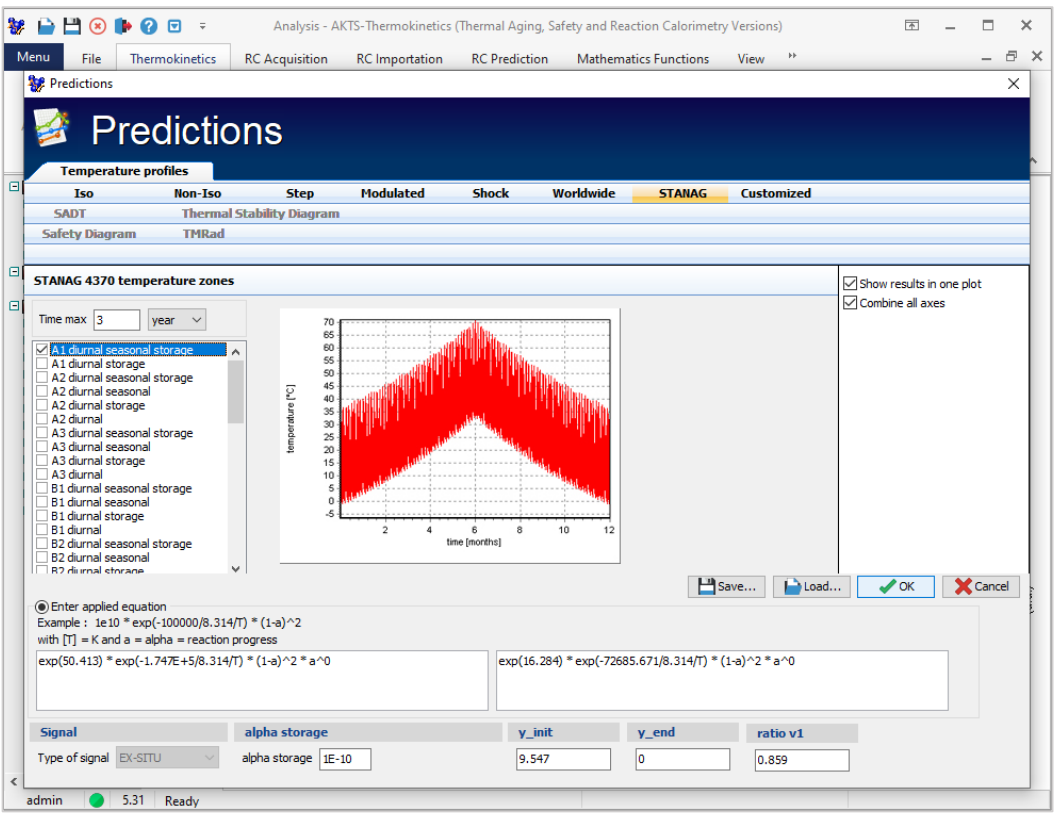

FIG. 1 – "STANAG" allows to predict the reaction course in places with different STANAG climate categories.

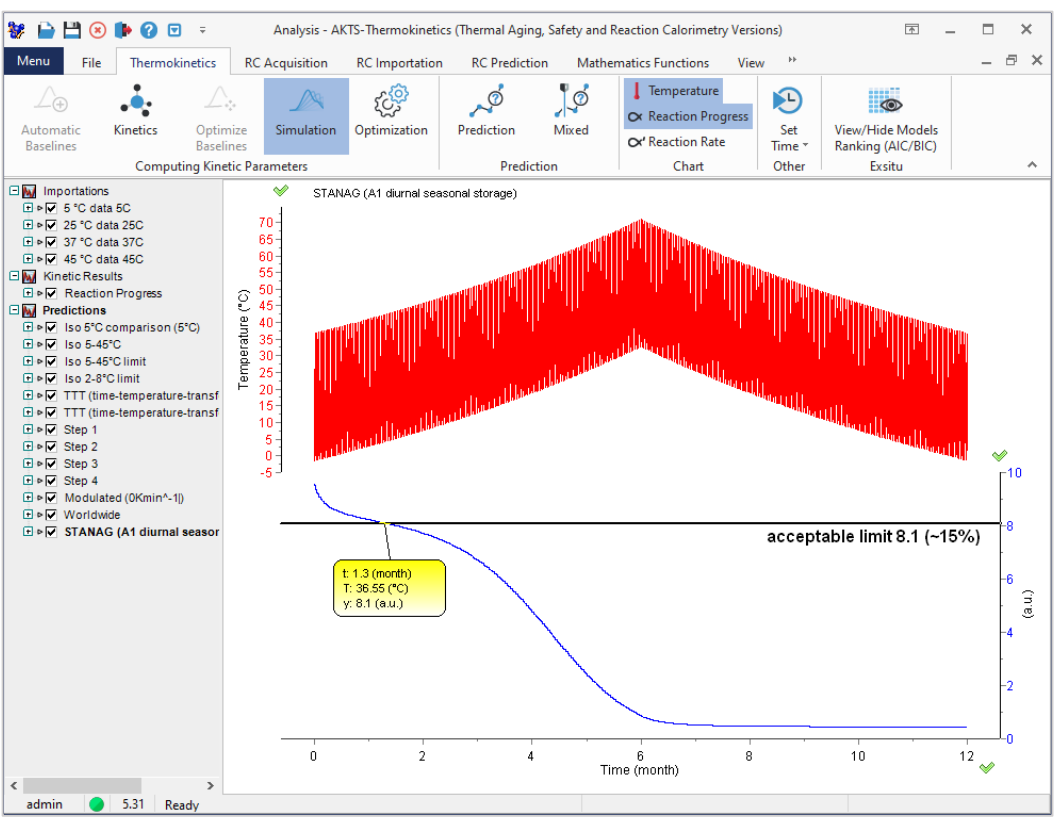

FIG. 2 - The value of 15% corresponding to the acceptable limit (8.1 a.u.) is reached after 1.3 months in STANAG climate category A1.

USER CUSTOMIZED TEMPERATURE MODE

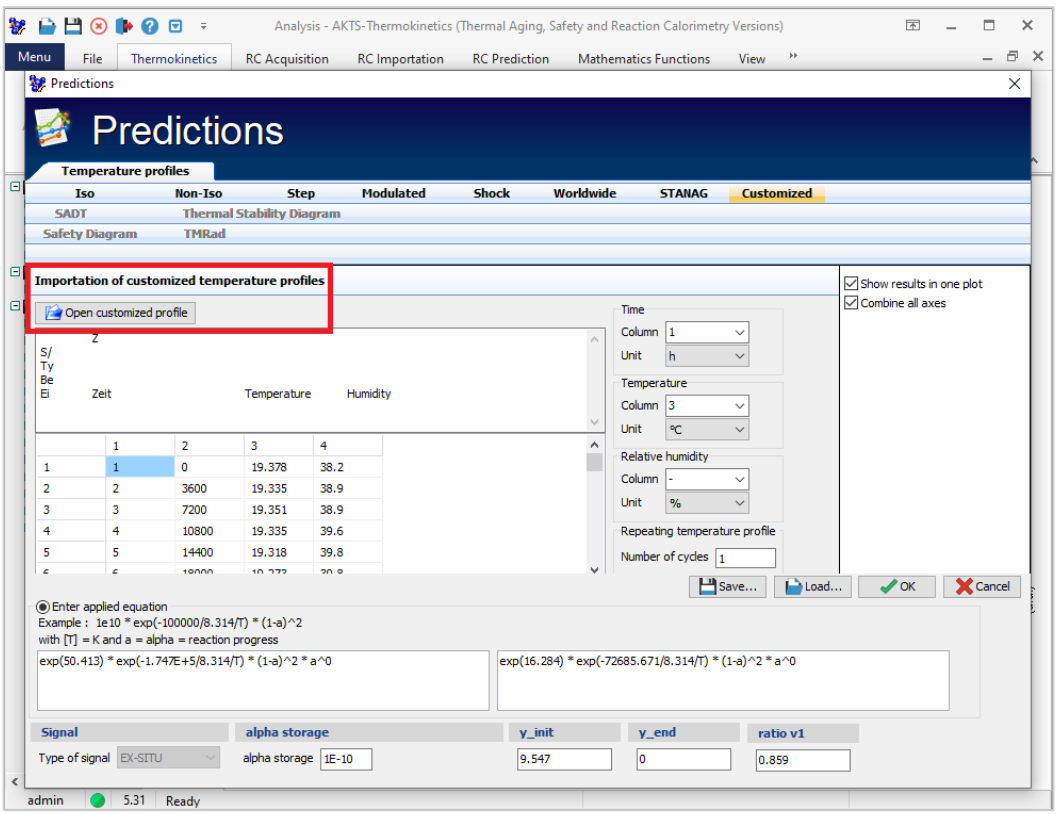

FIG. 1 - The user can predict the material properties at any customized temperature profile which has to be introduced in ASCII-format (.txt-files). The screen shows the importation of the customized profile.

The influence of the temperature fluctuations on the reaction course can be evaluated for any customized temperature profiles recorded by e.g. commonly applied data loggers that collect the temperature and humidity during a chosen period.

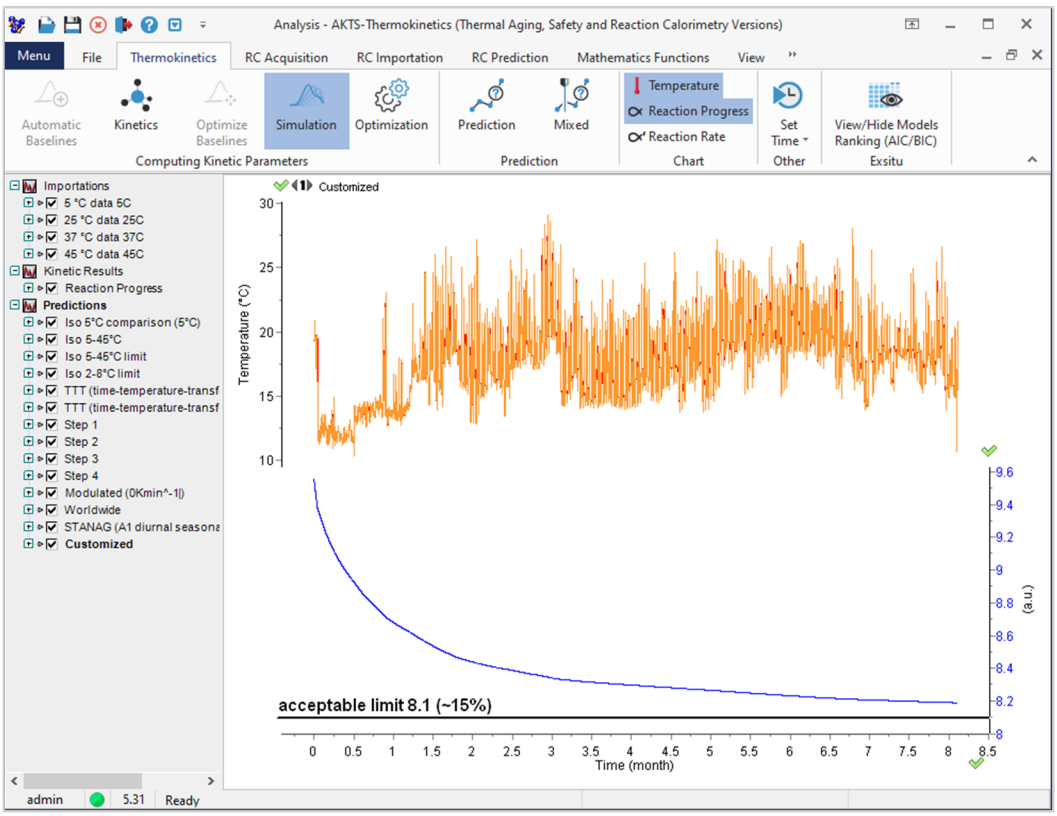

FIG. 2 - The change of the material properties at temperature profile recorded by data logger: the value of 15% corresponding to the acceptable limit (8.1 a.u.) is not reached after ca. 8 months.

MIXED TEMPERATURE MODES

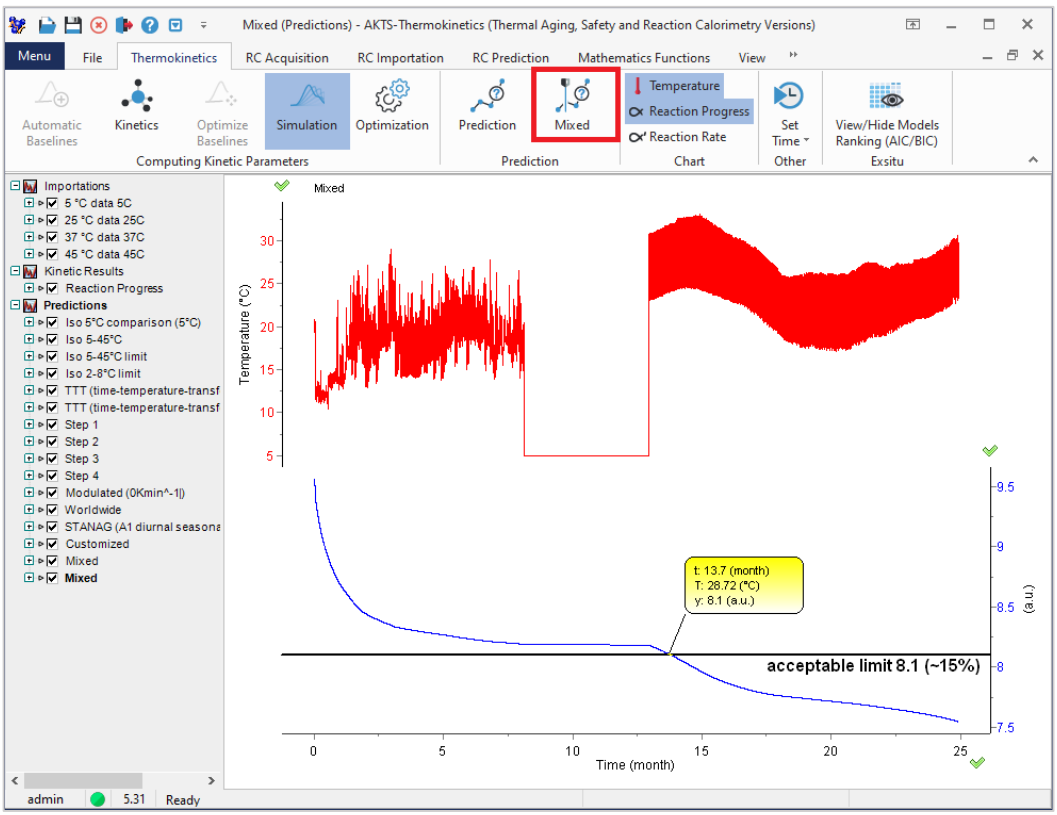

FIG. 1 - The "Mixed"-function allows to combine consecutively the different temperature conditions. This example displays the prediction of the decomposition course the following temperatures: recorded by the data logger, isothermal (5°C, characteristic for the cold chain) and daily climate fluctuations.
The value of 15% corresponding to the acceptable limit (8.1 a.u.) is reached after 13.7 months at these temperature fluctuations.

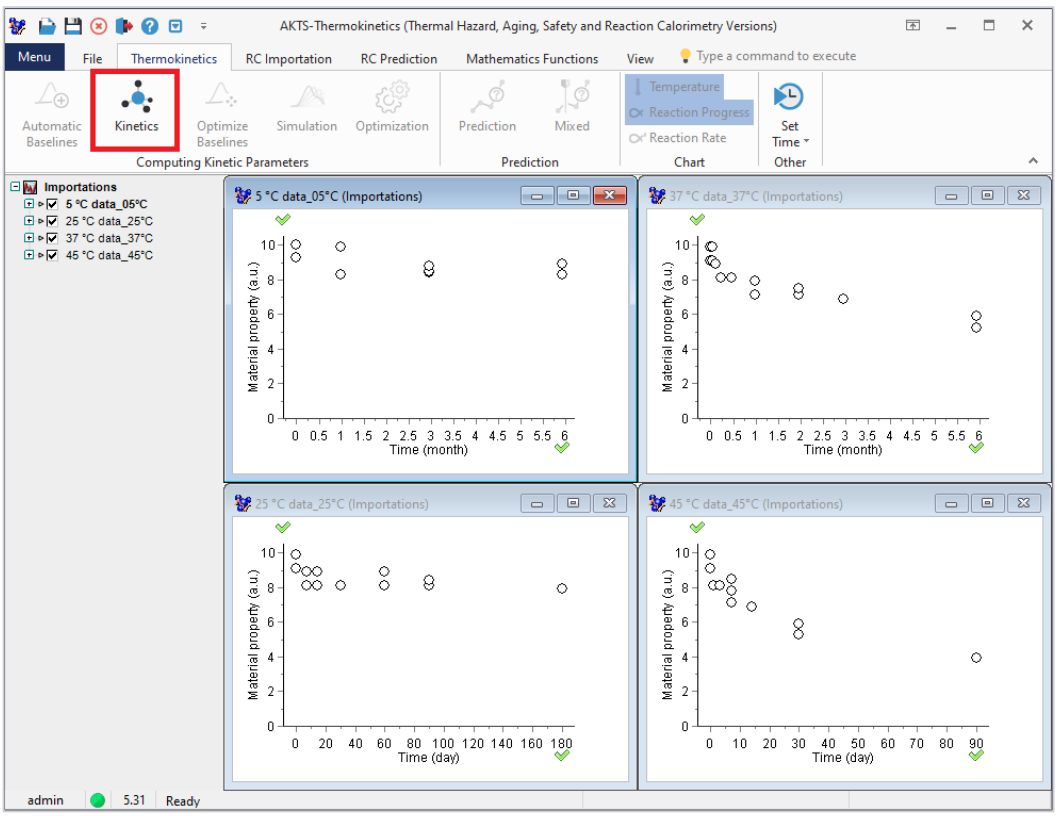

FIG. 1 – Noisy, sparse data collected at 5, 25, 37 and 45°C.

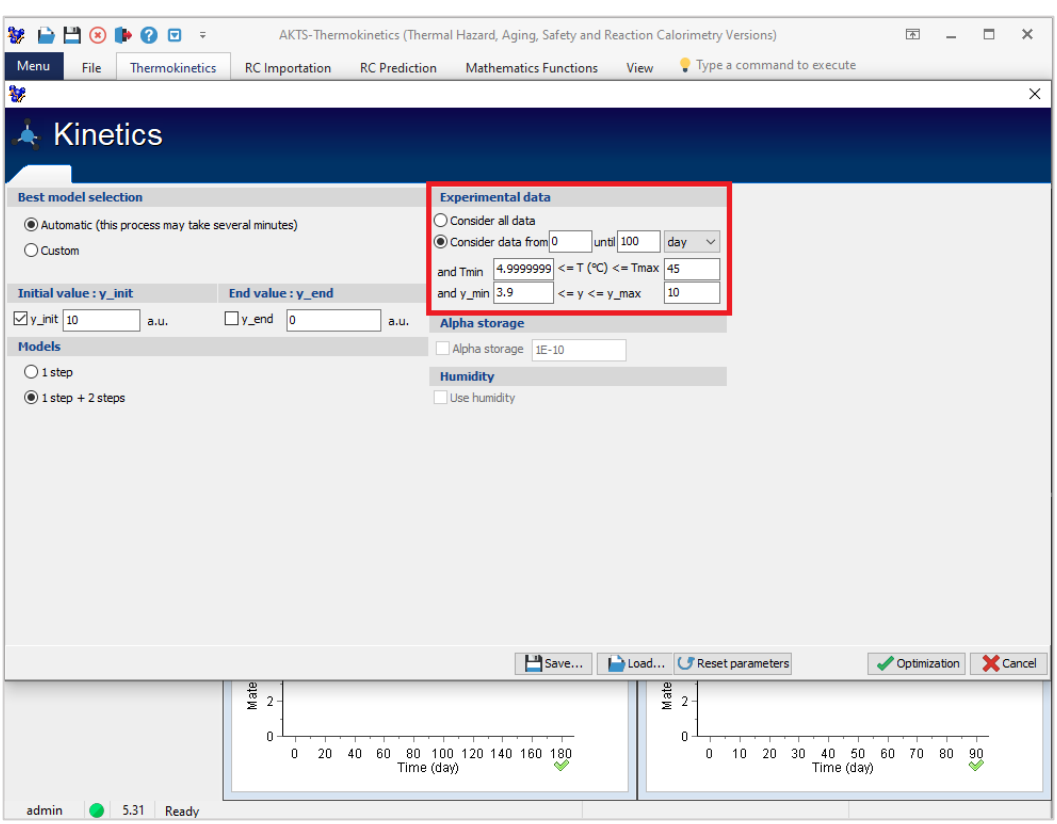

FIG. 2 - During determination of the best kinetic model one can change the range of data used in the kinetic analysis.

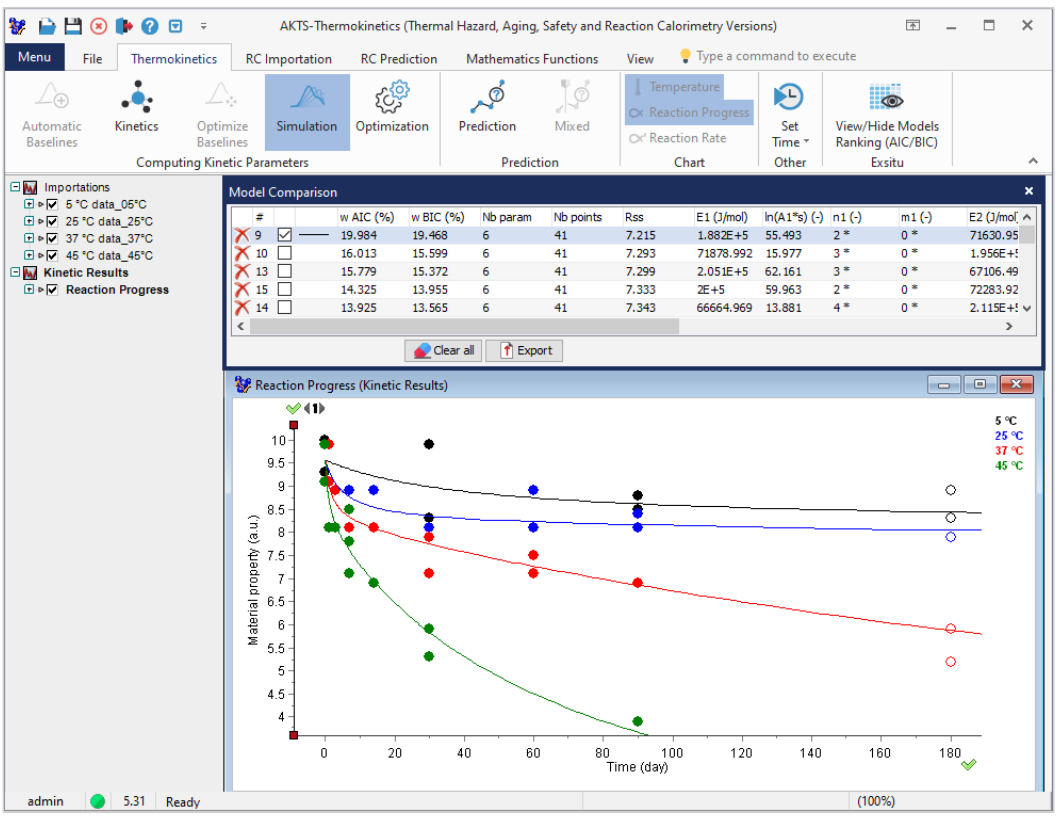

FIG. 3 - Kinetic parameters are determined for all considered models, fit of experimental points (solid circles) is displayed for the best model. Only the experimental points recorded until 100 days were considered during the kinetic analysis. The experimental points collected after 180 days (empty circles) serve for verification only.

DETERMINATION OF PREDICTION BANDS (E.G. 95% CONFIDENCE) AND VERIFICATION OF THE PREDICTIONS

The prediction bands are determined by the bootstrap method which is based on Monte Carlo approach frequently used in applied statistics. For the statistical analysis one can choose between resampling the residuals or data points.

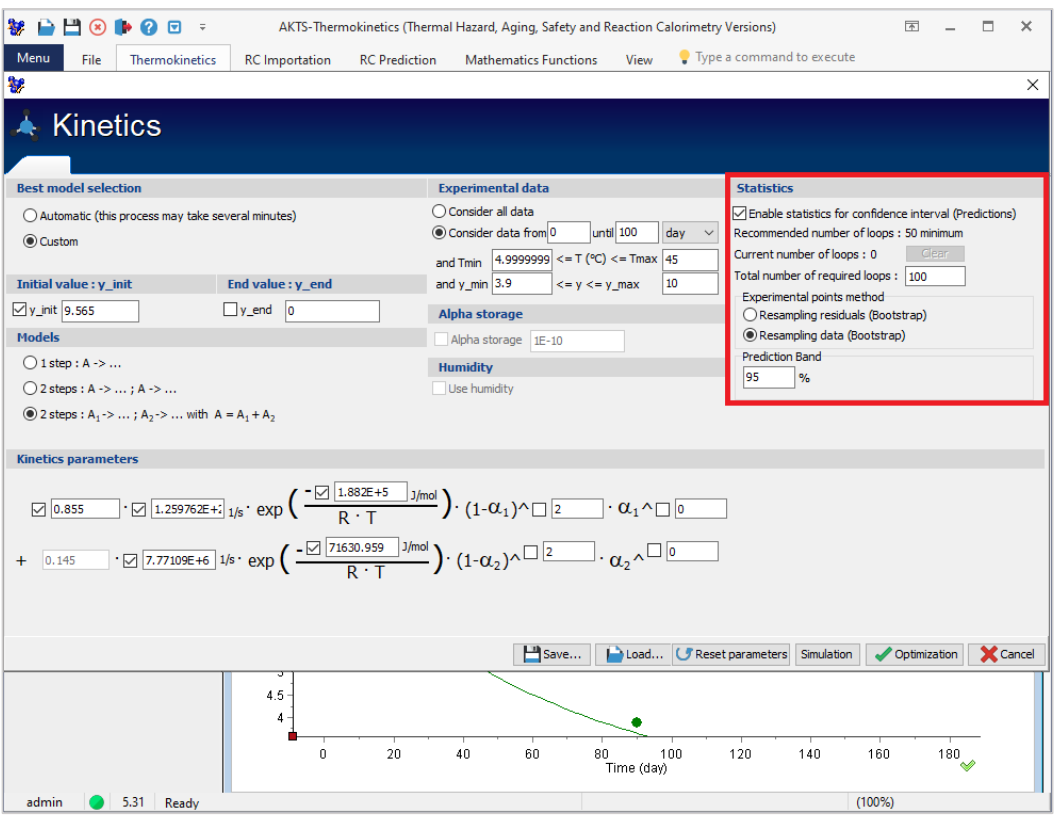

FIG. 1 - Determination of prediction bands (95% confidence). For the statistical analysis one can apply the residuals or the data points.

The plots below show the prediction of the reaction course at 5°C based on the best kinetic model evaluated from the data collected at 45, 37, 25 and 5°C (filled circles). The data points collected after 180 days serve for the verification of the predictions. The dashed lines depict the prediction bands with 95% confidence.

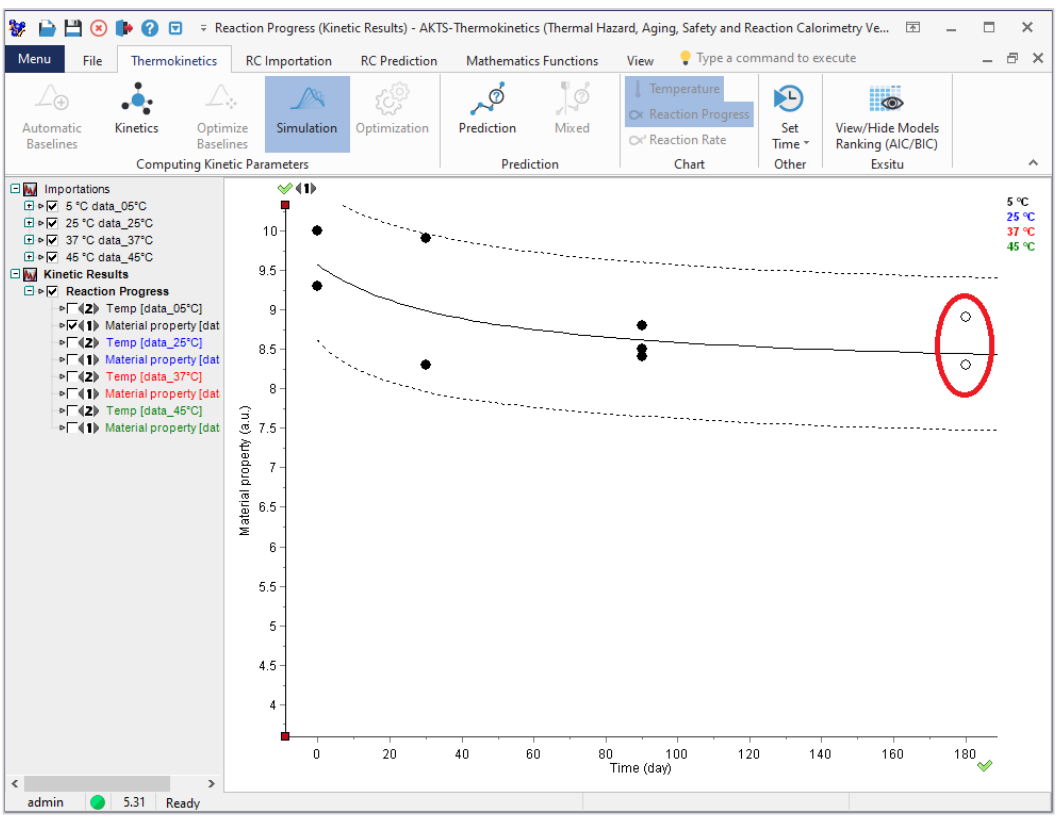

FIG. 2 - Prediction of the change of the material property at 5°C. The experimental points recorded after 6 months, which were not considered during kinetic analysis, serve for the verification of the predictions. With 95% probability all experimental points fall in the prediction band.

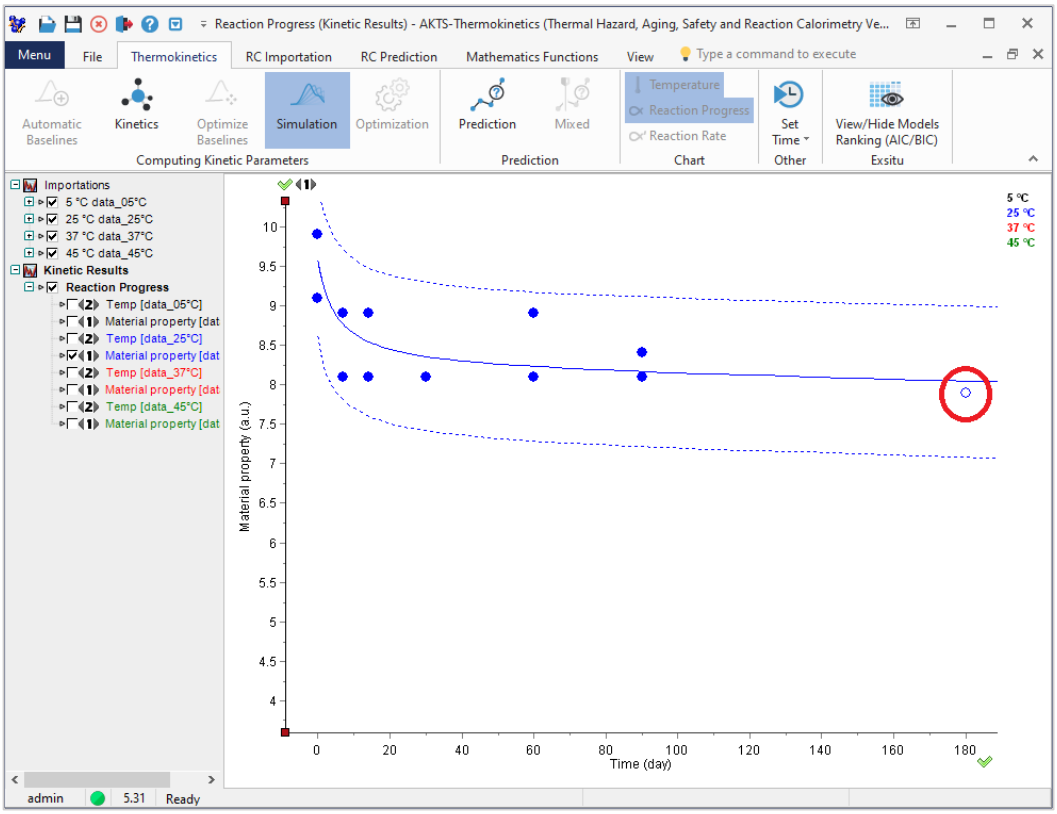

FIG. 3 - Prediction of the change of the material property at 25°C. The experimental point recorded after 6 months, which was not considered during kinetic analysis, serves for the verification of the predictions.

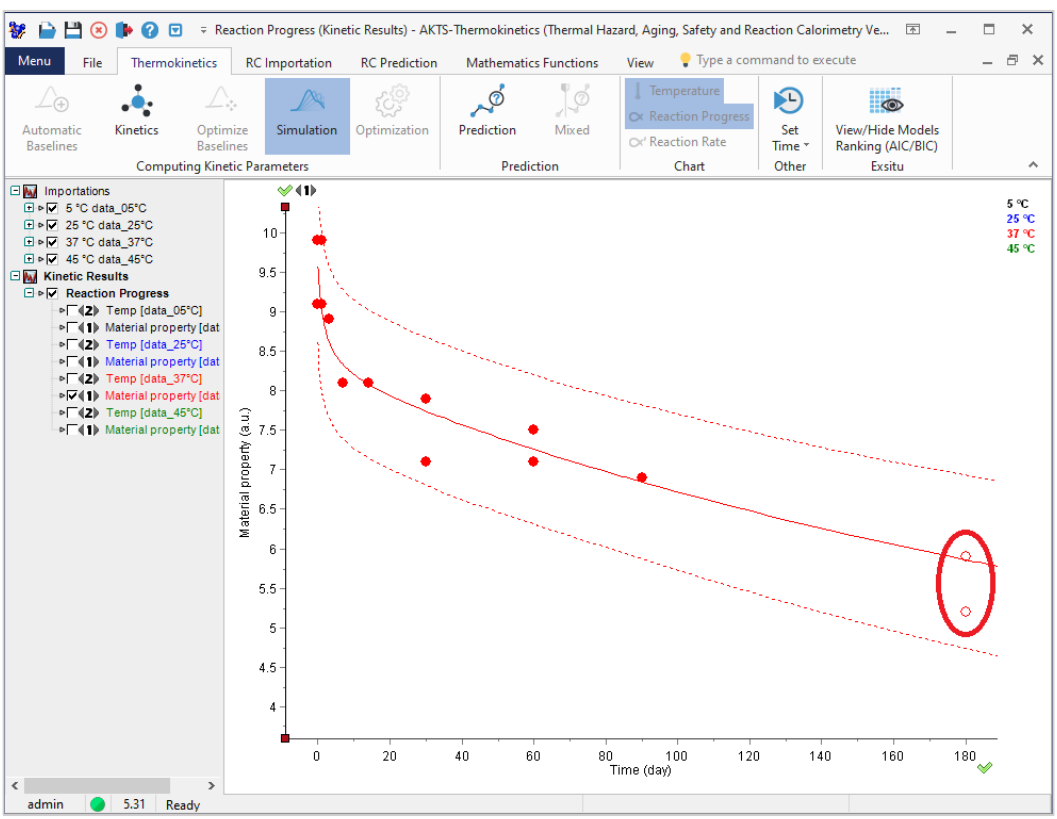

FIG. 4 - Prediction of the change of the material property at 37°C. The experimental points recorded after 6 months, which were not considered during kinetic analysis, serve for the verification of the predictions.

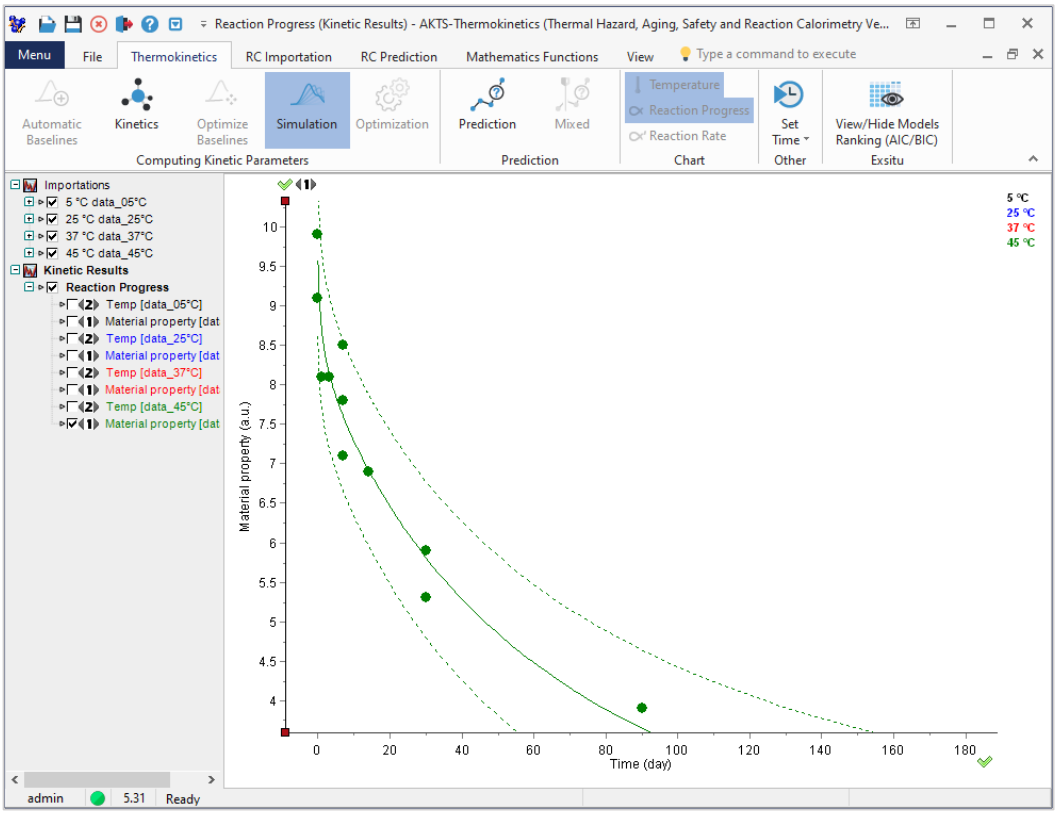

FIG. 5 - Prediction of the change of the material property at 45°C. The dashed lines depict the prediction bands with 95% confidence.

PREDICTION OF THE CHANGE OF MATERIAL PROPERTIES WITH THE PREDICTION BANDS AT RANDOMIZED TEMPERATURE FLUCTUATIONS

AKTS Thermokinetics Sparse Data software (TKsd) allows simulation of the stability of the materials and their degree of degradation under any temperature conditions occurring during their storage and transport before the final use. The software evaluates by the bootstrap method the prediction bands with 95% confidence (dashed lines in the plot).

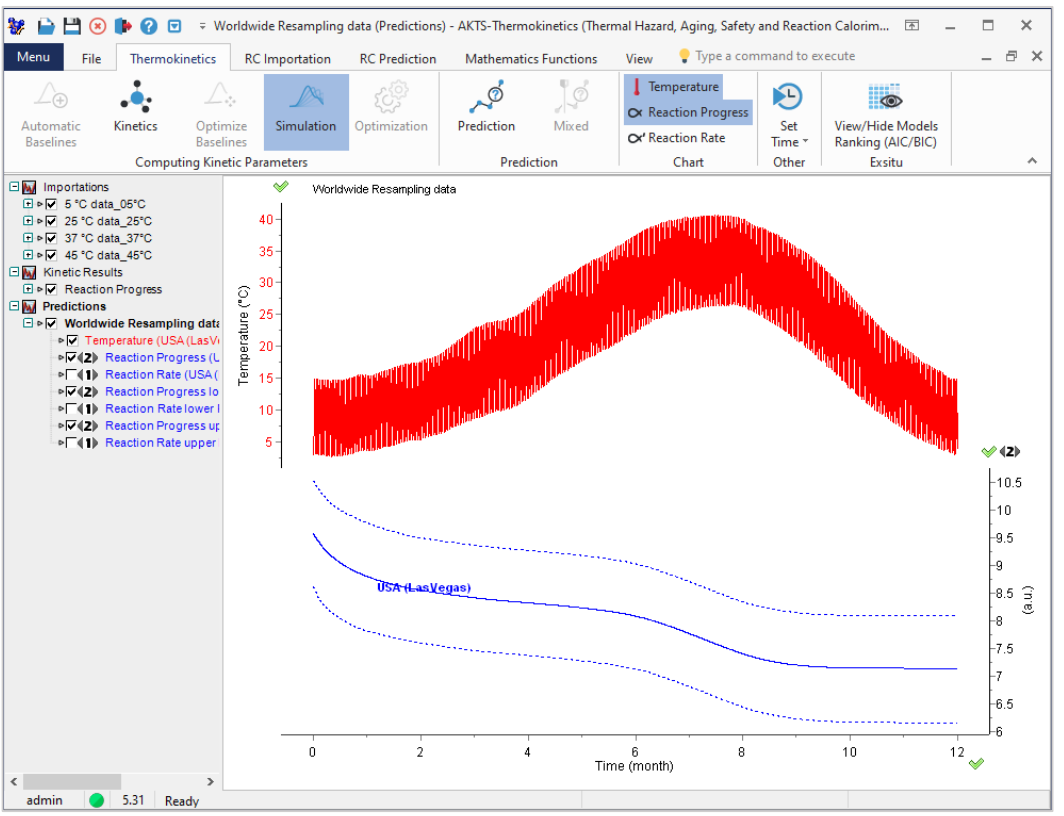

FIG. 1 - Influence of daily climate fluctuation temperatures (here Las Vegas) on the reaction extent. The dashed lines depict the prediction bands with 95% confidence.

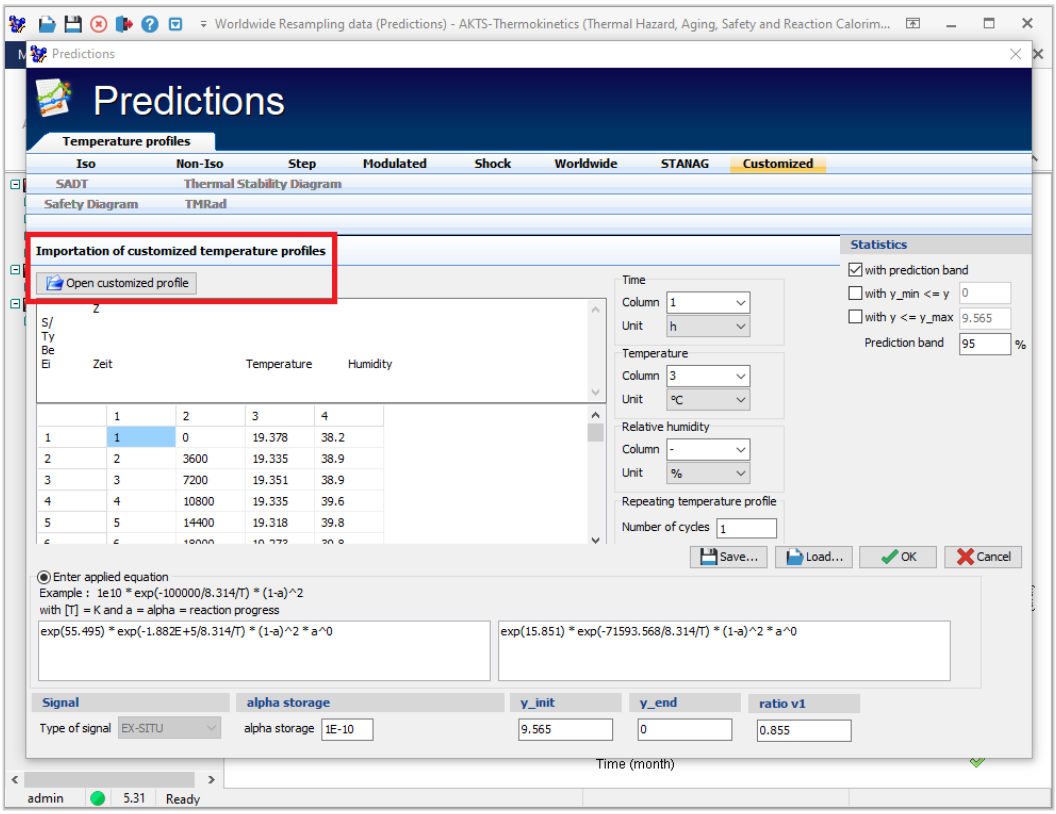

FIG. 2 - The influence of the temperature fluctuations on the reaction course can be evaluated for any customized temperature profiles.

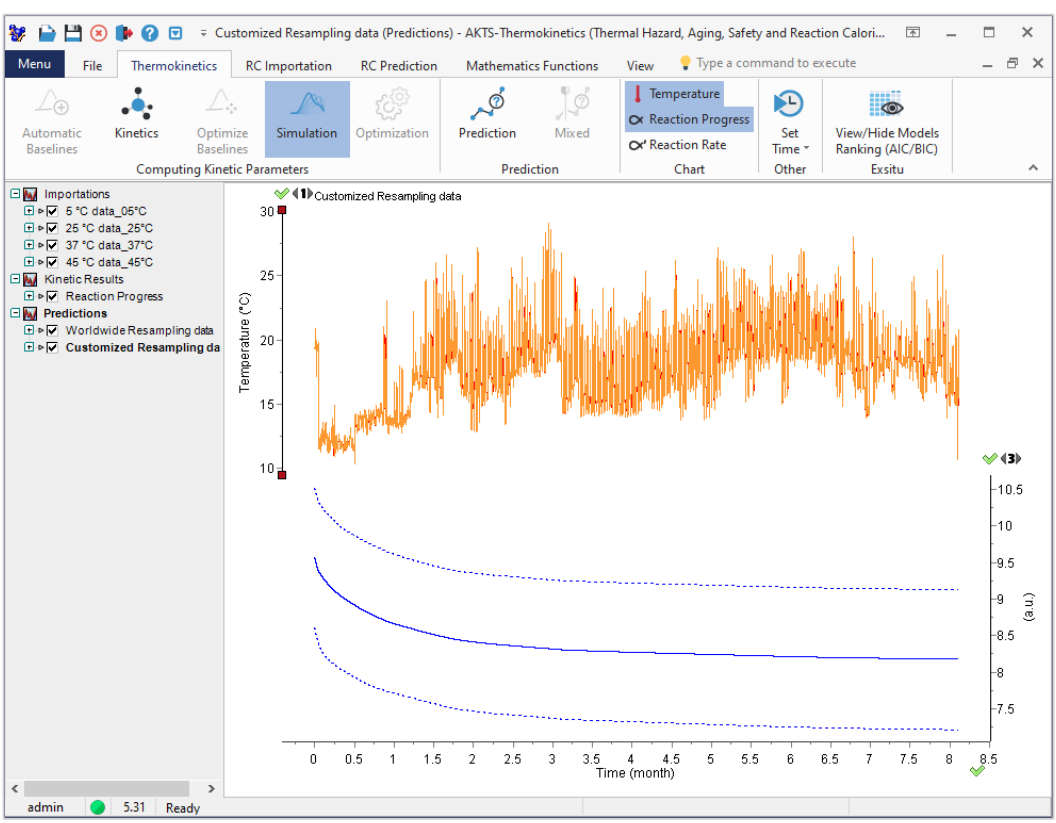

FIG. 3 - The influence of the temperature fluctuations recorded by commonly applied data loggers on the reaction course. The dashed lines depict the prediction bands with 95% confidence.

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