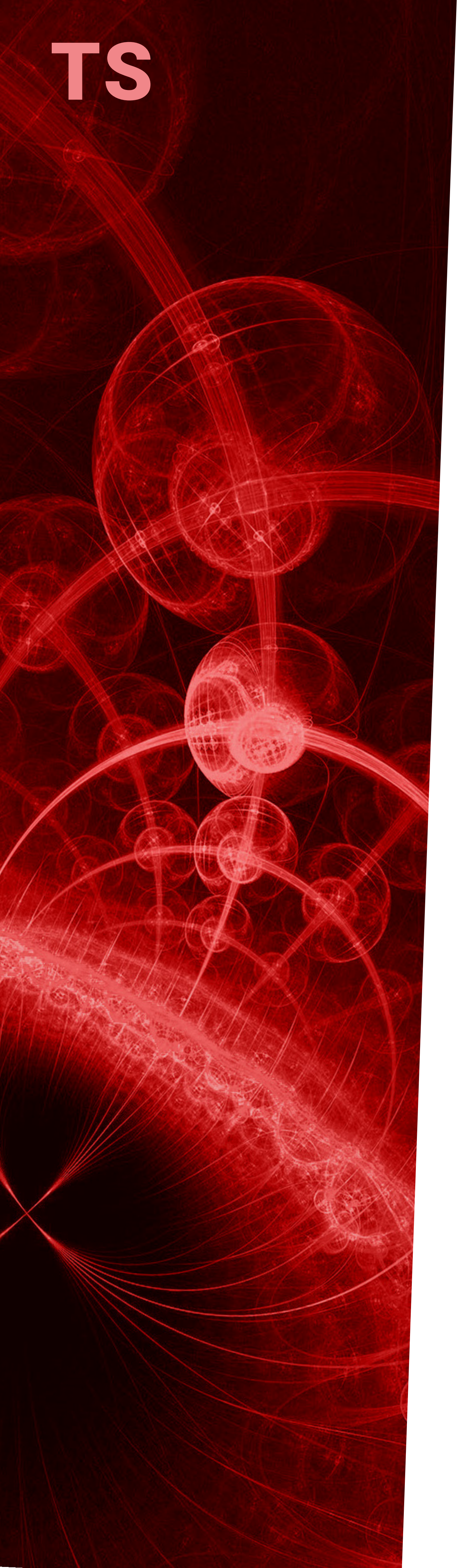

AKTS

THERMAL SAFETY Software (TS)

Evaluation of Safety Parameters TMRad, Safety Diagrams, Simulation of ARC and Runaway Reactions, Determination of SADT

CONTENT

AKTS E-Learning

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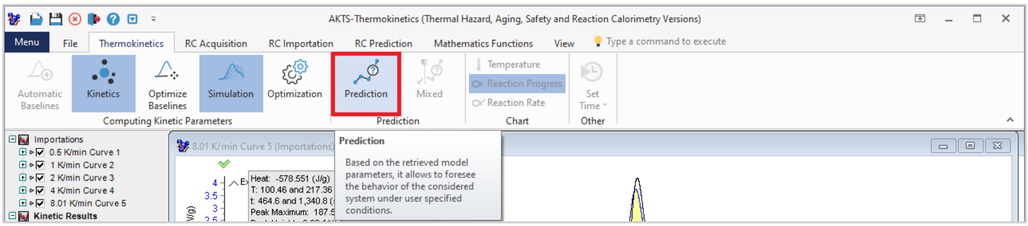
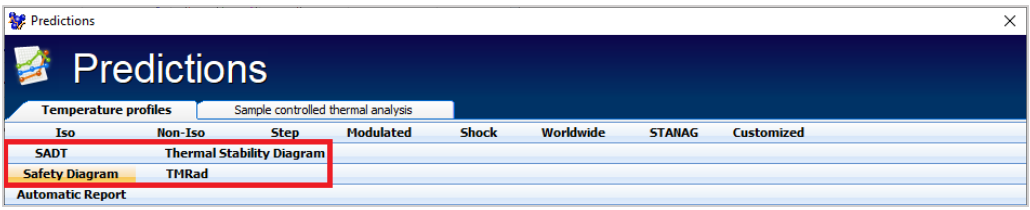
AKTS E-LEARNING

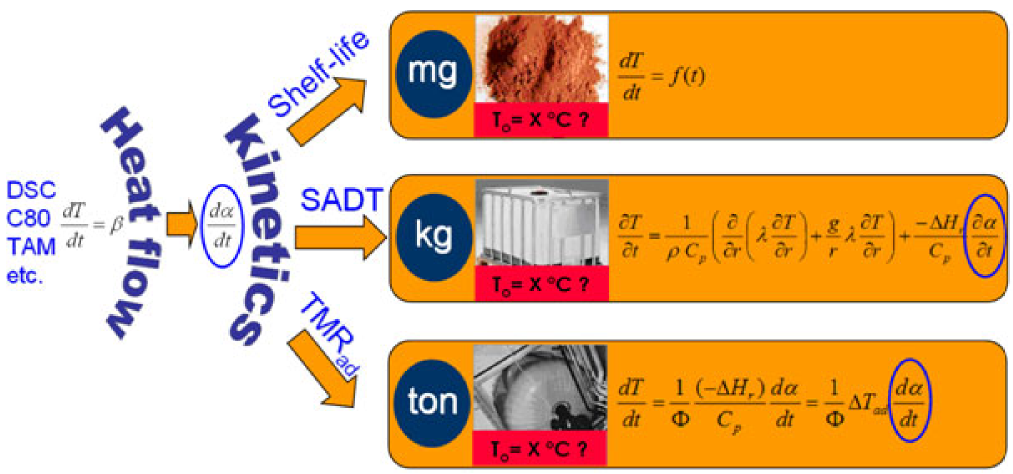
GENERAL INFORMATION

For the prediction of the thermal behaviour in kg-scale, in semi-adiabatic and ton-scale under adiabatic conditions under any temperature mode click the icon **“Prediction”.**

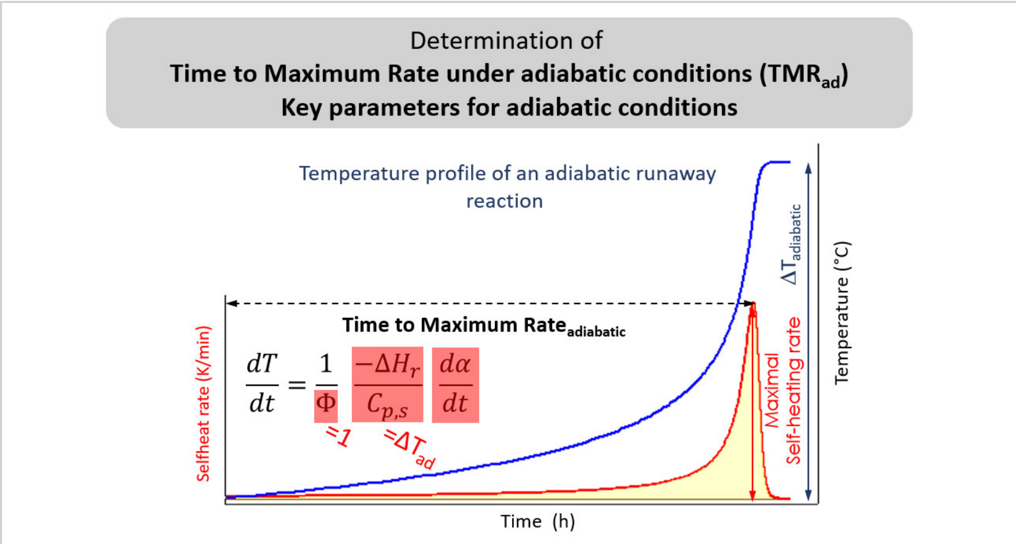




In all large-scale experiments dT/dt and T(t) are determined by applying appropriate heat balance equations (see figure below). In kg-scale the change of the sample temperature rate dT/dt depends among others, on the reaction rate da/dt and on the container radius r as well. The temperature of the sample will not be the same in the centre and at the surface of a package and, in addition, it will depend on its size, i.e. r value. In order to determine thermal behaviour in kg-scale, the convective heat transfer from the package (the boundary conditions) and the conductive heat transfer within the package are introduced into the calculating procedure.



TIME-TO-MAXIMUM RATE UNDER ADIABATIC CONDITIONS (TMRAD) / ADIABATIC THERMAL SAFETY DIAGRAM



$$\frac{dT}{dt} = \underbrace{\frac{1}{\Phi}}_{=1} \underbrace{\frac{-\Delta H_r}{C_{p,s}}}_{=\Delta T_{ad}} \frac{d\alpha}{dt}$$

FIG. 1 - The plot presents the temperature profile of an adiabatic reaction and depicts the meaning of its key parameters: ΔTad the adiabatic temperature rise, TMRad: Time to Maximum Rate and maximum Self-Heating Rate.

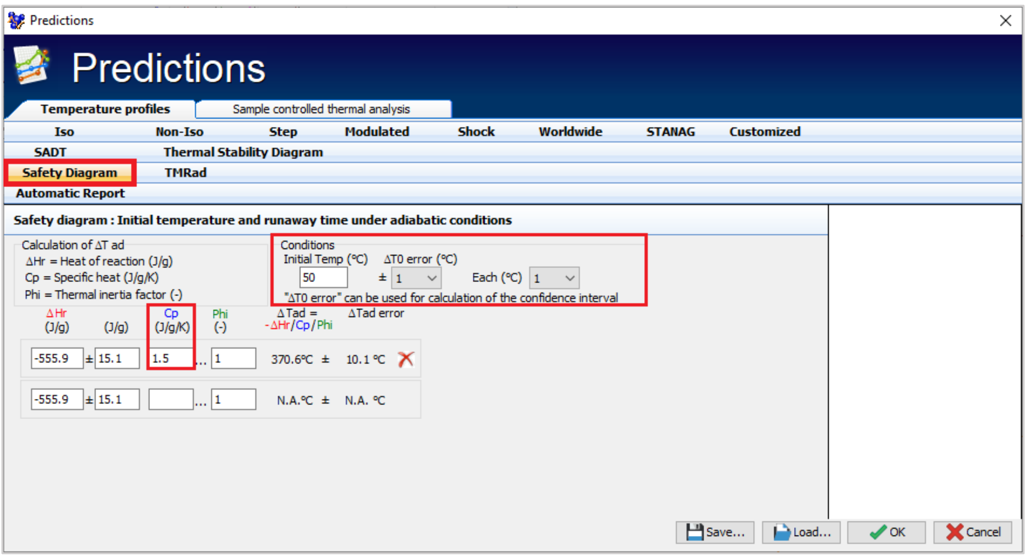


FIG. 2 - Click on the tab **"Adiabatic Safety Diagram"** to calculate the "Time to Maximum Rate" under adiabatic conditions for any arbitrarily starting temperature. Introduce the lowest required initial temperature (in presented example 50°C) and the heat capacity value (here 1.5 J/g/K) of the substance.

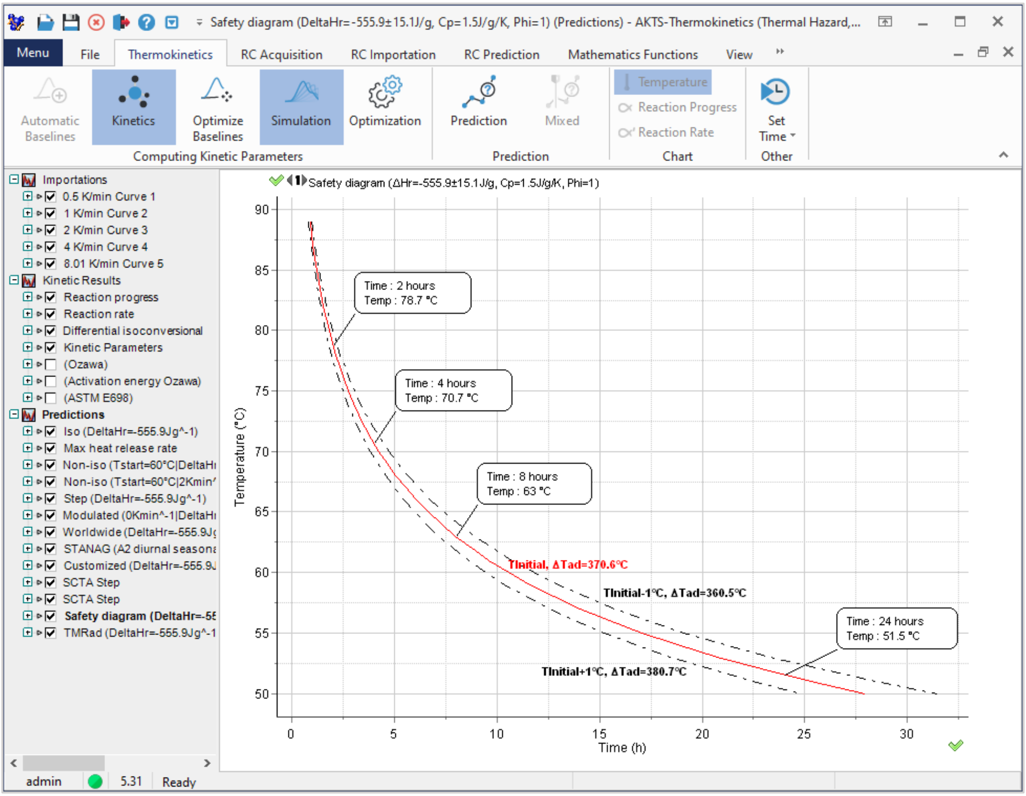


FIG. 3 - Adiabatic safety diagram - Influence of the initial temperature on the corresponding adiabatic induction time TMRad for following conditions: ΔHr = -555.9±15.1 J/g and ΔTad=(-ΔHr)/Cp)= 370.6±10.1°C for Φ = 1 and Cp = 1.5 J/g/K.

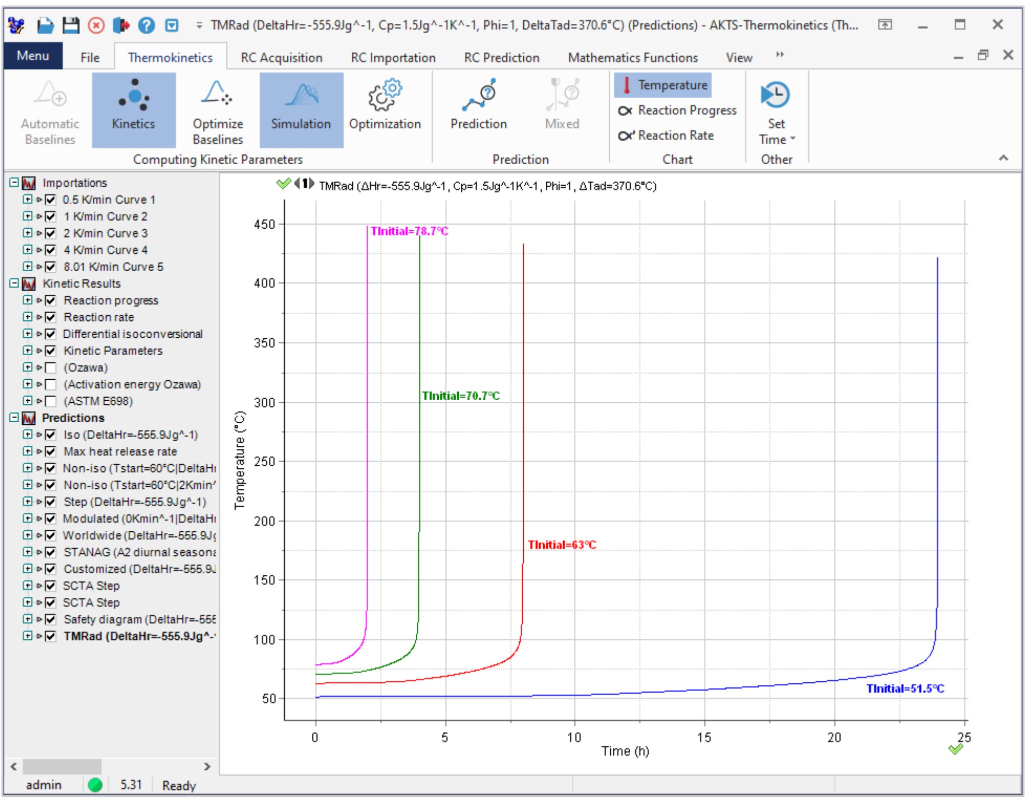


FIG. 4 - The simulation of T-time relationships under adiabatic conditions. For an initial temperature of 51.5°C TMRad amounts to 24 h.

Safety data for following input parameters: ΔHr=-555.9±15.1J/g, Cp=1.5J/g/K, Phi=1			
TStart °C	**TMRad (mean value) (TInitial, DeltaTad=370.6°C)**	**TMRad (lower value) (TInitial+1°C, DeltaTad=380.7°C)**	**Confidence interval %**
89	52.27 min	47.64 min	8.87
88	56.55 min	51.51 min	8.92
87	61.21 min	55.72 min	8.97
86	66.28 min	60.31 min	9.02
85	71.82 min	65.30 min	9.07
84	77.85 min	70.75 min	9.12
83	84.43 min	76.69 min	9.17
82	91.61 min	83.17 min	9.22
81	99.45 min	90.24 min	9.27
80	108.03 min	97.96 min	9.32
79	117.4 min	106.39 min	9.37
78	127.65 min	115.62 min	9.43
77	138.87 min	125.7 min	9.48
76	151.15 min	136.74 min	9.53
75	164.61 min	148.83 min	9.59
74	179.37 min	162.08 min	9.64
73	195.55 min	176.59 min	9.70
72	213.31 min	192.51 min	9.75
71	232.82 min	209.98 min	9.81
70	254.25 min	229.17 min	9.86
69	277.8 min	250.24 min	9.92
68	5.06 hours	273.41 min	9.98
67	5.54 hours	298.89 min	10.04
66	6.06 hours	5.45 hours	10.10
65	6.64 hours	5.96 hours	10.16
64	7.27 hours	6.53 hours	10.22
(*)63	(*) 7.98 hours	(*) 7.16 hours	10.28
(*)Means that determined TMRad is about 8 hours (7.98 h) for an initial temperature of about 63°C, (a more conservative value is 7.16 h)			
62	8.75 hours	7.85 hours	10.34
61	9.61 hours	8.61 hours	10.40
60	10.55 hours	9.45 hours	10.46
59	11.6 hours	10.38 hours	10.52
58	12.75 hours	11.4 hours	10.59
57	14.04 hours	12.54 hours	10.65
56	15.46 hours	13.8 hours	10.71
55	17.03 hours	15.2 hours	10.78
54	18.78 hours	16.74 hours	10.84
53	20.72 hours	18.46 hours	10.91
(**)52	(**)22.87 hours	(**)20.36 hours	10.97
(**) Means that determined TMRad is about 24 hours (22.87 h) for an initial temperature of about 52°C, (a more conservative value is 20.36 h)			
51	25.27 hours	22.48 hours	11.04
50	27.94 hours	24.83 hours	11.11

TABLE. 1 - Thermal safety table: Dependence of TMRad on initial temperatures under adiabatic conditions.

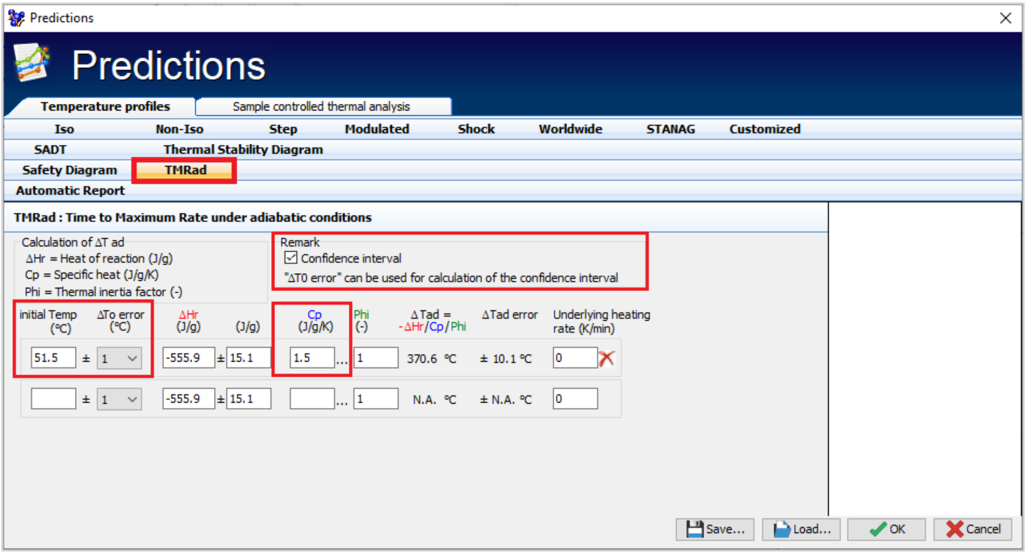


FIG. 1 - Click on the tab **"TMRad"** to calculate the "Time to Maximum Rate" with or without confidence interval for any arbitrarily chosen initial temperature. Specify the values of initial temperature (in this example 51.5°C) and heat capacity (here 1.5 J/g/K).

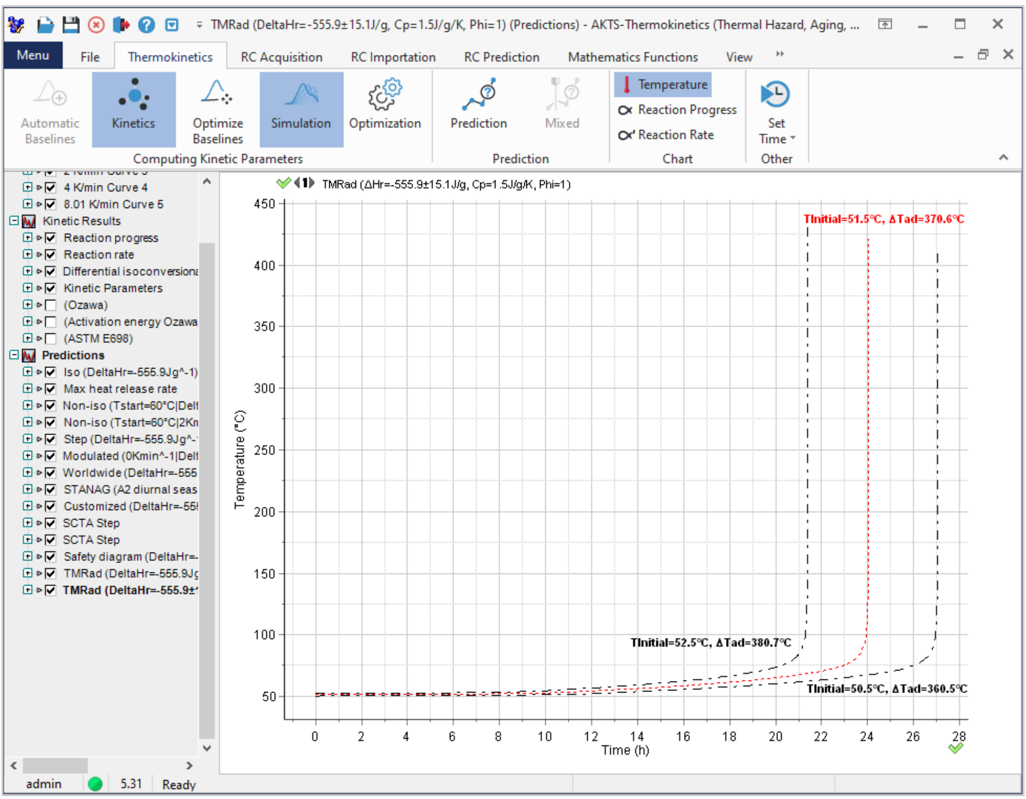


FIG. 2 - Adiabatic runaway curve for the reaction with ΔHr = -555.9±15.1 J/g and Cp = 1.5 J/g/K with the confidence interval for the prediction: Tinitial =51.5±1°C. ΔTad=(-ΔHr)/Cp)=370.6±10.1°C for Φ =1.

The TS software also allows the calculation of self-heating rate curves in adiabatic conditions (see below):

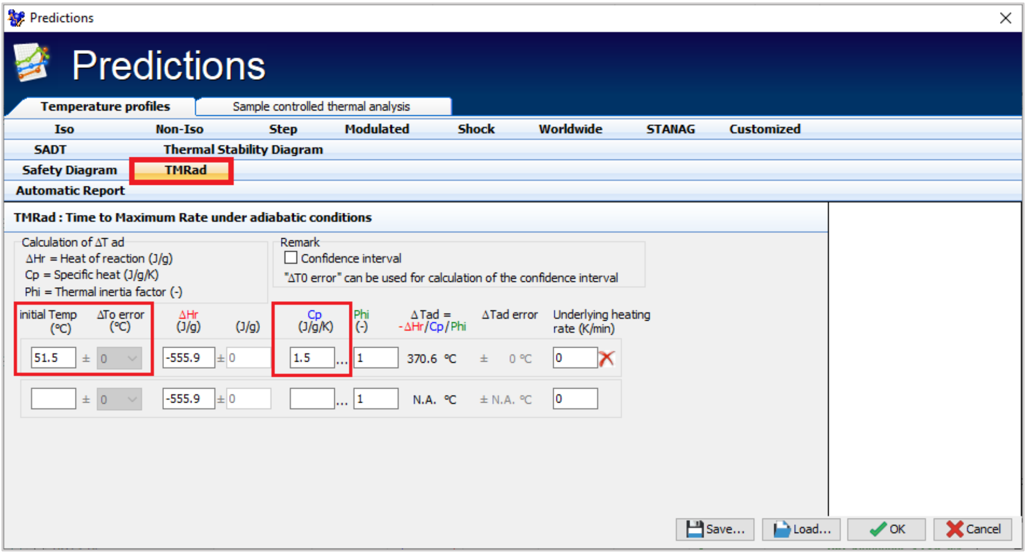


FIG. 3 - Click on the tab "TMRad" to calculate the "Time to Maximum Rate" for any arbitrarily chosen initial temperature. Specify the values of initial temperature (in this example 51.5°C) and heat capacity (here 1.5 J/g/K).

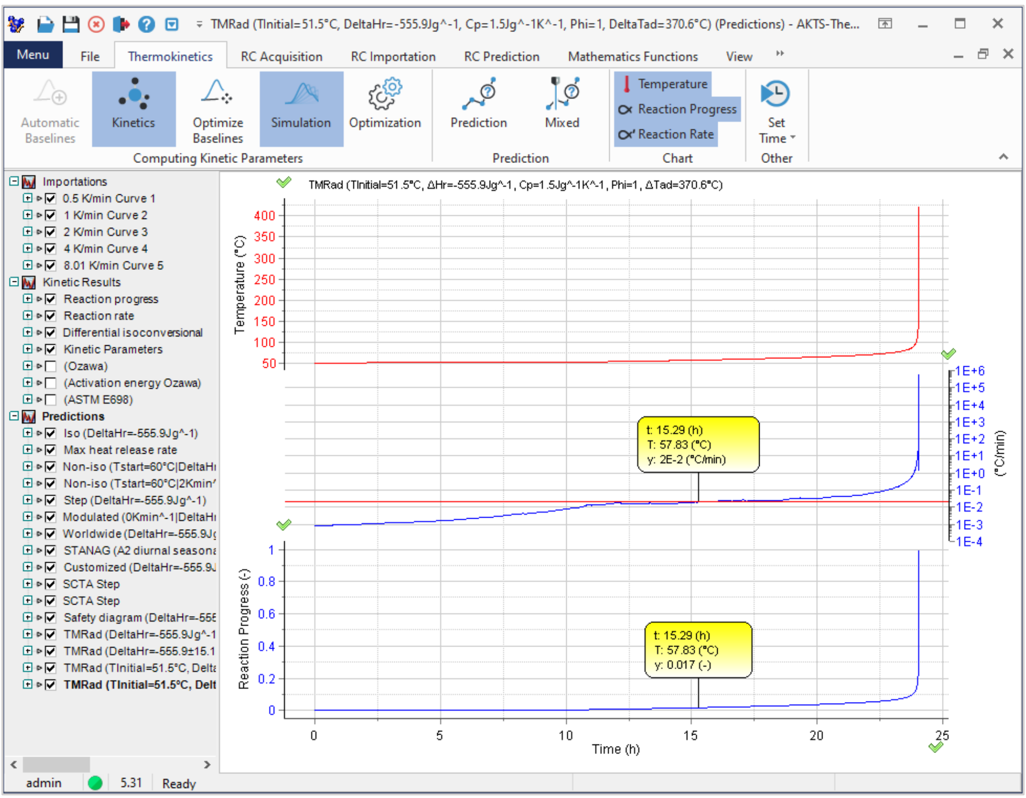


FIG. 4 - Adiabatic runaway curve with TMRad = 24h as a function of time for following conditions: ΔHr = -555.9±15.1 J/g, ΔTad=(-ΔHr)/Cp)=370.6±10.1°C, Φ = 1 and Cp = 1.5 J/g/K. The graph displays the time-dependence of the temperature (top), self-heating rate (middle) and reaction extent (bottom).

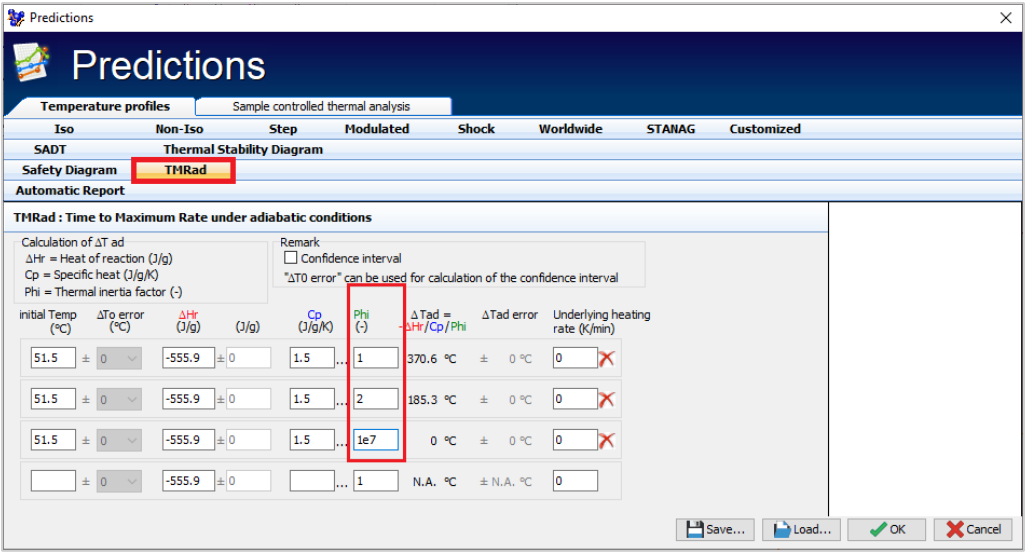


FIG. 5 - Heat exchange properties of the system characterized by Phi factor significantly influence the TMRad, ΔTad and the temperature dependence of the reaction progress.

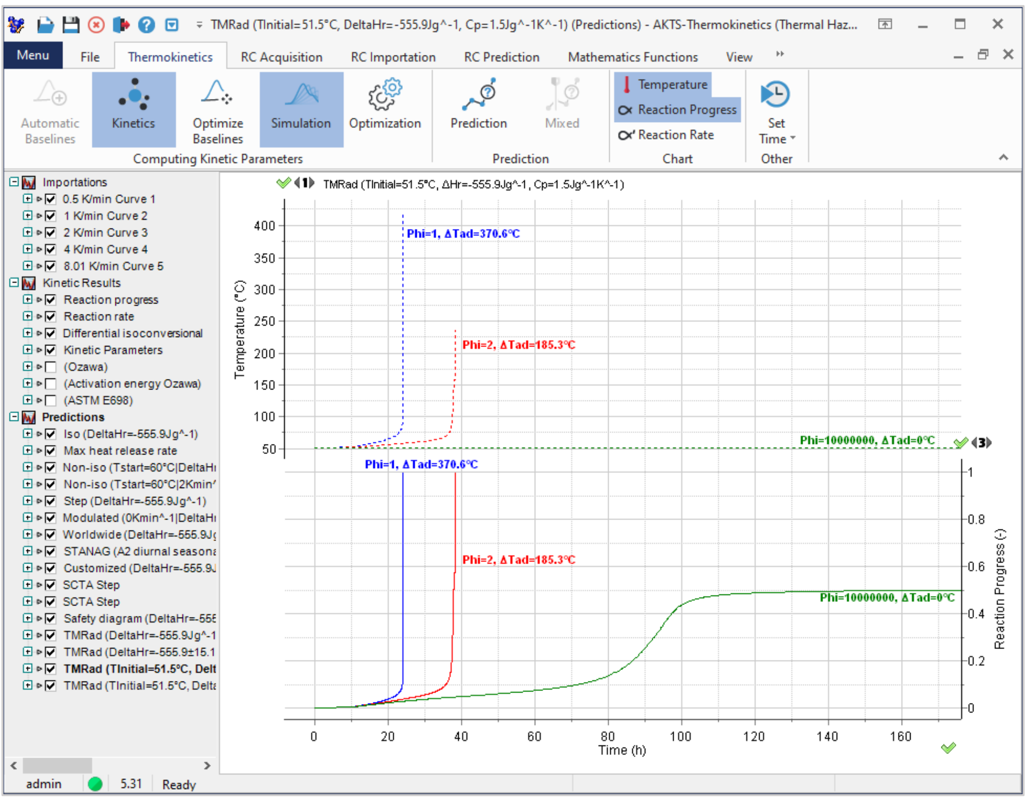


FIG. 6 - (Top) Dependence of TMRad and ΔTad on the values of phi-factor marked on curves. (Bottom) Influence of the phi-factor on the reaction progress at 51.5°C under isothermal conditions (Φ = 1e+7) and the adiabatic runaway curves for an initial temperature of 51.5°C with Φ = 2 and 1 (for Φ =1 TMRad amounts to 24h), respectively. ΔHr = -555.9±15.1 J/g and Cp = 1.5 J/g/K.

The blue curve in the graph above presents the simulation of the reaction course in ton-scale (fully adiabatic conditions, Phi=1), the green curve in mg-scale (total exchange of the reaction heat with surrounding, Phi taken as 1e+7). The red curve displays the reaction behaviour in semi-adiabatic conditions for Phi=2. For checking the influence of the thermal inertia (Phi factor) on TMRad introduce required values of phi-factor in respective fields as shown below:

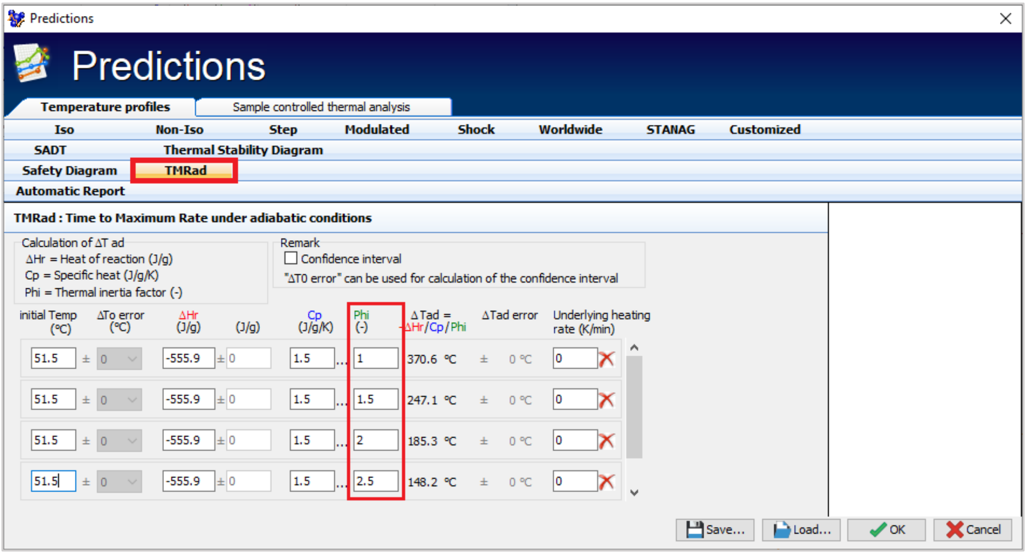


FIG. 7 - Heat exchange properties of the system characterized by Phi factor significantly influence the TMRad, ΔTad and the temperature dependence of the reaction progress. The graph displays the input of specific Phi factor values.

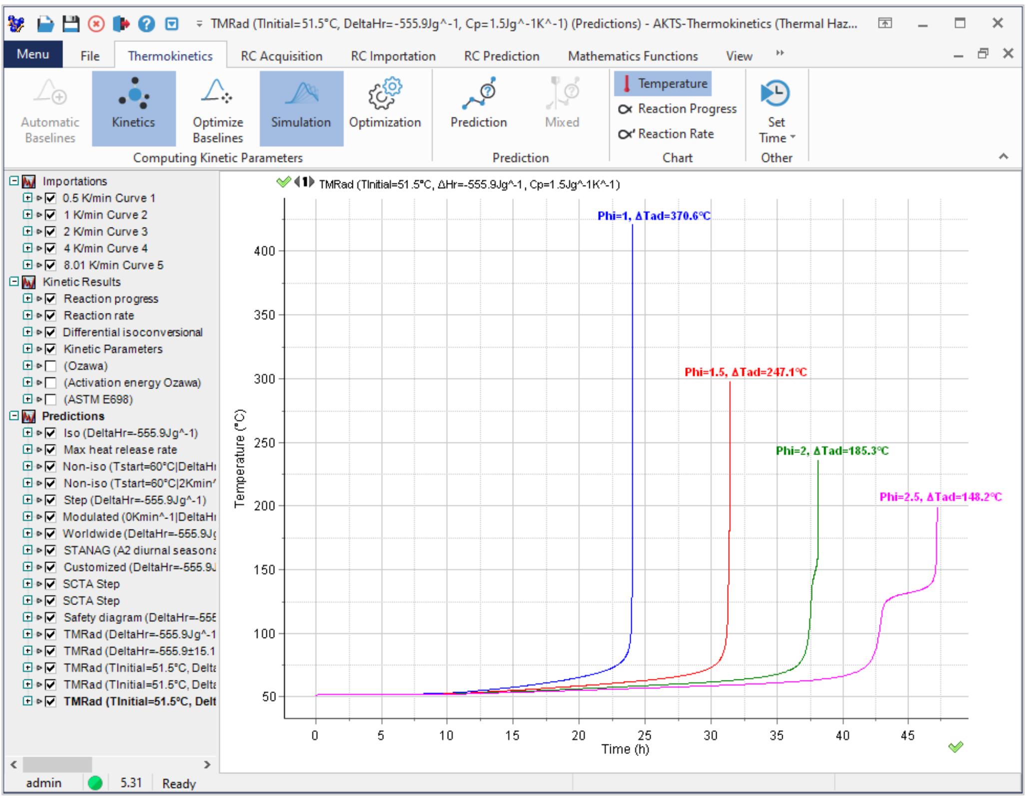


FIG. 8 – Adiabatic runaway curves for different Phi factors.

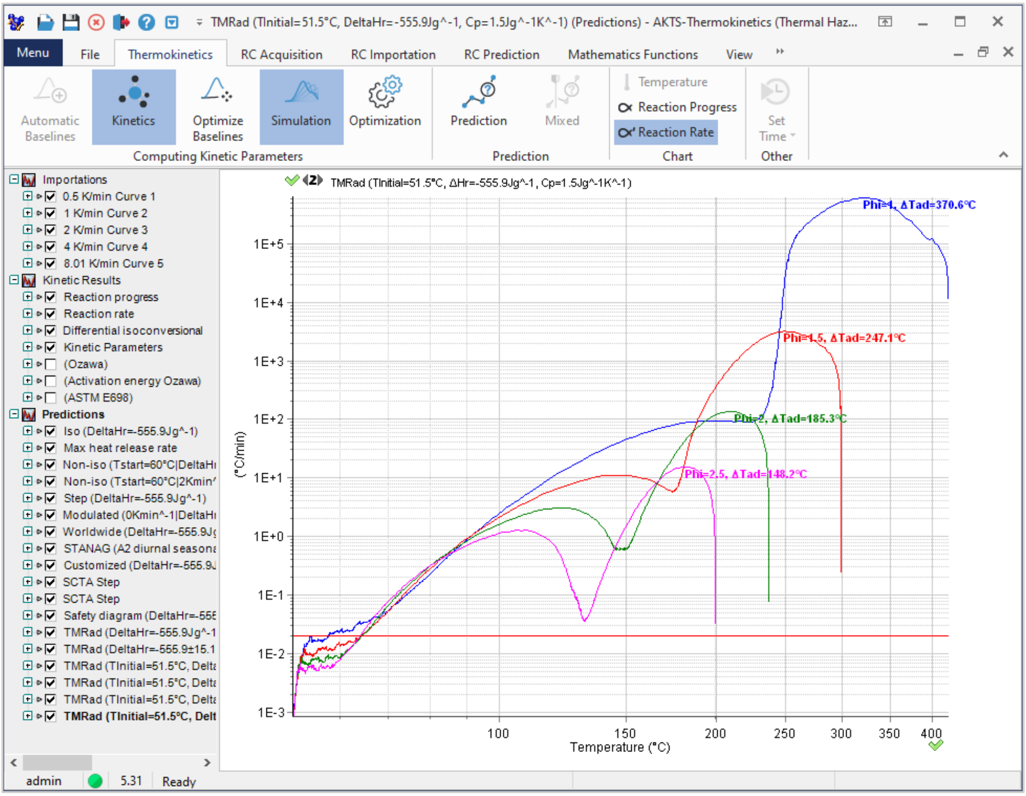


FIG. 9 – Self-heating rate curves for different Phi factors.

Φ	ΔTad /K
1	370.6
1.5	247.1
2	185.3
2.5	148.2

TABLE. 1 - Influence of the Phi factor on the ΔTad at following conditions: Tinitial =51.5°C, ΔHr = -555.9±15.1 J/g and Cp = 1.5 J/g/K

THERMAL SAFETY DIAGRAM FOR NON-ADIABATIC CONDITIONS

Click on the tab **“Thermal Stability Diagram”** to calculate the Time to the Maximum Rate under non-adiabatic conditions as a function of the external conditions and the sample properties.

The Thermal Stability Diagram allows evaluating the dependence of the Time to Maximum Rate under any, non-adiabatic conditions, as a function of the external- (temperature, size and geometry of the container) and internal parameters, specific to the sample (such as density, specific heat, thermal conductivity, etc).

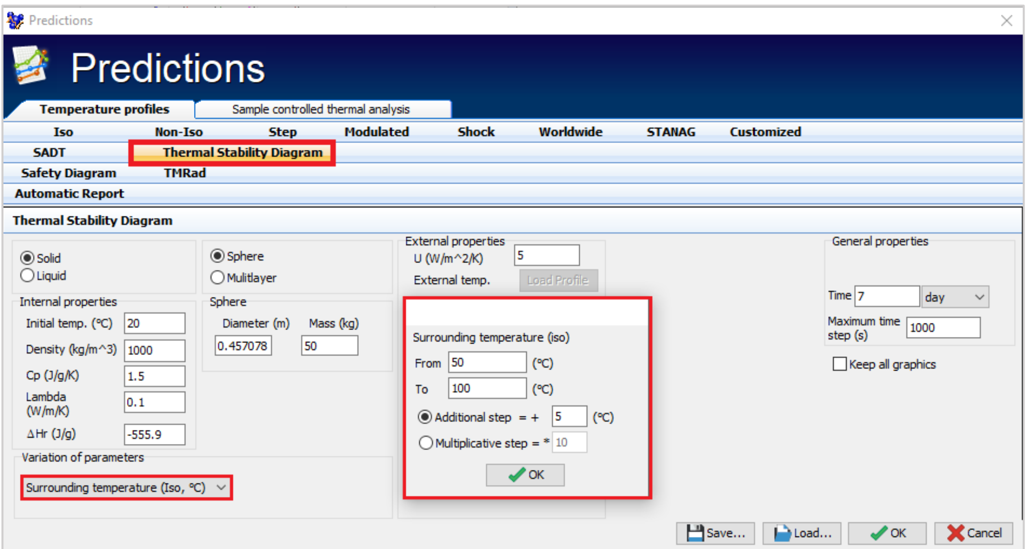


FIG. 1 - Input of the surrounding temperature during the evaluation of the dependence of the time to maximum rate under non-adiabatic conditions.

The diagram shown below displays two zones: safe and unsafe and transparently presents the time in which the operations with the material are safe. The plot depicted below shows the impact of the surrounding temperature on the time of reaching the maximal rate of the reaction for parameters introduced by user.

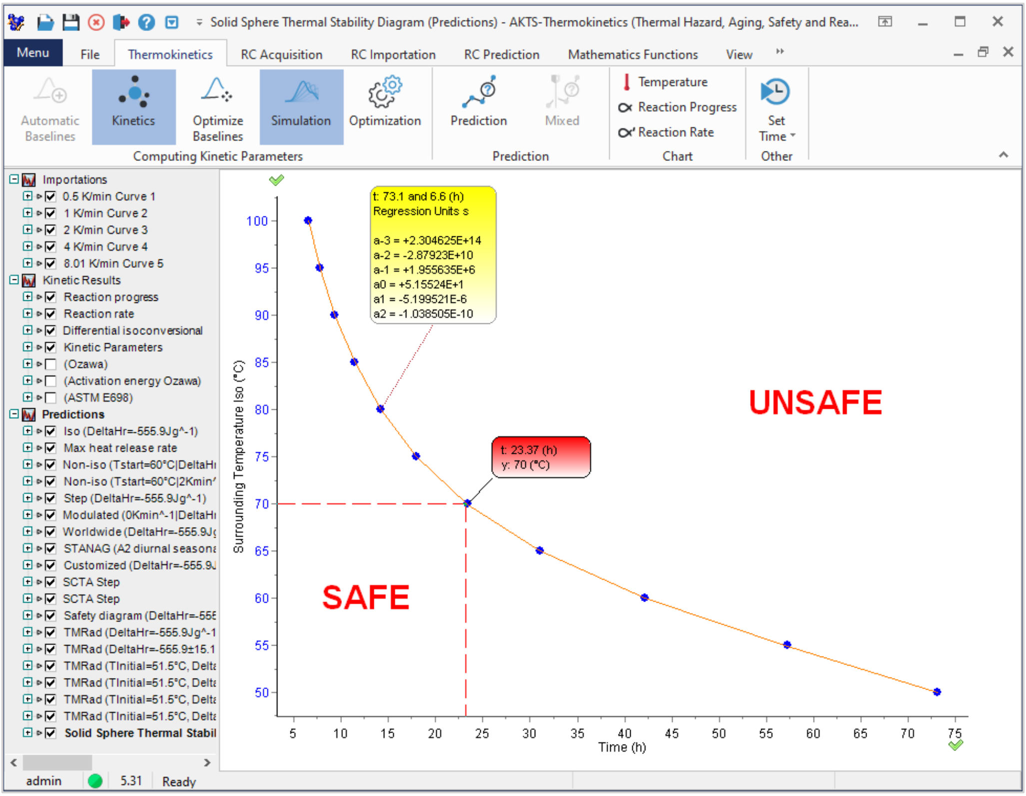


FIG. 2 - Influence of the surrounding temperature on time to maximum rate (TMR) under non-adiabatic conditions for a sample mass m = 50kg and initial sample temperature Ts = 20°C. The time to explosion is increasing, if the surrounding temperature Te is decreasing. At Te = 70°C the TMR amounts to 23.37 hrs.

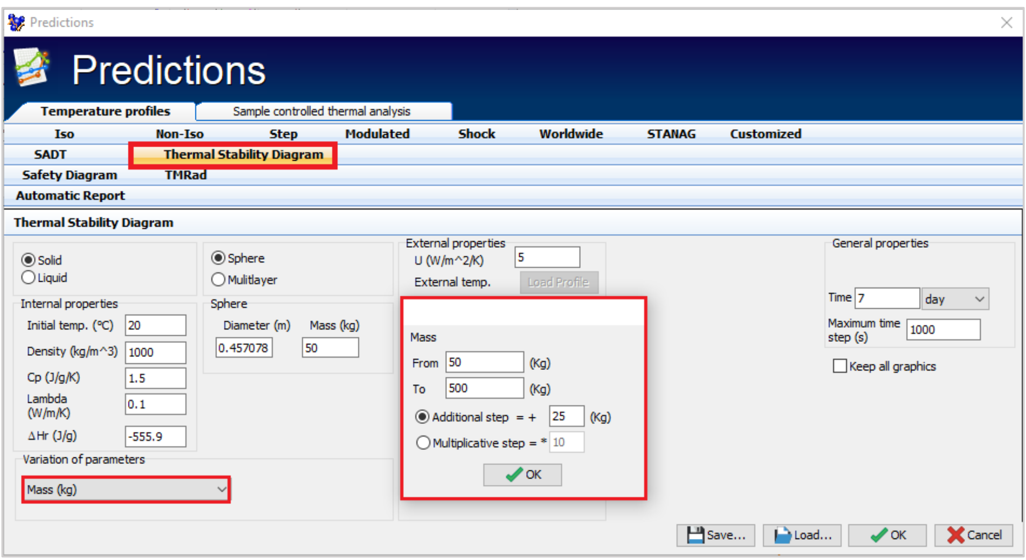


FIG. 3 - Input of the mass required for the evaluation of the dependence of the time to maximum rate under non-adiabatic conditions.

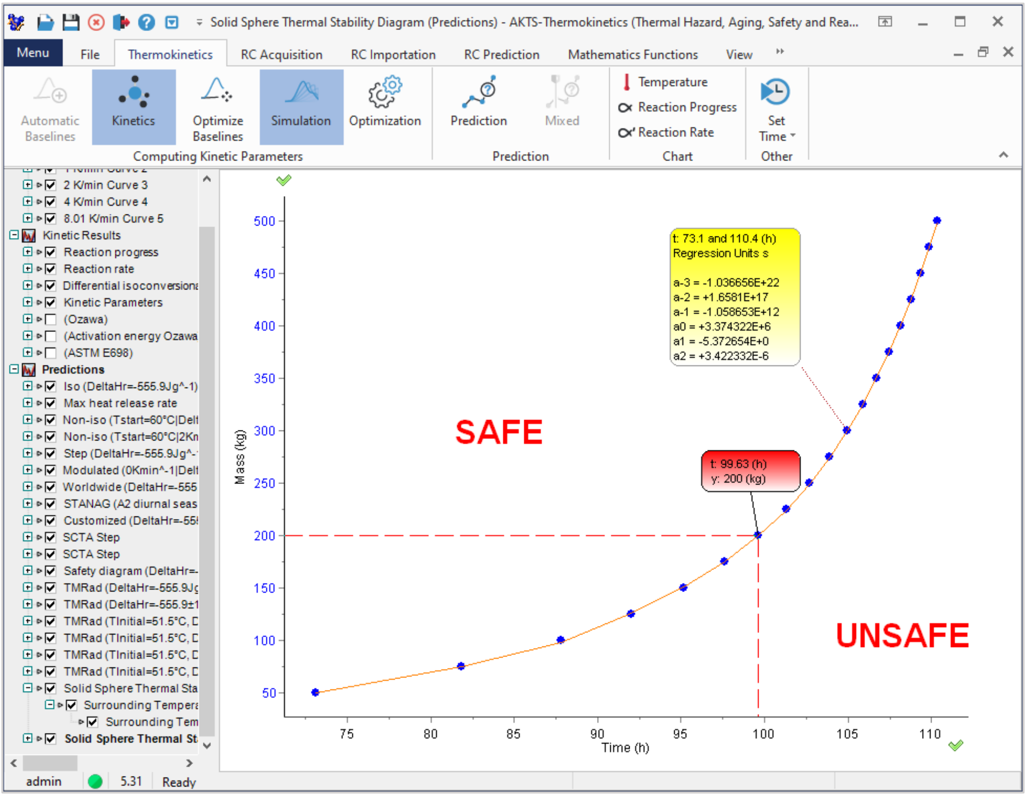


FIG. 4 - Influence of the sample mass on time to maximum rate under non-adiabatic conditions for an initial sample temperature Ts=20°C and external temperature Te = 50°C. The time to maximum rate under non-adiabatic conditions is increasing, if the sample mass is increasing. For the sample mass of 200kg duration of the safe zone amounts to 99.63 hrs.

SIMULATION OF THE SELF-ACCELERATING-DECOMPOSITION TEMPERATURE (SADT)

The prediction of the thermal behaviour in kg-scale is illustrated by the determination of the Self-Accelerating Decomposition Temperature (SADT) according to the recommendations of Manual of Tests and Criteria of the United Nations on the transport of dangerous goods (the so-called “Orange Books”). One can find few different definitions of SADT, however in our Software we apply the definition given in the 'Orange Books'.

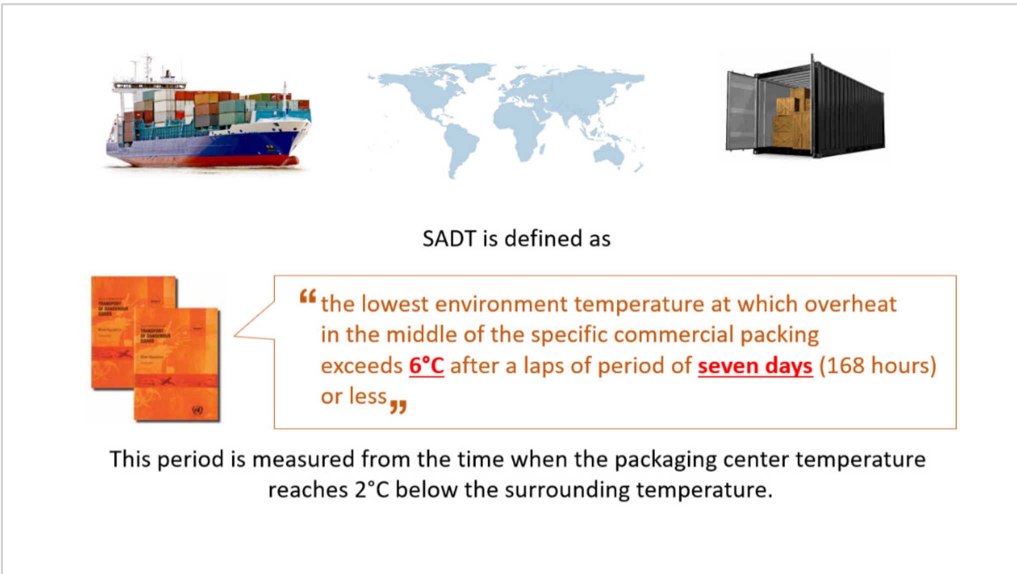


FIG. 1 - Definition of the Self-Accelerating-Decomposition Temperature (SADT) given in the Orange Book.

Click on the tab SADT to proceed with calculations.

SADT calculation requires specifying:

- The physico-chemical properties of the examined material such as its density, specific heat capacity, heat of reaction and thermal conductivity (solids)
- Container’s geometry and size
- Sample mass

Thermal Saftey Software allows to determine the effect of properties of containers on the reaction progress and heat accumulation conditions. The user can evaluate the critical container parameters such as its critical radius, the necessary thickness of insulation, and the influence of the surrounding temperature on storage and transport safety.

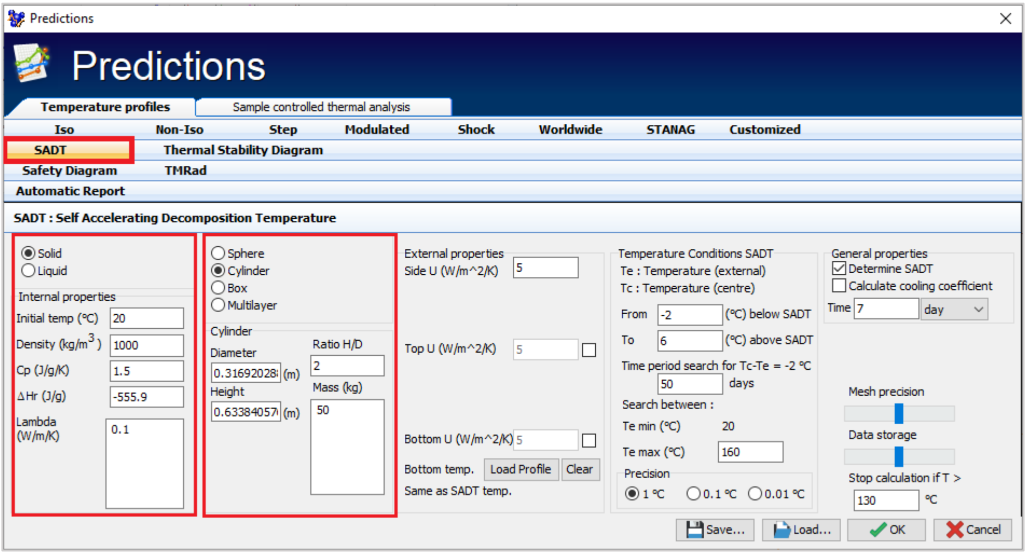


FIG. 2 - Input of parameters required for SADT calculation.

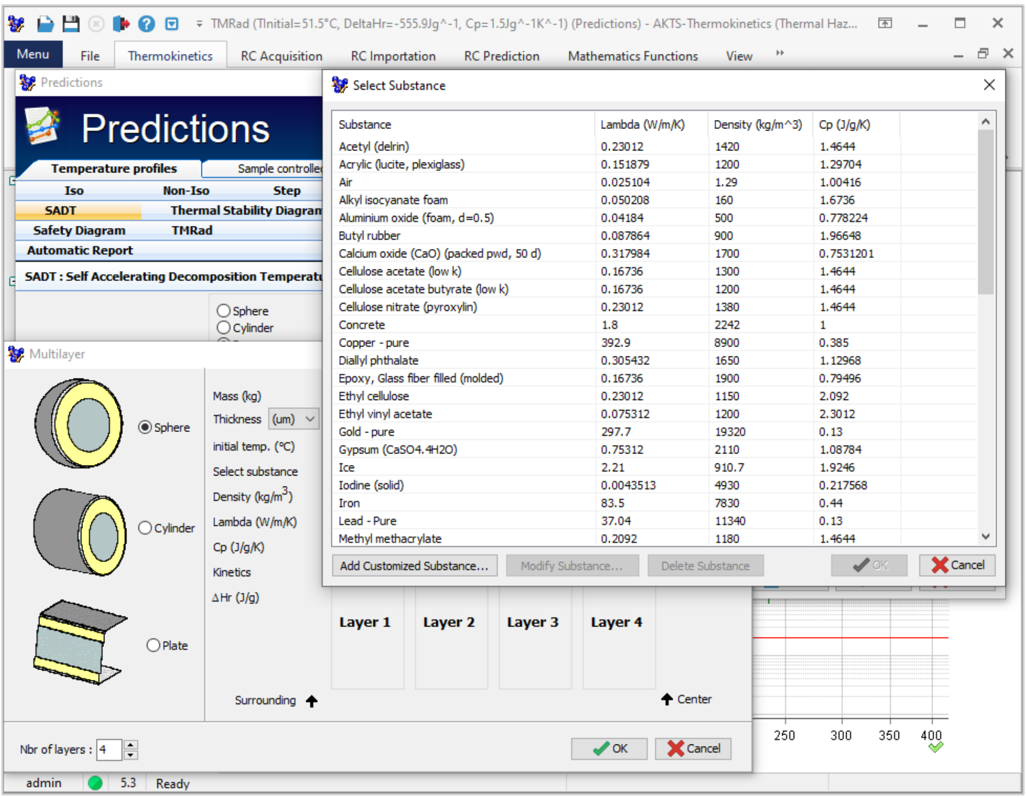


FIG. 3 - Input of parameters (placed in scrolled table) required for SADT calculation.

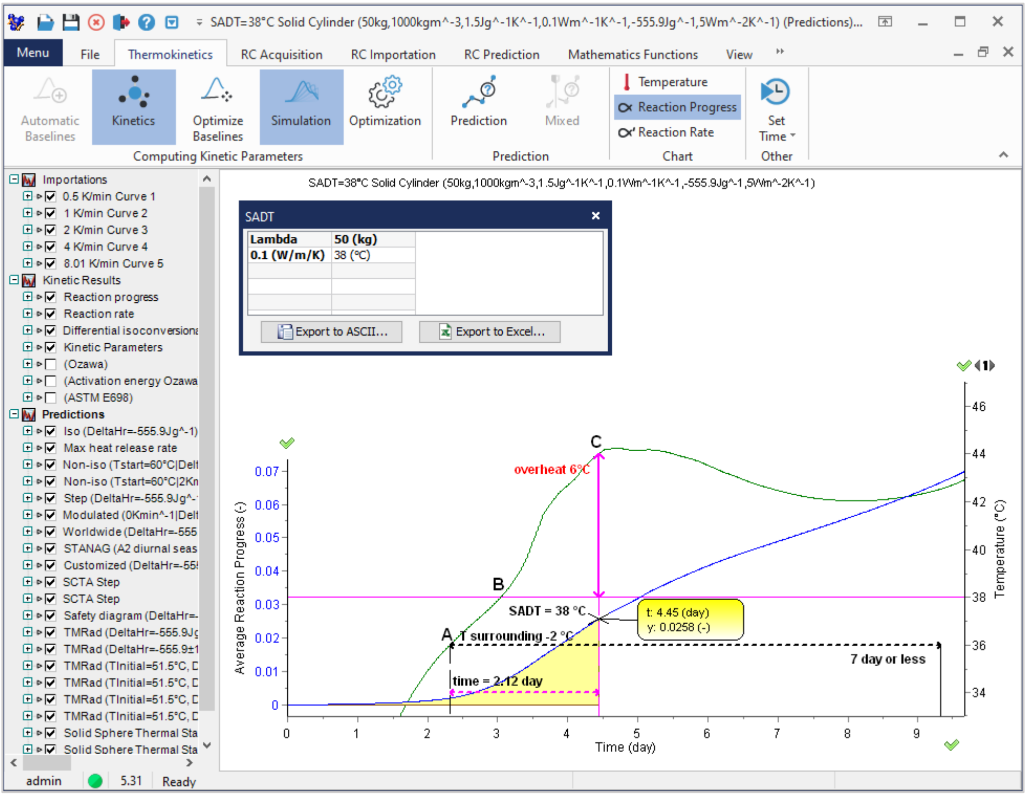


FIG. 4 - Simulation of the SADT for 50 kg sample placed in a drum with filling height H = 63.4 cm and diameter D = 31.7 cm. (pink: surrounding temperature Te = 38°C, green: sample temperature in the centre of the drum Tc, blue: reaction extent α). Point A indicates the time when the packaging centre temperature reaches 2°C below the surrounding temperature. The overheat of 6°Cin the centre of the container (point C) is reached after 4.45 days. 38°C is the lowest surrounding temperature fulfilling the SADT criterion.

SIMULATIONS OF THE SPATIAL DISTRIBUTION OF TEMPERATURE AND REACTION PROGRESS

Software allows the SADT determination and the simulation of the thermal behaviour of the material in the container at any temperature (e.g. at points A, B and C in the plot above).

Uncheck **"Determine SADT"** and introduce in **"External properties"** any requested temperature profiles.

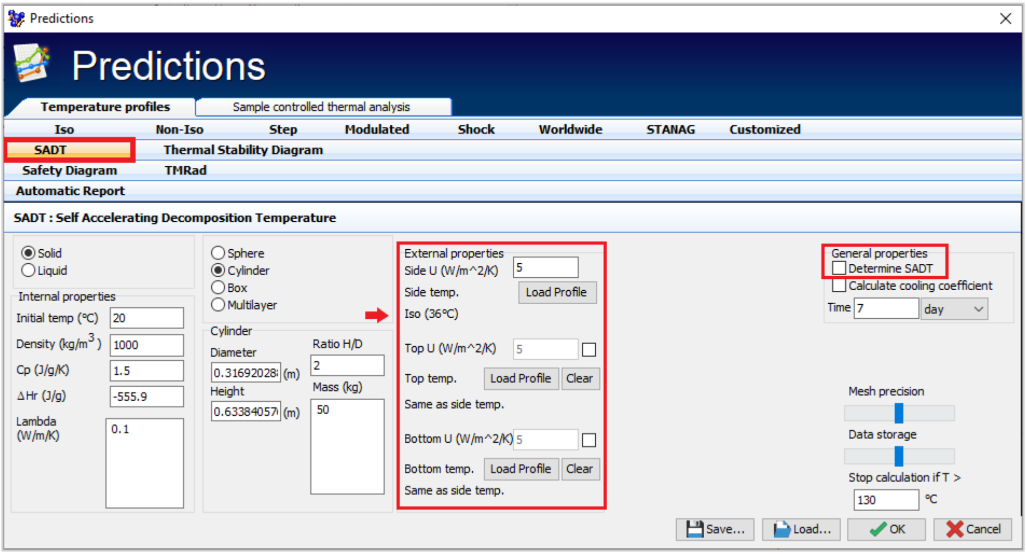


FIG. 1 - Input of parameters for simulation of the thermal behaviour of the material in the container at any temperature (here at point A = 36°C, marked by an arrow).

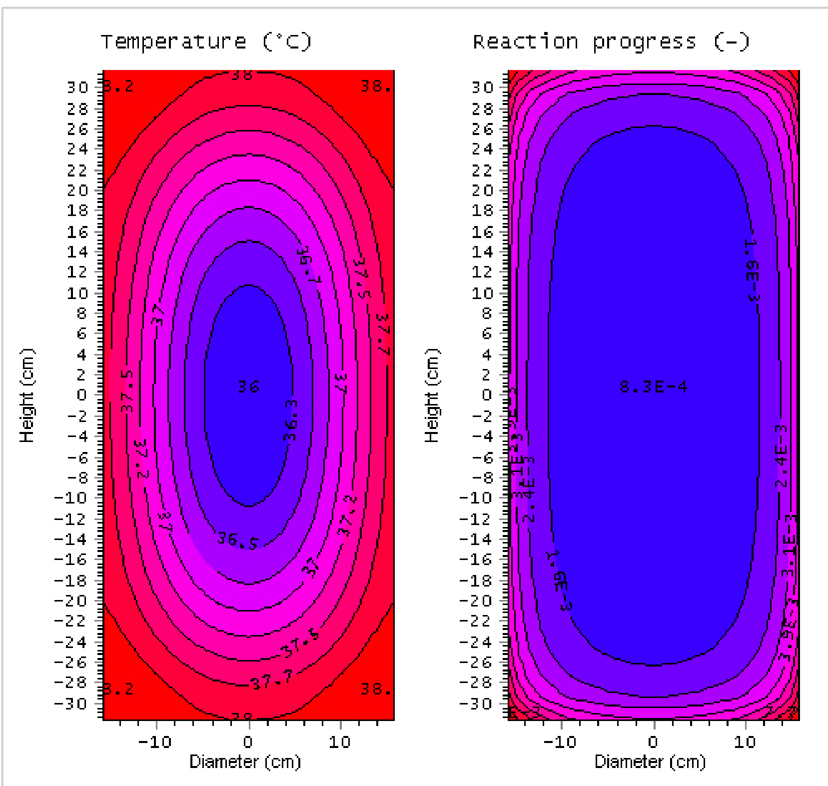


FIG. 2 - Simulations of the spatial distribution of temperature (left) and reaction progress α (right) for a mass of 50 kg in a drum with ratio H/D = 2 after period at which the point A (36°C) was reached – see Fig.4 in the previous section.

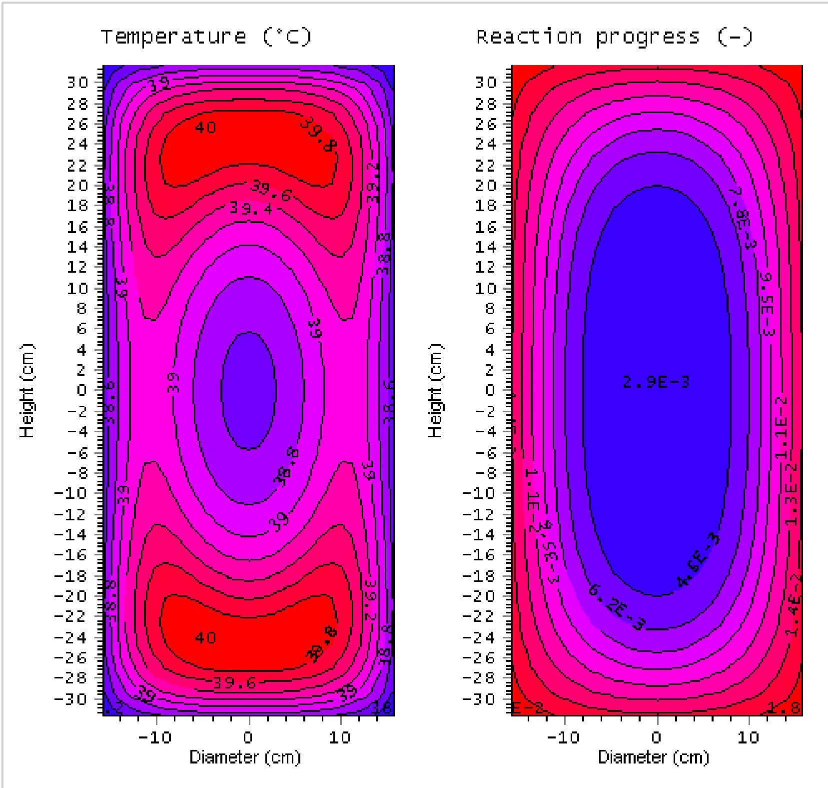


FIG. 3 - Simulations of the spatial distribution of temperature (left) and reaction progress α (right) for a mass of 50 kg in a drum with ratio H/D = 2 after period at which the point B (38°C) was reached – see Fig.4 in the previous section.

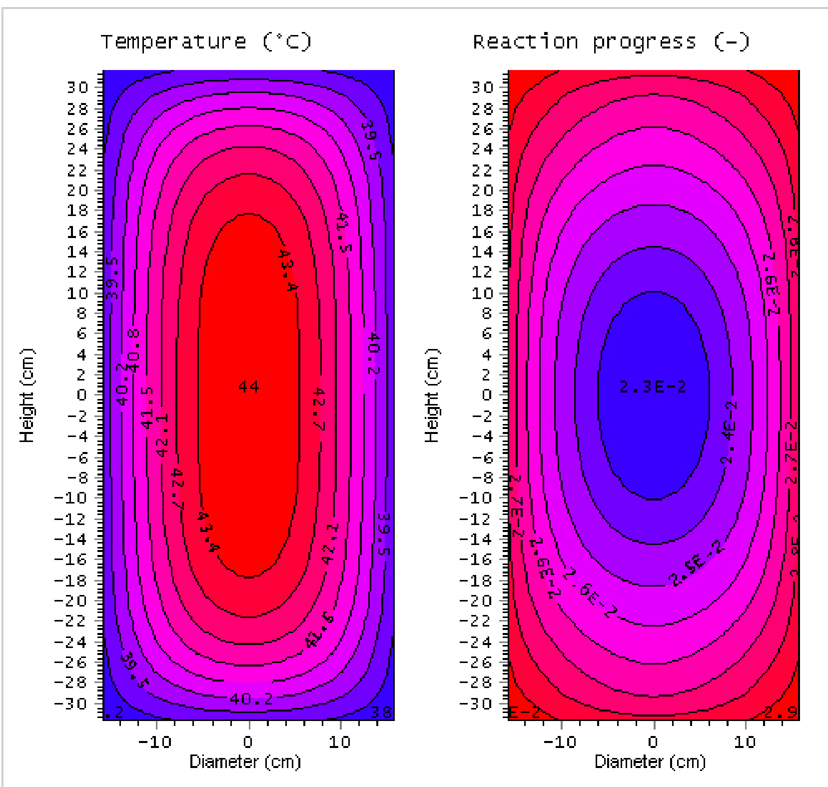


FIG. 4 - Simulations of the spatial distribution of temperature (left) and reaction progress α (right) for a mass of 50 kg in a drum with ratio H/D = 2 after period at which the point C (44°C) was reached – see Fig.4 in the previous section.

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