



THERMAL SAFETY Software (TS)

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

CONTENT

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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"**.

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Automatic	Report														

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



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.

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Temperature p	rofiles	Sample co	ntrolled therm	nal analysis						
Iso	Non-Iso	Ste	ep M	odulated	Shock	Worldwide	STANAG	Customized		
SADT	Therm	al Stability Dia	agram							
Safety Diagram	TMRad	1								
Automatic Report										
Safety diagram : Ini	tial tempera	ature and run	away time u	under adiabati	c conditions		_			
Calculation of ΔT ad ΔHr = Heat of reaction Cp = Specific heat (J) Phi = Thermal inertia ΔHr (J/g) (J/g) -555.9 \pm 15.1	on (J/g) /g/K) factor (-) (J/g/K) 1.5 ,.	Рhi Д (-) -ДН , 1 370	Conditions Initial Temp (° 50 "ATO error" ca Tad = A Ir/Cp/Phi 0.6°C ± 10	C) $\Delta T0 \text{ error (} \pm 1 \sim$ an be used for ca Tad error 0.1 %	(°C) Each (°C) Iculation of the	1 V confidence interval				
-555.9 ± 15.1]	. <u>1</u> N	.A.ºC ± N	A. ℃						
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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: Δ Hr = -555.9±15.1 J/g and Δ Tad=(- Δ Hr)/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 parar	neters: ∆Hr=-555.9±15.1J/g, Cp=1.5J/g/ł	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
(*)Meai	ns that determined TMRad is about 8 h (a more conse	nours (7.98 h) for an initial temperature ervative value is 7.16 h)	of about 63°C,
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
(**) Mear	ns that determined TMRad is about 24 (a more conse	hours (22.87 h) for an initial temperatur rvative value is 20.36 h)	e of about 52°C,
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.

— ADIABATIC RUNAWAY AND SELF-HEATING RATE CURVES –

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Temperature pr	ofiles Sam	ple controlled thermal a	nalysis						
Iso	Non-Iso	Step Modu	ilated Sl	hock V	Vorldwide	STANAG	Customized		
SADT	Thermal Stabil	ity Diagram							
Safety Diagram	TMRad								
Automatic Report								1	
TMRad : Time to Max	kimum Rate under a	idiabatic conditions							
Calculation of ∆T ad ∆Hr = Heat of reaction Cp = Specific heat (J/ Phi = Thermal inertia	on (J/g) (g/K) factor (-)	Remark ☑ Confidence int "∆T0 error" can be	erval e used for calculati	ion of the confi	idence interval				
initial Temp ∆To erro (°C) (°C)	or <u>AHr</u> (J/g) (J/g	() (J/g/K) (-)	∆Tad = -∆Hr/Cp/Phi	∆Tad error	Underlying heat rate (K/min)	ting			
51.5 ± 1 ~	-555.9 ± 15.1	1.5 1	370.6 ℃	± 10.1 °C	0 🗙				
± 1 ~	-555.9 ± 15.1	1	N.A. °C	± N.A. °C	0				
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The TS software also allows the calculation of self-heating rate curves in adiabatic conditions (see below):

₩ Predictions				×
Predictions				
Temperature profiles Sample	e controlled thermal analysis			
Iso Non-Iso	Step Modulated	Shock Worldwide	STANAG Customized	
SADT Thermal Stability	/ Diagram			
Safety Diagram TMRad				
	- L - M MM			
Trikad : Time to Plaximum kate under ad	labatic conditions			
Δ Hr = Heat of reaction (J/g)	Confidence interval			
Cp = Specific heat (J/g/K) Phi = Thermal inertia factor (-)	"ΔT0 error" can be used for calcu	lation of the confidence interval		
initial Temp ∆To error (°C) (°C) (J/g) (J/g)	Cp Phi ∆Tad = (J/g/K) (-) -∆Hr/Cp/R	∆Tad error Underlying he Phi rate (K/min)	ating	
51.5 ± 0 -555.9 ± 0	1.5 1 370.6 °C	± 0°C 0 ★		
± 0 ~ -555.9 ± 0	1 N.A. °C	± N.A. °C 0		
			💾 Save 📔 Load	i 🗸 OK 🗙 Cancel





FIG. 4 - Adiabatic runaway curve with TMRad = 24h as a function of time for following conditions: Δ Hr = -555.9±15.1 J/g, Δ Tad=(- Δ Hr)/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).

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Temperature pro	files [Sample	controlled then	mal analysis	s						
Iso	Non-Iso		Step I	lodulated	i Sh	ock	Worldwide	STANAG	Customized		
SADT	Therm	al Stability	Diagram								
Safety Diagram	TMRad										
Automatic Report											
TMRad : Time to Maxi	mum Rate	e under adi	abatic conditi	ons							
Calculation of ∆T ad ∆Hr = Heat of reaction	(1/a)		Remark	e interval							
Cp = Specific heat (J/g	(5/g) (K)		"ΔT0 error" c	an be used	for calculation	on of the cor	nfidence interval				
Phi = Thermal inertia fa	ctor (-)										
initial Temp ∆To error (°C) (°C)	∆Hr (J/g)	(J/g)	(J/g/K)	Phi (-) -	∆Tad = ∆Hr/Cp/Phi	∆Tad erro	r Underlying hea rate (K/min)	ating			
51.5 ± 0 ~	-555.9	± 0	1.5	1	370.6 °C	± 0 °C	0 🗙				
51.5 ± 0 ~	-555.9	± 0	1.5	2	185.3 °C	± 0 °C	0 🗙				
51.5 ± 0 ~	-555.9	± 0	1.5	1e7	0 °C	± 0 °C	0 🗙				
± 0 ~	-555.9	± 0		1	N.A. °C	± N.A. °C	0				
									Save 📔 Load	I 🗸 ок	Cancel

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



FIG. 6 - (Top) Dependence of TMRad and Δ Tad 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. Δ Hr = -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. 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 Δ Tad at following conditions: Tinitial =51.5°C, Δ Hr = -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 nonadiabatic 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).

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Predict	ions						
Temperature profiles	Sample controlled th	nermal analysis					
Iso Non-Is	o Step	Modulated	Shock	Worldwide	STANAG	Customized	
SADT Ther	nal Stability Diagram						
Safety Diagram TMRa	d						
Automatic Report							
Internal Scability Diagram ● Solid □ Liquid Internal properties Initial temp. (°C) Density (kg/m^3) 1000 Cp (J/g/K) Lambda (W/m/K) △ Hr (J/g) -555.9 Variation of parameters Surrounding temperature (Iso, °	Sphere Mulitlayer Sphere Diameter (m) Mass (0.457078 50	(kg) (kg) To ©	nal properties W/m^2/K) ernal temp. rounding tempe m 50 100 Additional step Multiplicative s	5 Load Profie rature (iso) (°C) (°C) • = + 5 (°C) tep = * 10 ✓ OK			General properties Time 7 day Maximum time 1000 Step (s) Keep all graphics

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.

Predictions								×
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Temperature p	rofiles	Sample controlled th	ermal analysis					
Iso	Non-Is	o Step	Modulated	Shock	Worldwide	STANAG	Customized	
SADT	Therr	nal Stability Diagram						
Safety Diagram	TMRa	ıd						
Automatic Report								
Solid Liquid Internal properties Initial temp. (°C) 2 Density (kg/m^3) 1 Cp (1/g/K) 1 Lambda (W/m/K) O Variation of paramete Mass (kg)	00000000000000000000000000000000000000	Sphere Multitayer Sphere Diameter (m) Mass 0.457078 50	(kg) (kg) (kg) (kg) (kg) (kg) (kg) (kg)	nal properties W/m^2/K) ernal temp. s m 50 500 Additional step Multiplicative st	5 Load Profile (Kg) (Kg) = + 25 (Kg) tep = * 10 OK]		General properties Time 7 day Maximum time 1000 tep (s) Keep all graphics
						- -	Save 📄 Loa	d 🗸 OK 🎇 Cancel

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.

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.

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Predict	ions			
Temperature profiles	Sample controlled thermal analy	vsis		
Iso Non-Is	o Step Modulat	ed Shock Worldwide	STANAG Customized	
SADT Therr	nal Stability Diagram			
Safety Diagram TMRa	b			
Automatic Report				
5ADT : Self Accelerating Decon	nposition Temperature			
Sold Liquid Internal properties Initial temp (°C) 20 Density (kg/m ³) 1000 Cp (J/g/K) 1.5 ΔHr (J/g) -555.9 Lambda (W/m/K) 0.1	Sphere © Cylinder Box Multilayer Cylinder Diameter (0.31692028) (m) Height 0.63384057) (m)	External properties Side U (W/m^2/K) Top U (W/m^2/K) 5 Bottom U (W/m^2/K) Bottom U (W/m^2/K) Same as SADT temp.	$\label{eq:constraints} Temperature Conditions SADT Te : Temperature (external) Tc : Temperature (centre) From \frac{-2}{2} (°c) below SADT To 6 (°c) above SADT To 6 (°c) above SADT Time period search for Tc-Te = -2 °C SO days Search between : Te min (°c) 20 Te max (°c) 160 Precision (© 1 °C 0.0.1 °C 0.0.1 °C)$	General properties Determine SADT Calculate cooling coefficient Time 7 day ~ Mesh precision Data storage Stop calculation if T > 130 °C

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

Predict	ions	Substance			Lambda (W)	m/K) Density (kg/m^3) Cp (J/g/K)	
		Acetyl (delrin)		0.23012	1420	1.4644	
Temperature profiles	Sample controller	Acrylic (lucite	, plexiglass)		0.151879	1200	1.29704	
Ico Non-I	co Stop	Air			0.025104	1.29	1.00416	
ISU NUI-I	so Step	Alkyl isocyana	ate foam		0.050208	160	1.6736	
SAUT The	mai Stability Diagram	Aluminium oxi	de (foam, d=0.5)	0.04184	500	0.778224	
atety Diagram TMR	ad	Butyl rubber			0.087864	900	1.96648	
utomatic Report		Calcium oxide	(CaO) (packed p	owd, 50 d)	0.317984	1700	0.7531201	
DT : Self Accelerating Deco	mposition Temperatu	Cellulose ace	tate (low k)		0.16736	1300	1.4644	
		Cellulose ace	tate butyrate (lov	w k)	0.16736	1200	1.4644	
	○ Sphere	Cellulose nitra	ate (pyroxylin)		0.23012	1380	1.4644	
	Ocylinder	Concrete			1.8	2242	1	
lultilaver		Copper - pure	2		392.9	8900	0.385	
latenayer		Diallyl phthala	ite		0.305432	1650	1.12968	
		Epoxy, Glass	fiber filled (molde	ed)	0.16736	1900	0.79496	
(\land)	Mass (kg)	Ethyl cellulose	2		0.23012	1150	2.092	
Sohere	Thickness (um) 🗸	Ethyl vinyl ac	etate		0.075312	1200	2.3012	
	initial temp (90)	Gold - pure			297.7	19320	0.13	
	initial temp. (-C)	Gypsum (CaS	04.4H2O)		0.75312	2110	1.08784	
	Select substance	ICe			2.21	910.7	1.9246	
	Density (kg/m ³)	Todine (solid)			0.0045515	4930	0.21/508	
	Looph de Anti-MO	Iron Dure			03.5	7630	0.12	
Cylinder	Lambda (W/m/K)	Methyl methy	crulate		0.2092	11340	1 4644	
	Cp (J/g/K)	meanymeana	ici yidite		0.2092	1100	1.1011	
	Kinetics	Add Customiz	ed Substance	Modify Sub	ostance	Delete Substance	✓ OK	Cance
-	ΔHr (J/g)					1		
and a state of the		Layer 1	Layer 2	Layer 3	Layer 4			
OPlate								
and a state of the								

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.

😵 Predictions 🛛 🕹						
Predictions						
Temperature profiles	Sample controlled thermal	analysis				
Iso Non	i-Iso Step Mod	ulated Shock	Worldwide	STANAG	Customized	
SADT Thermal Stability Diagram						
Safety Diagram TI	MRad					
Automatic Report						
SADT : Self Accelerating Decomposition Temperature						
	O Sphere © Cylinder Box Multilayer Cylinder Diameter 2 Indeptition 2 Height 0.63384057/(m) So 50	External properties Side U (W/m^2/K) Side temp. Iso (36°C) Top U (W/m^2/K) Top temp. Load Same as side temp. Bottom U (W/m^2/K) Bottom temp. Load Same as side temp.	5 Load Profile S Profile Clear S Profile Clear			General properties Determine SADT Calculate cooling coefficient Time 7 day Mesh precision Data storage Stop calculation If T > 130 °C









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.

FOR FURTHER INFORMATION VISIT: www.akts.com/ts





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