Consideration of Autocatalytic Behavior in Determination of Self Accelerating Decomposition Temperature

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Presented to:
NATAS 2011

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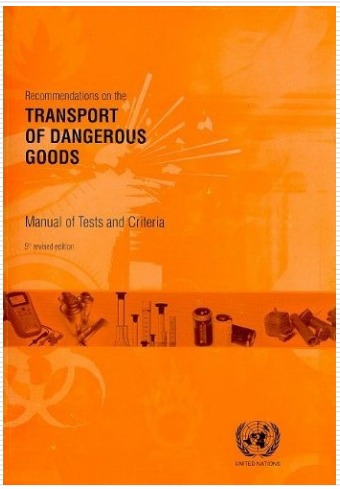
What is a Self Accelerating Decomposition Temperature?

United States SADT Test: SADT is defined as the lowest environmental temperature at which the center of the material within the package heats to a temperature 6°C greater than the environmental temperature after a lapse of a seven day period or less. This period is measured from the time when the temperature in the center of the package reaches 2°C below the environmental temperature



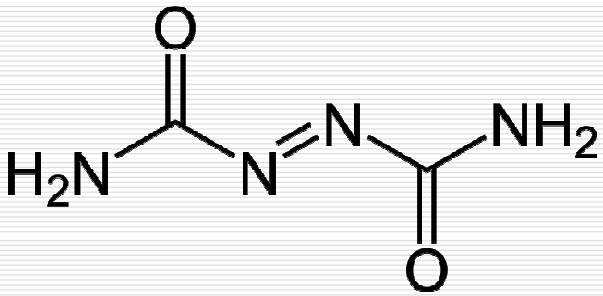
What is Needed to Estimate a SADT?

- Package properties
  - Size
  - Heat transfer coefficient
- Physical properties of self-reactive substance
  - Density
  - Specific heat
  - Thermal conductivity
- Decomposition kinetics

Azodicarbonamide

(CAS: 123-77-3)

- Package properties
  - Size (50 kg)
  - Heat transfer coefficient (5 $W/m^2 \cdot K$)
- Physical properties of self-reactive substance
  - Density (1650 kg/m^3)
  - Specific heat (1050 $J/kg \cdot K$)
  - Thermal conductivity (0.1 $W/m \cdot K$)
- Decomposition kinetics



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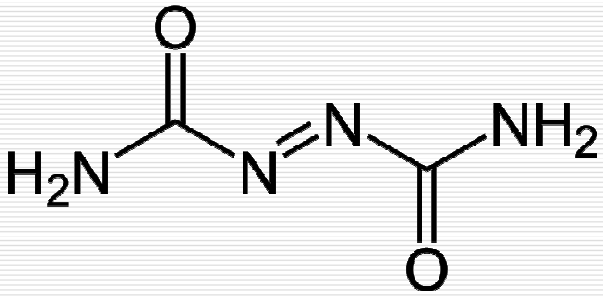

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Methods of Investigating Decomposition Reactions

- Adiabatic Calorimetry
  - ARC
  - VSP2
  - ARSST
- Heat Flow Calorimetry
  - TAM
  - C80
  - DSC

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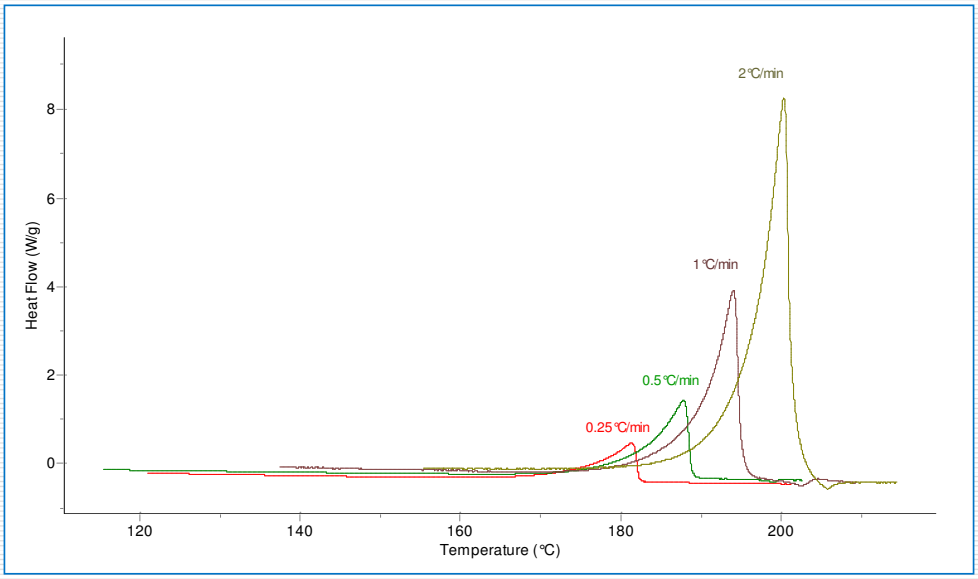
Non-isothermal DSC Signals



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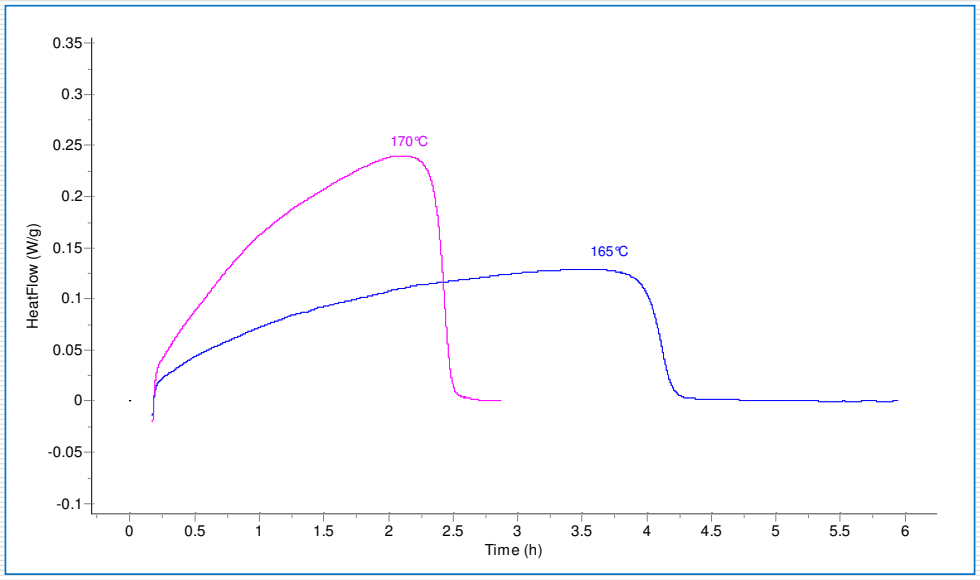
Isothermal DSC Signals



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Basic Kinetic Equation

- Reaction rate is expressed by the equation

$$\frac{d\alpha}{dt} = A \cdot \exp\left(-\frac{E}{R \cdot T(t)}\right) f(\alpha)$$

  - Where A, E, f(α), T, and t mean: pre-exponential factor in Arrhenius equation, activation energy, function of the reaction extent α which form depends on the decomposition mechanism, temperature and time, respectively

- Isoconversional methods (model free)
  - Reaction model is not required

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Isoconversional Methods

- Isoconversional methods (model free):

  Three main modifications of isoconversional method are applied in the literature:
  - Differential (Friedman)
  - Integral (Flynn-Ozawa-Wall)
  - ASTM E698

  Reaction rate expressed by the Arrhenius equation

$$\ln\left(\frac{d\alpha}{dt}\right)_{\alpha} = \underbrace{\ln\left(A'(\alpha)\right)}_{\| \; A(\alpha)\cdot f(\alpha)} - \frac{E(\alpha)}{R}\frac{1}{T}$$

Reaction rate at a given reaction progress α is only a function of the temperature

$A'(\alpha)$ and $E(\alpha)$ are the pre-exponential factor and apparent activation energy

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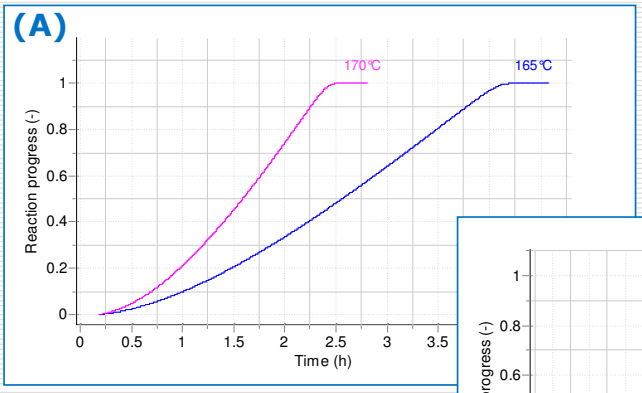
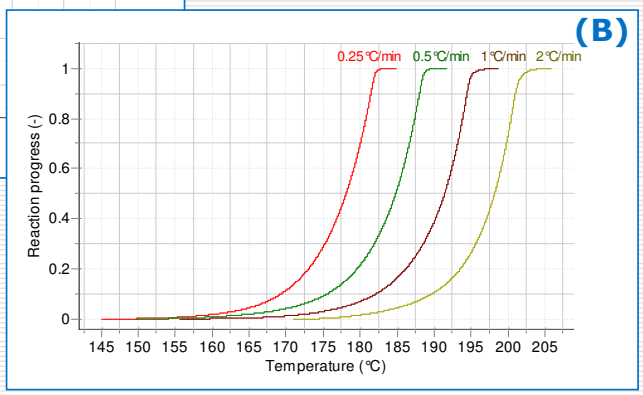
Reaction Progress in Isothermal (A) and Non-isothermal (B) Conditions





$$\alpha = \frac{Q}{\Delta H_r}$$

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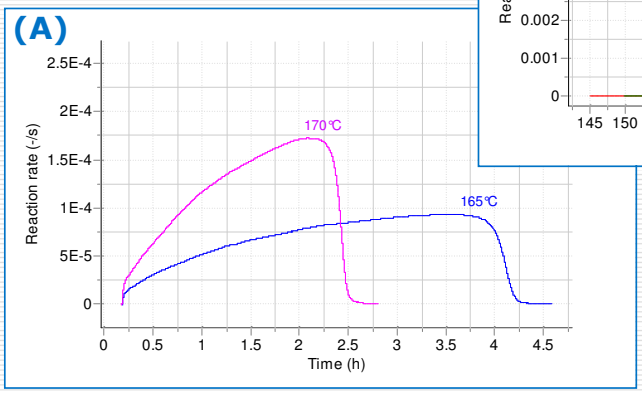
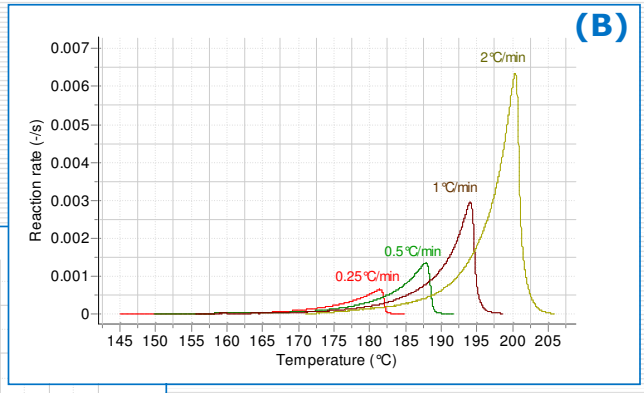
Reaction Rate in Isothermal (A) and Non-isothermal (B) Conditions

$$\frac{d\alpha}{dt} = \frac{\dot{Q}}{\Delta H_r}$$





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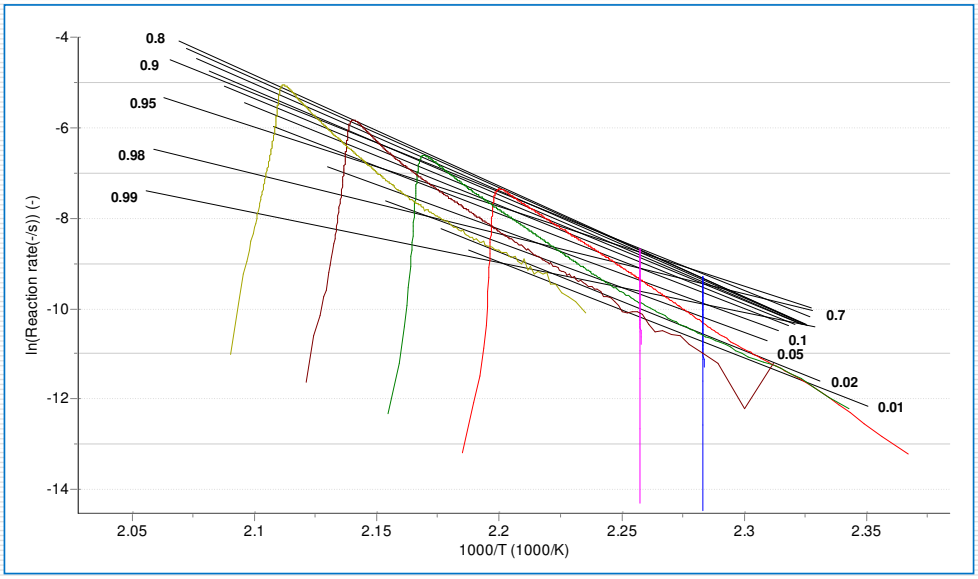
Differential Isoconversional Method



The activation energy is determined from the slope of the lines connecting points plotted in coordinates: reaction rate vs. 1/T obtained for the same reaction progress α at different heating rates

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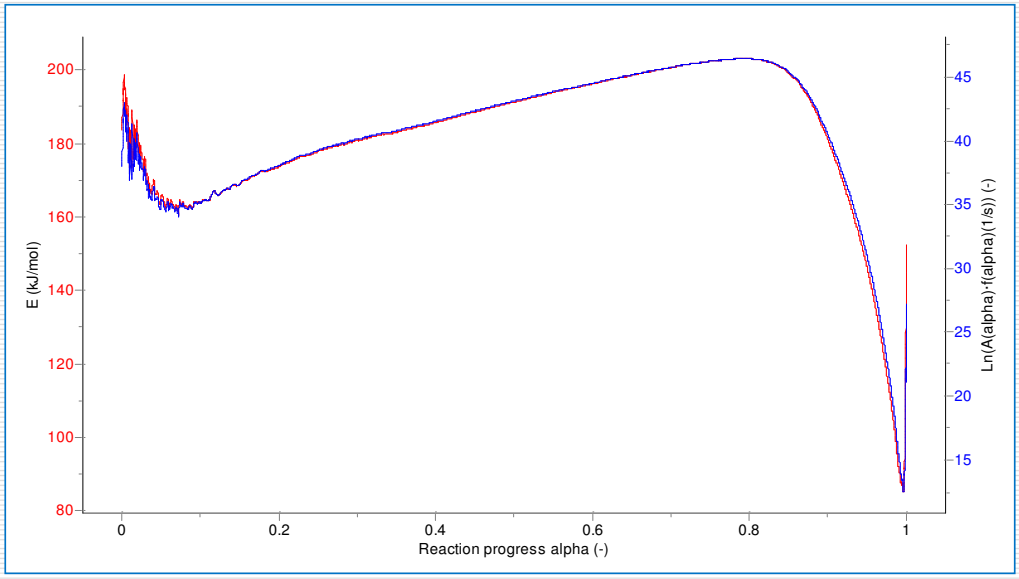
Dependence of E_a and ln(A) on the Reaction Progress



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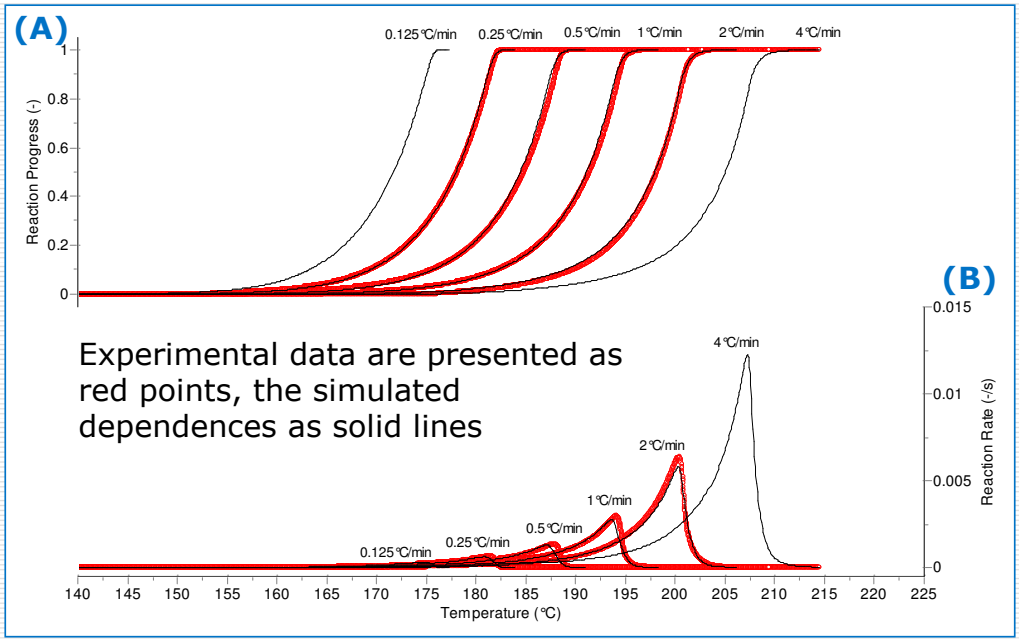
Simulation of the Reaction Progress (A) and Reaction Rate (B) in Non-isothermal Conditions



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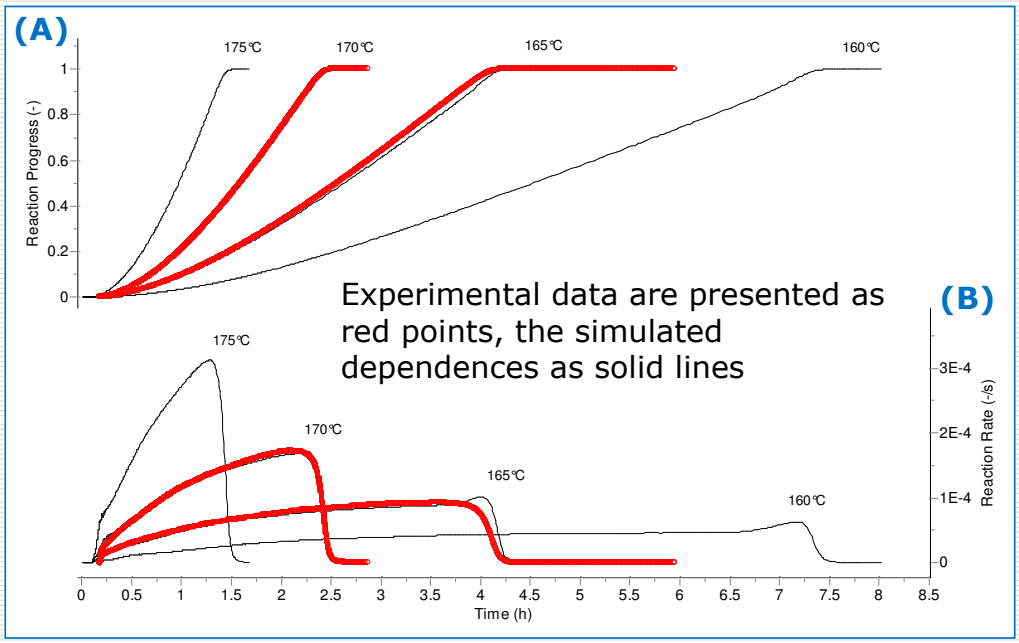
Simulation of the Reaction Progress (A) and Reaction Rate (B) in Isothermal Conditions



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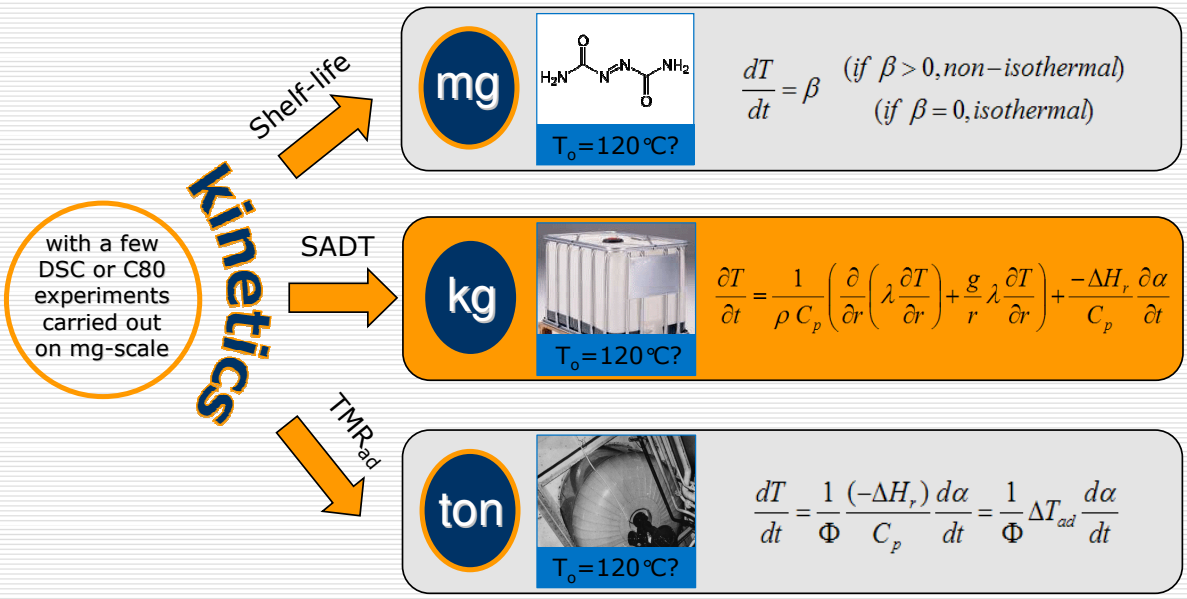
Temperature-Time Dependence for Different Sample Masses

Azodicarbonamide (CAS: 123-77-3)



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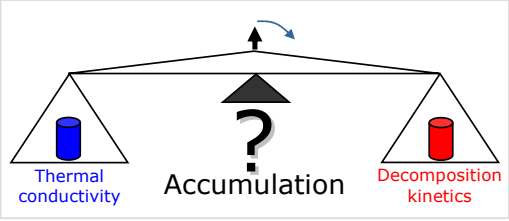
Heat Balance: Kilogram Scale



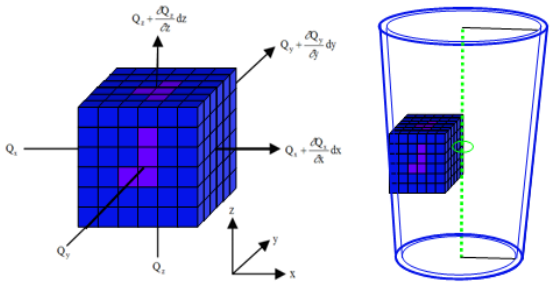
Heat balance combined with numerical analysis enables the determination of the

(i) heat accumulation and

(ii) reaction rate and progress

for any surrounding temperature profile

$$\frac{\partial T}{\partial t} = \frac{1}{\rho C_p}\left(\frac{\partial}{\partial r}\left(\lambda \frac{\partial T}{\partial r}\right) + \frac{g}{r}\lambda \frac{\partial T}{\partial r}\right) + \frac{-\Delta H_j}{C_p}\frac{\partial \alpha}{\partial t}$$



input (heat conducted in) + reaction (heat generated within) = output (heat conducted out) + accumulation (change in energy stored within)

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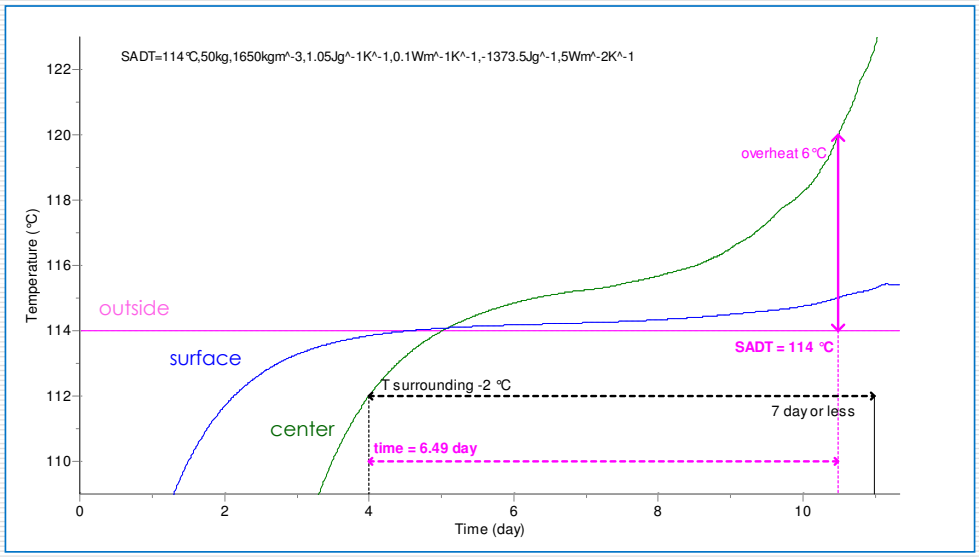
Prediction of SADT Applying Heat Balance and Kinetic Data



The SADT is 114℃. This temperature is the lowest environment temperature at which overheat in the middle of the specific packaging exceeds 6℃ (ΔT6) after a lapse of the period of seven days (168 hours) or less. This period is measured from the time when the packaging centre temperature reaches 2℃ below the surrounding temperature. This overheat of 6℃ occurs after about 6.5 days.

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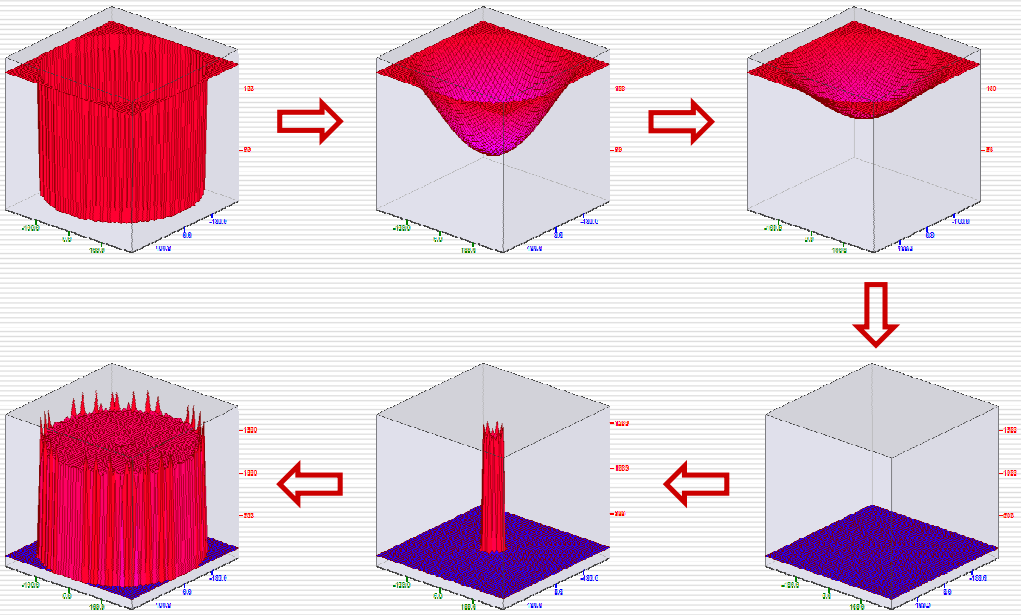
Simulation of Thermal Explosion of a 50 kg Package of Azodicarbonamide (T_{amb} = 120°C)



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SADT predicted: 114°C

SADT literature: 115°C

(M.W. Whitmore, J.K. Wilberforce, J. Loss Prev. Process Ind., 6 (1993) 95.)

The simulated SADT values of azodicarbonamide being in very good agreement with those already determined indicate the

(i) correct collection of the experimental DSC data,

(ii) accurate procedure of the determination of kinetic parameters, and

(iii) precise evaluation of the thermal safety behavior implemented in AKTS-Thermokinetics software.

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Conclusion

Thermal safety simulation of self-reactive chemicals in kg-scale (SADT) based on:

(i) the kinetics of the reaction investigated by DSC applying differential isoconversional method

(ii) the heat balance of the system

allow the precise prediction of SADT.

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