Influence of Polymorphic Transition on the Thermal Behavior of Quasi-Autocatalytically Decomposed Solids

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Scale-up of Thermal Behavior of Quasi-Autocatalytically Decomposed Solids: How the Phase Transition and Melting can Influence the Experimental Workflow

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To say it in another way:

Based on few thermoanalytical experiments carried out in high pressure sealed crucibles with few mg sample, can one predict the thermal behavior of few kg sample?
mg  kg
For the illustration of my remarks
I will use as example
the results of a study of the thermal behavior of

AIBN (Azobisisobutyronitrile)

The applied method will be based on
kinetic and heat balance approaches.
Why AIBN?

Why KINETICS?
DSC traces of AIBN recorded by DSC at 2 K/min⁻¹

5 zones

A) range of existence of low temperature (L-T) polymorph
B) polymorphic transformation
C) decomposition of (H-T) phase in solid state
D) melting
E) decomposition in the liquid phase

(15mg, high pressure sealed crucible)
Because it decomposes exothermally, and may be potentially dangerous during storage. Additionally:

(i) it has a polymorphic transition and melting before decomposition

(ii) and its decomposition is quasi-autocatalytic.

Why KINETICS?

Because with small amount of material one can determine the rate of heat evolution which can lead to thermal hazard of larger amount of substance.
Based on few heat flow experiments carried out with few mg of AIBN,

is it possible to predict

if 50 kg of AIBN
at surrounding temperature of 45°C
will be stable during a laps period of 10 days?
DSC traces of AIBN recorded by DSC at 2 Kmin⁻¹

5 zones

A) range of existence of low temperature (L-T) polymorph
B) polymorphic transformation
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50 kg at 45°C for 10 days?

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DSC traces of AIBN recorded by DSC at 2 Kmin⁻¹

5 zones

It seems to be obvious that the kinetics of the decomposition must be investigated for this phase which is stable at ambient temperatures during the long-term storage.

50 kg at 45°C 10 days?

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DSC traces of AIBN recorded by DSC at 2 Kmin⁻¹

- **A)** range of existence of low temperature (L-T) polymorph
- **B)** polymorphic transformation
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50 kg at 45°C for 10 days?


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(15mg, high pressure sealed crucible)
DSC traces of AIBN recorded by DSC at 2 Kmin\(^{-1}\)

- **A)** range of existence of low temperature (L-T) polymorph
- **B)** polymorphic transformation
- **C)** decomposition of (H-T) phase in solid state

Roduit et al., JTAC (2014)

- 50 kg at 45°C 10 days?

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(15mg, high pressure sealed crucible)
DSC traces of AIBN recorded by DSC at 2 Kmin⁻¹

A) range of existence of low temperature (L-T) polymorph

50 kg at 45°C 10 days?

Roduit et al., TCA (2018)

(15mg, high pressure sealed crucible)
Ultra-sensitive heat flow measurements with Heat Flow Calorimetry (HFC) which sensitivity is about 1000 times better than in DSC.
Heat Flow Calorimetry (HFC) traces of AIBN recorded at 55, 60, 65 and 70°C with the Thermal Activity Monitor (TAM)

ΔH_{r,avg} = -1103.6 \text{ J g}^{-1}

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Heat Flow Calorimetry (HFC) traces of AIBN recorded at 55, 60, 65 and 70°C with the Thermal Activity Monitor (TAM)

- **70°C**
  - 30 mg
  - $\Delta H_{r,avg} = -1103.6 \text{ J g}^{-1}$

- **65°C**
  - 15 mg
  - $\Delta H_{r,avg} = -1109.1 \text{ J g}^{-1}$
Heat Flow Calorimetry (HFC) traces of AIBN recorded at 55, 60, 65 and 70°C with the Thermal Activity Monitor (TAM)

- **30 mg** at 70°C: $\Delta H_{r,avg} = -1103.6 \text{ J g}^{-1}$
- **15 mg** at 70°C: $\Delta H_{r,avg} = -1109.1 \text{ J g}^{-1}$
- **60°C**: $\Delta H_{r,avg} = -1080 \text{ J g}^{-1}$
- **65°C**: $\Delta H_{r,avg} = -1109.1 \text{ J g}^{-1}$
Heat Flow Calorimetry (HFC) traces of AIBN recorded at 55, 60, 65 and 70°C with the Thermal Activity Monitor (TAM)

- **55°C**: 
  - 30 mg: \[ \Delta H_{r,\text{avg}} = -1103.6 \text{ J g}^{-1} \]
  - 15 mg: \[ \Delta H_{r,\text{avg}} = -1109.1 \text{ J g}^{-1} \]

- **60°C**: 
  - 65°C: 
  - 30 mg: \[ \Delta H_{r,\text{avg}} = -1080 \text{ J g}^{-1} \]
  - 15 mg: \[ \Delta H_{r,\text{avg}} = -1094.1 \text{ J g}^{-1} \]

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The kinetic parameters were calculated by the differential isoconversional kinetic analysis.

Activation energy $E(\alpha)$ and \{A(\alpha) f(\alpha)\} of AIBN decomposition as a function of the reaction progress $\alpha$ calculated from HFC traces of AIBN recorded at 55, 60, 65 and 70°C.

\[ \frac{d\alpha}{dt_\alpha} = A'(\alpha) \cdot \exp \left( -\frac{E(\alpha)}{R} \cdot \frac{1}{T(t)} \right) \]
Having kinetic parameters of the reaction we can predict the rate of the decomposition of AIBN at any temperature.
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**Experimental domain**

*Black: experiments*

*Red: simulations*

(Sample mass: 30 mg)
Having **kinetic parameters** of the reaction we can predict the rate of the decomposition of AIBN at **any temperature**.

**Experimental domain**

- **Black**: experiments
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(Sample mass: 30 mg)
The kinetic parameters are the same for the 1mg, 1g or 1kg sample.

But for scale-up of HFC results, knowledge of the kinetics is one prerequisite only. The second one, also very important is the correct heat balance in the system.

Why?
The kinetic parameters are the same for the 1mg, 1g or 1kg sample.

But for scale-up of HFC results, knowledge of the kinetics is one prerequisite only. The second one, also very important is the correct heat balance in the system.

Because for samples with larger mass the heat cannot be fully exchanged with an environment (as during HFC) what may result in increase of the temperature of the samples and the thermal runaway.
with few HFC (TAM) experiments carried out in mg scale

\[
\frac{dT}{dt} = f(t) \neq f(m)
\]

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with few HFC (TAM) experiments carried out in mg scale

\[ \frac{dT}{dt} = f(t) \neq f(m) \]

\[ \rho C_p \left( \frac{\partial^2 T}{\partial r^2} + \frac{1}{r} \frac{\partial T}{\partial r} + \frac{\partial^2 T}{\partial z^2} \right) + \frac{-\Delta H_r}{C_p} \frac{d\alpha}{dt} \]

\[
\begin{align*}
0.127 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1} & \quad -1097.3 \text{ J} \cdot \text{g}^{-1} \\
650 \text{ kg} \cdot \text{m}^{-3} & \quad 1.55 \text{ J} \cdot \text{g}^{-1} \cdot \text{K}^{-1}
\end{align*}
\]
Having kinetic parameters and heat balance we can predict the rate of decomposition of AIBN under any, temperature mode and scale.

- **Sample temperature**: 50 mg
- **Set temperature**
Having kinetic parameters and heat balance we can predict the rate of decomposition of AIBN under any temperature mode and scale.
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Having **kinetic parameters** and **heat balance** we can predict the rate of decomposition of AIBN under any, **temperature mode and scale**.
Are 50 kg of AIBN stable at surrounding temperature of 45°C during a lapse period of 10 days?

Yes ☑
Experimental validation with a drum containing 50kg AIBN and exposed at 47°C during 10 days.
Having kinetic parameters and heat balance we can predict the rate of decomposition of AIBN under any temperature mode and scale.

50 kg at 45°C ~21 days

50 kg at 45°C 10 days?
Having kinetic parameters and heat balance, we can predict the rate of decomposition of AIBN under any temperature mode and scale.
Having kinetic parameters and heat balance we can predict the rate of decomposition of AIBN under any, temperature mode and scale.
It is possible to predict the thermal behavior during scale-up in which sample mass is increased by one million times.

For substances with polymorphic transition and melting before the exothermic event, ultra-sensitive heat flow measurements (HFC) may be applied. HFC has a sensitivity that is about 1000 times better than in DSC and can be applied to collect the heat flow data of this phase which is stable at ambient temperatures during the long-term storage.

But summarizing, for successful scale-up, we need:
- Kinetic description of the process
- Correct heat balance
Thank you for your attention

More information: www.akts.com or info@akts.com