

Leading Thermal Analysis ■

# NETZSCH KINETICS NEO SOFTWARE DEMONSTRATION

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Sitzung der ERFA-BCI ‚Gefährliche Reaktionen‘, Sisseln, 24 January 2019

## Academic

1. **Activation energy** for the **peak point**
2. **Activation energy** for different stages of **process**
3. **Scientific research** of the process, including information about each reaction step.

## Industrial

1. **Prediction** at the same ranges of temperature and heating rate as in experiment (**no extrapolation**), based on kinetic analysis
2. **Predictions** at the **temperatures** and/or **heating rates** outside of the experimental range (**extrapolation**), based on kinetic analysis
3. **Optimization** of industrial processes



- A Software for studying **chemical kinetics** (reaction kinetics) and **crystallization kinetics**.
- It investigates the **reaction rates** of chemical processes or crystallization depending on **time** and **temperature**.
- Kinetics Neo contains **10 model-free methods** including numerical methods for the best model-free results.
- Kinetics Neo features a unique **model-based method** that allows for analyzing multi-step processes, determines a kinetic model, makes predictions and optimizations based on this model.

- Experiment
- Analysis
- Predictions

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## Experimental data

## TGA, DSC

- Dynamic DSC, different heating rates
- Isothermal DSC: different temperatures

## Calorimetric data:

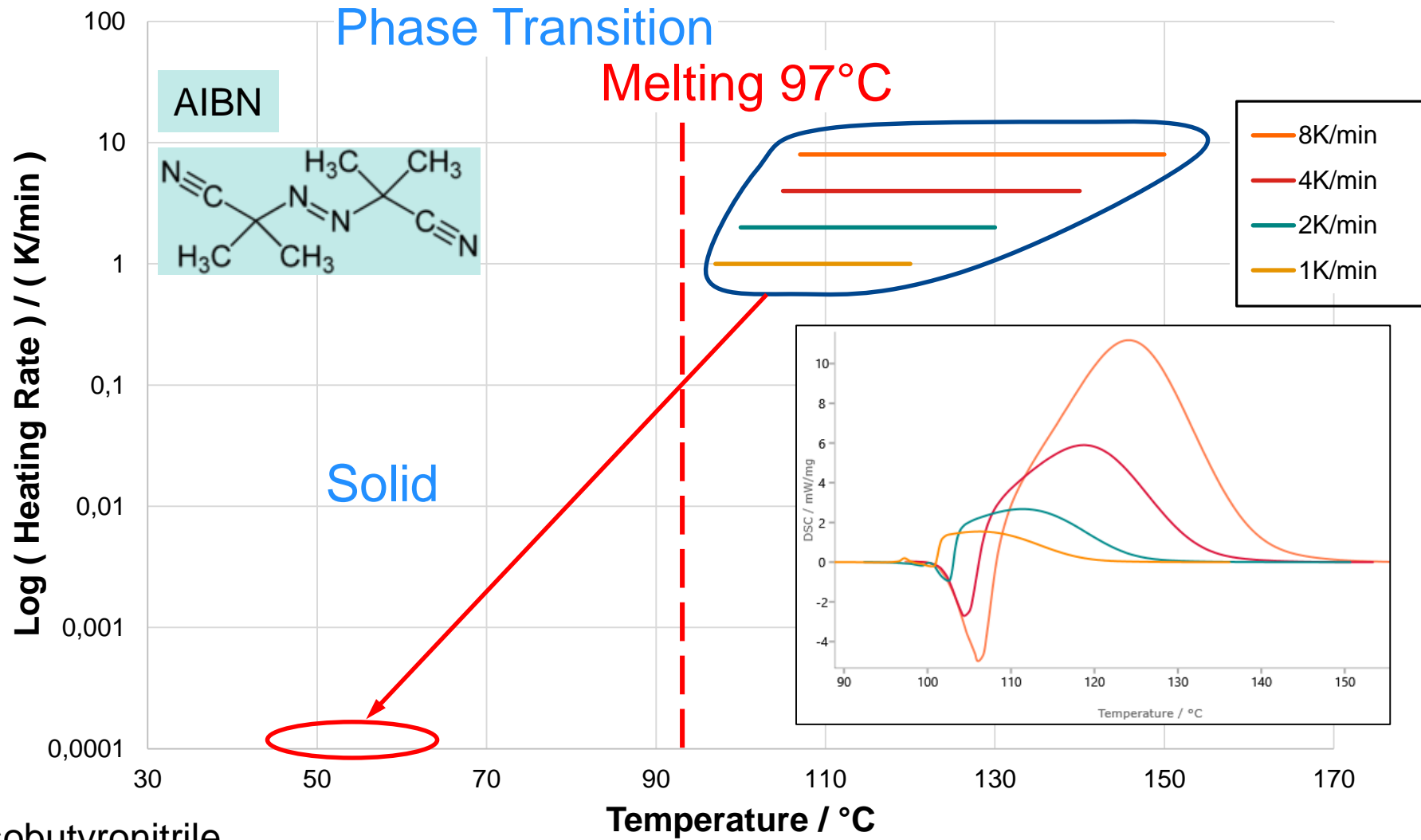
- HFC different temperatures
- ARC, APTAC, MMC

## Additional

- DIL, DEA, Viscosity, Rheometry

# Data field depends on the target

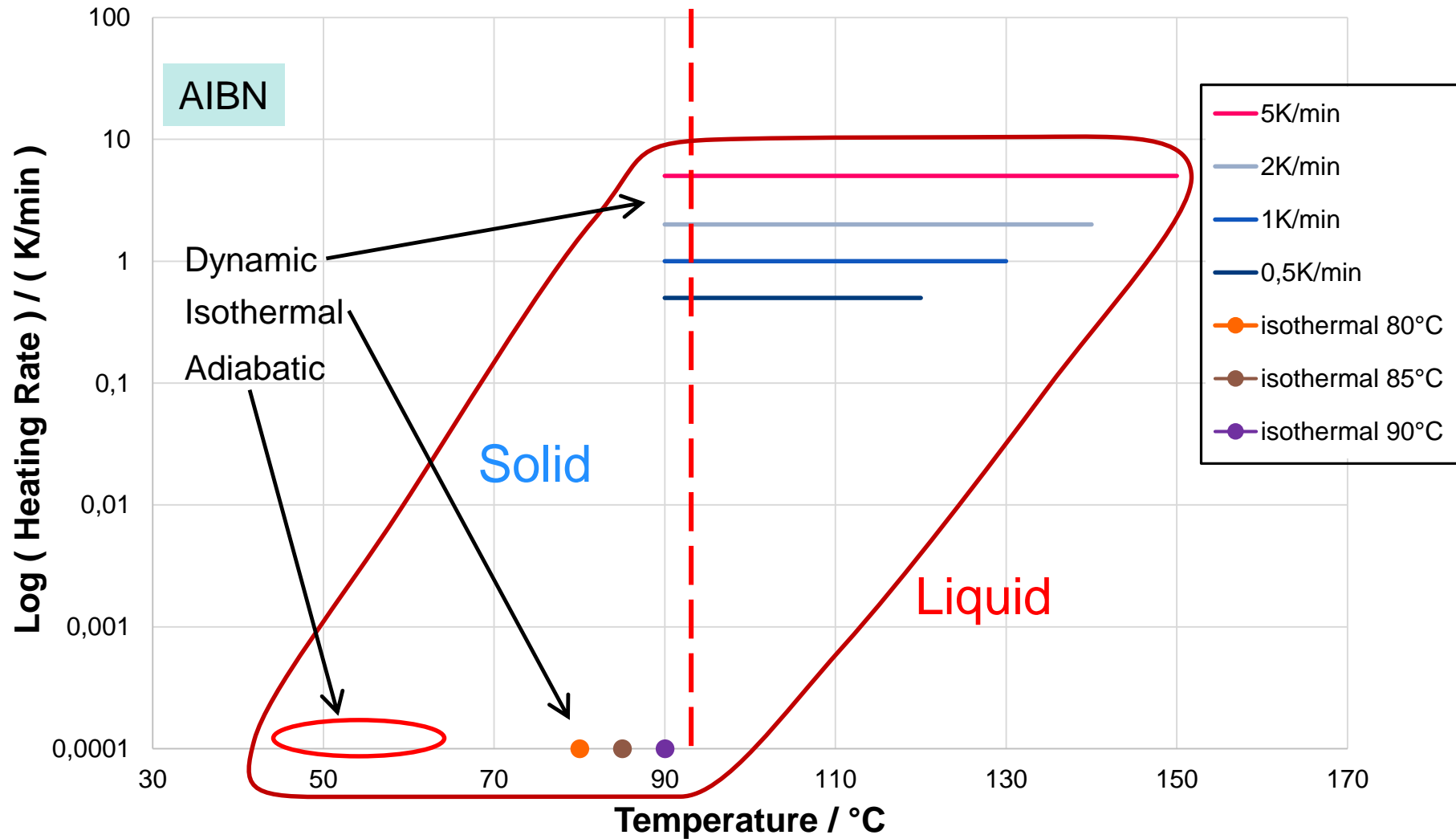
## Different temperatures – different kinetics



AIBN: Azobisisobutyronitrile

S.Guo, J.Therma Anal Calorim (2013) 113:1169-1176 **SADT:63°C** for 50kg (AKTS)

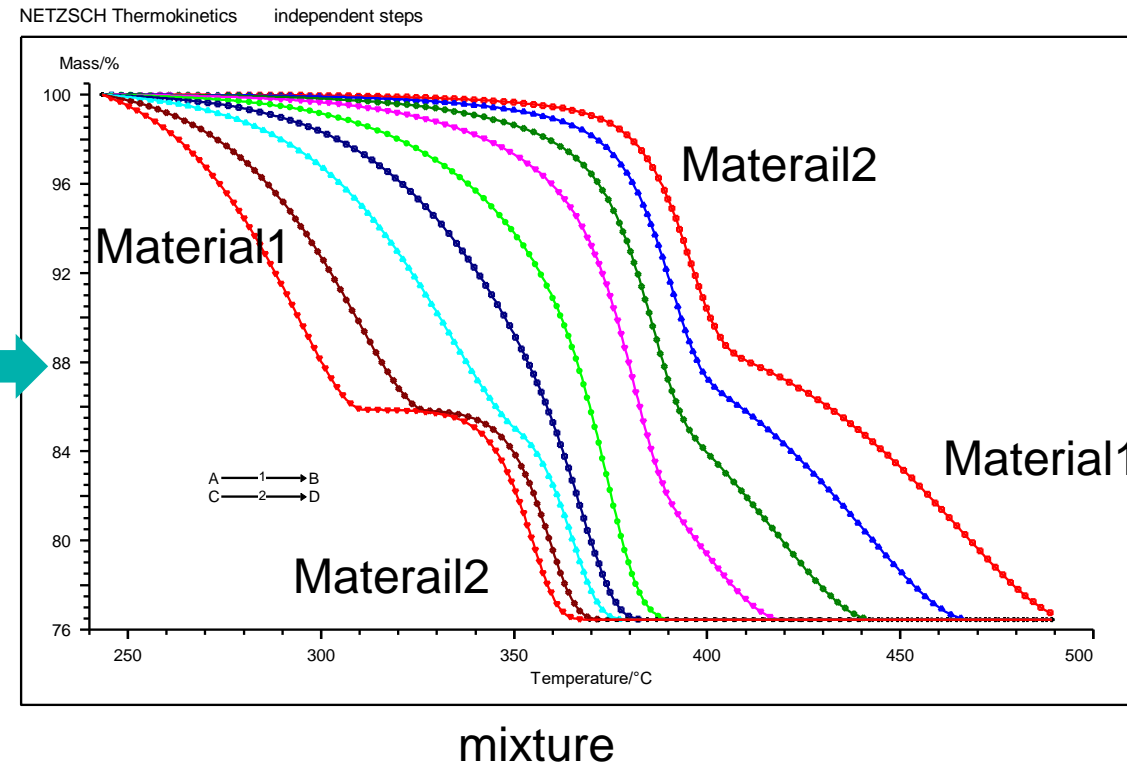
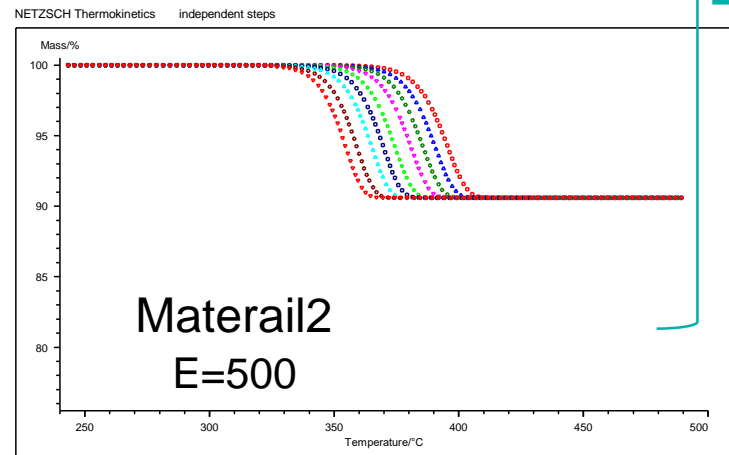
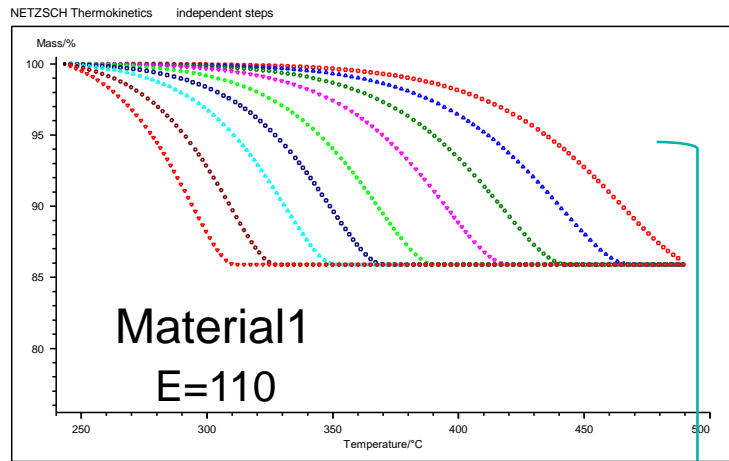
Data field depends on the target  
Experiment must be done for the same state of material



Moukhina, Thermochemica Acta 621(2015) 25-35, **SADT 46°C**, measurements: BAM



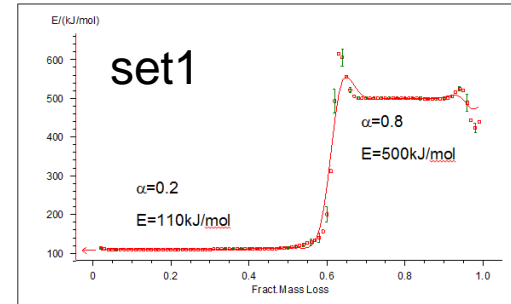
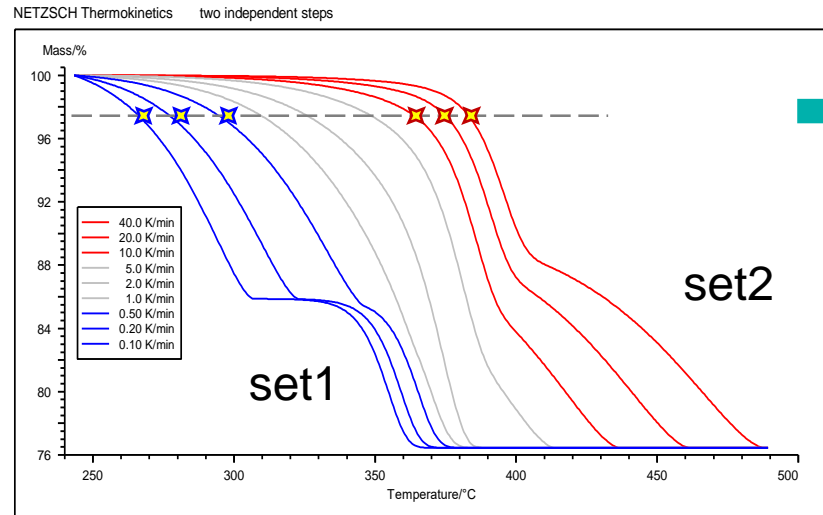
# Different heating rates different kinetics Decomposition of mixtures



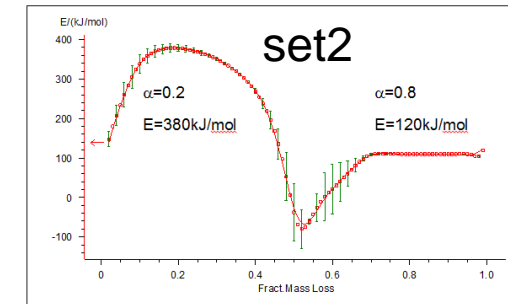
Heating Rate from 0.1K/min to 50K/min

Moukhina, J Therm Anal Calorim (2012) 109:1203–1214

## Dynamic data: two data sets

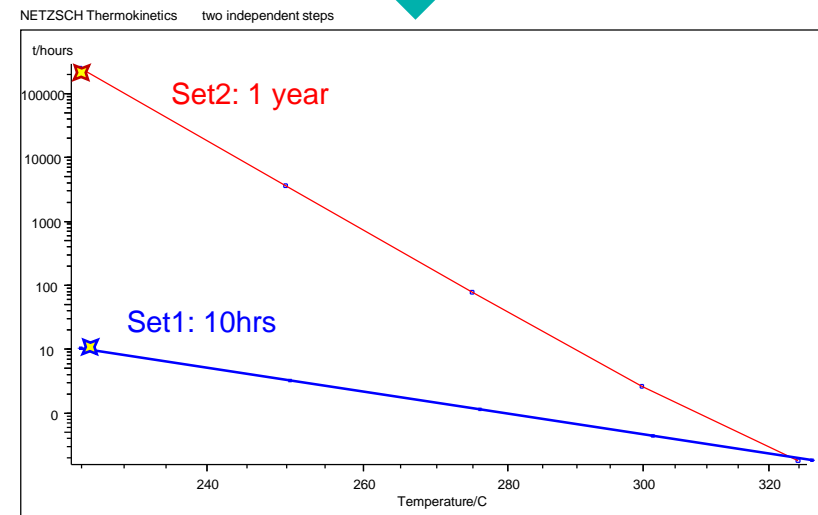


Simulation  $E=110, 500$ ,  
Model-free  $E=110, 500$ ,



Simulation  $E=110, 500$ ,  
Model-free  $E=380, 120$ ,

Lifetime predictions by model-free  
are different



Moukhina, ASTM Journal of Testing and evaluation (2014) V42,N6: 1376-1386

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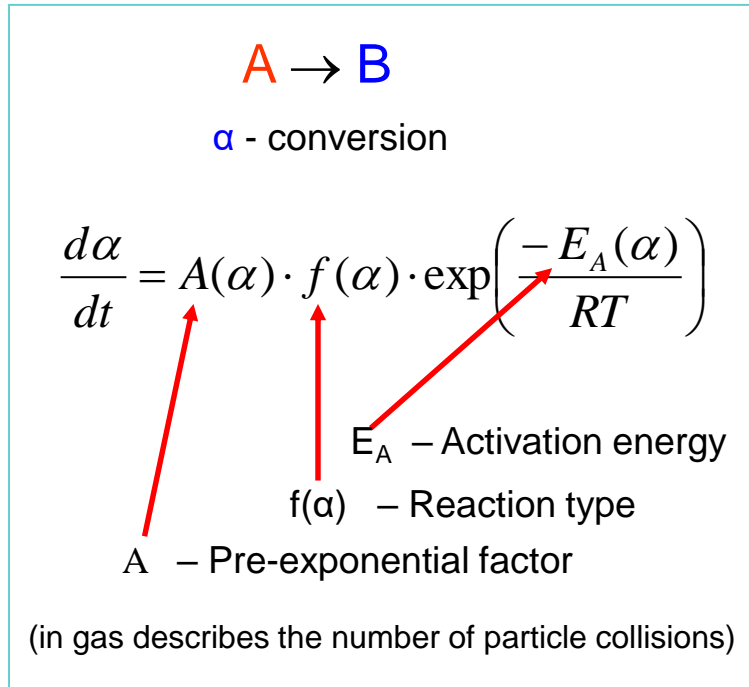
# Analysis Method

## **Model-free and model-based methods.**

The results of these methods can be statistically compared with one another.

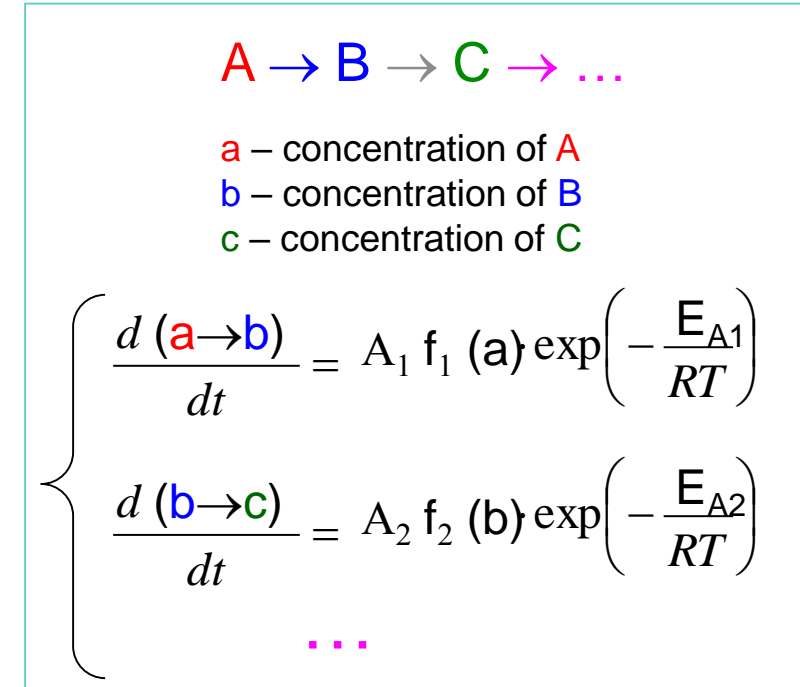
- **Model-free**
  - activation energy and pre-exponential factor as functions of the conversion degree.
- **Model-based**
  - kinetics model including
  - Number of reaction steps
  - Step contribution to the total effect
- **Parameters for each reaction step:**
  - Reaction type
  - Activation energy
  - Reaction order
- **Parameters for crystallization:**
  - Dimension of nucleation
  - Melting temperature and glass transition temperature

## Model-free



1. One equation for any reaction
2. Activation energy depends only on conversion  
And independent on measurement conditions
3.  $f(\alpha)$  is assumed to be n-th order reaction

## Model-based (any model)



1. Reaction has several steps
2. Reaction steps can be parallel or consecutive
3. Each reaction step has own kinetic equation
4. Kinetic parameters of each step are constant values



## Conversion-dependent methods

• Ozawa-Flynn-Wall	Integral isoconversional method for each conversion point	heating
• Kissinger-Akahira-Sunose	Integral isoconversional method for each conversion point	heating
• Friedman method	differential isoconversional method for each conversion point	heating+iso
• Numerical optimization	modified Friedman method	
	to get minimum of $\psi = \sum_{curves} \sum_{points} (\alpha_i^{calc} - \alpha_i^{exp})^2$	heating+iso

## Methods based on the single conversion

• ASTM E698	integral Ozawa method for points with Maximum rate	heating
• ASTM E2890	integral Kissinger Method for points with maximum rate	heating
• ASTM E1641	integral Ozawa method for points with 5% conversion	heating
• ASTM E2070	Integral isoconversional method for isothermal data	isothermal
• Dynamic Arrhenius	integral Ozawa method for failure temperature at heating	heating
• Isothermal Arrhenius	integral isoconversional method for time-to-event (e.g. OIT)	isothermal

1. **No scientific research, no predictions:**

ASTM, Friedman, Ozawa, Kissinger, model based for 1-2steps

2. **Deep scientific research:** both model free and model based

Model free: Friedman or numerical methods produce best fit

Model based: allow to find parallel steps: independent or competitive

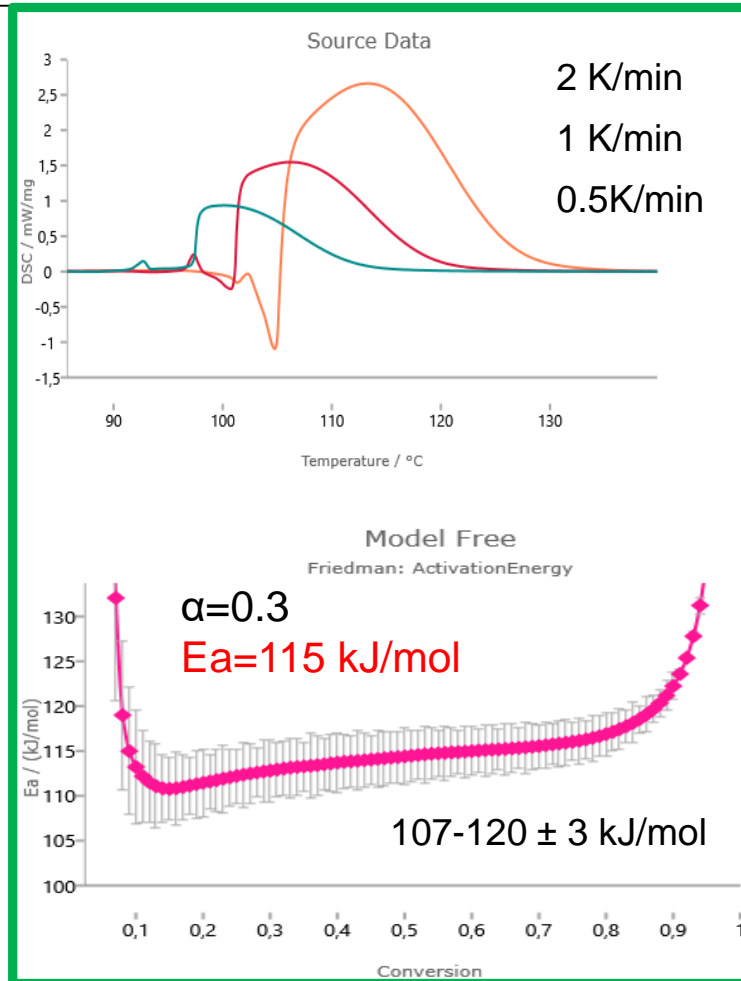
3. **Predictions with extrapolation on heating rate:**

Model free, if it has the same result for isothermal and dynamic data

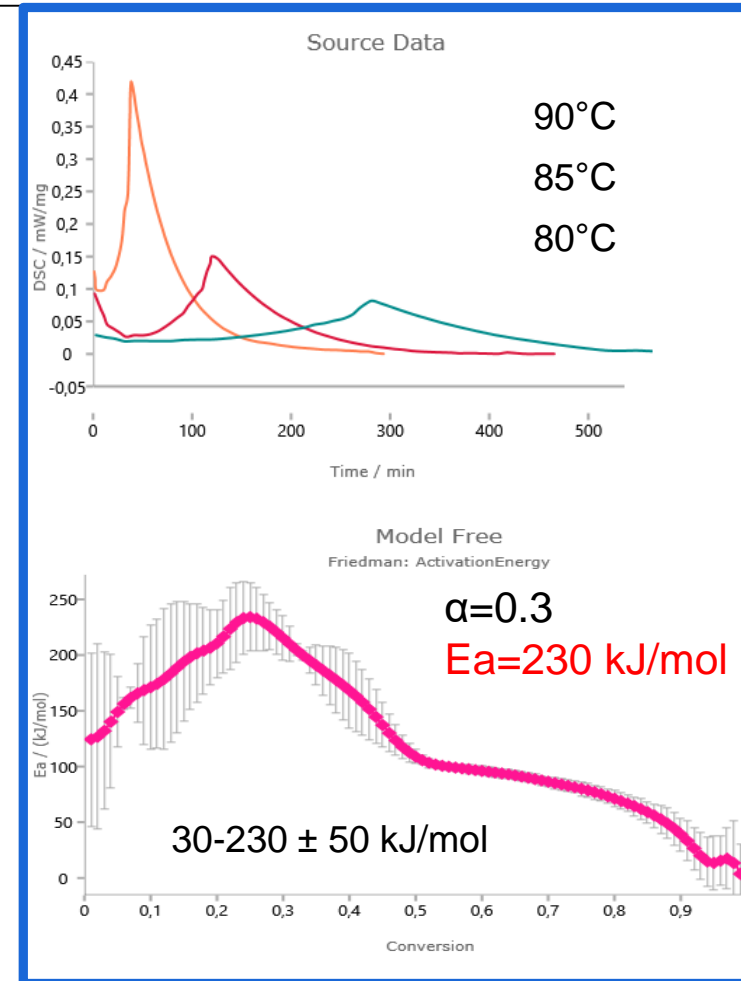
Model based, if isoconversional lines have crossing by decreasing of HR

# Why and when model free analysis is inapplicable?

Example: model free analysis for dynamic and isothermal data is not the same



Dynamic

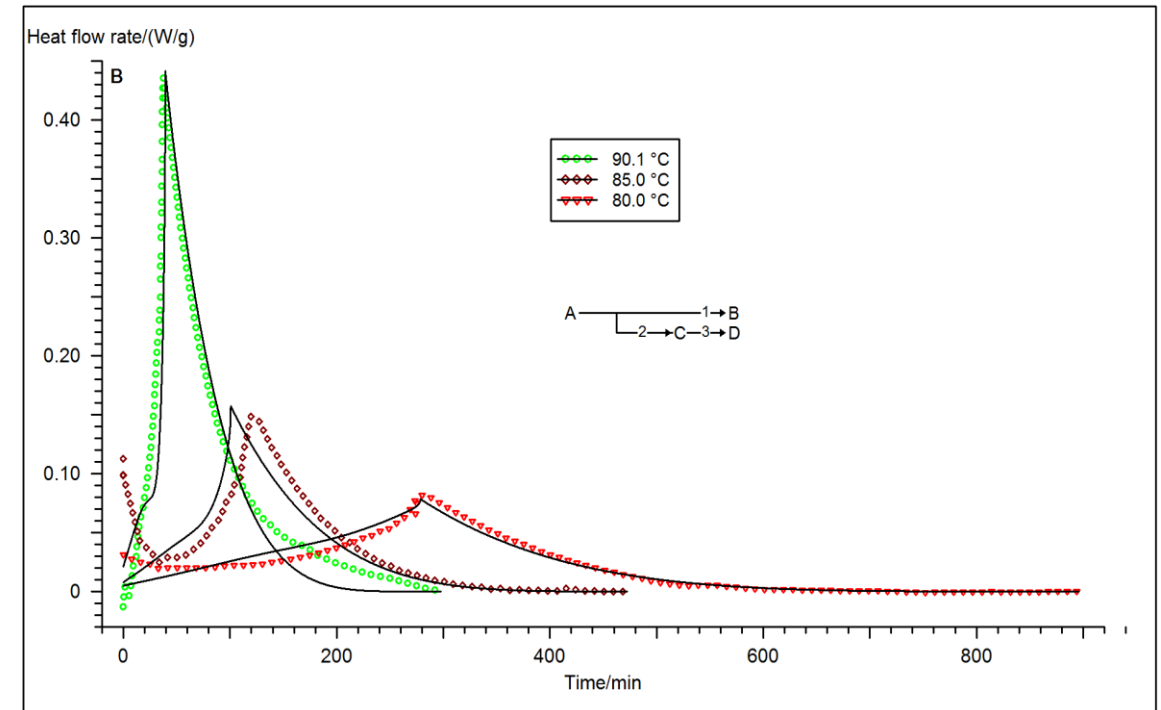
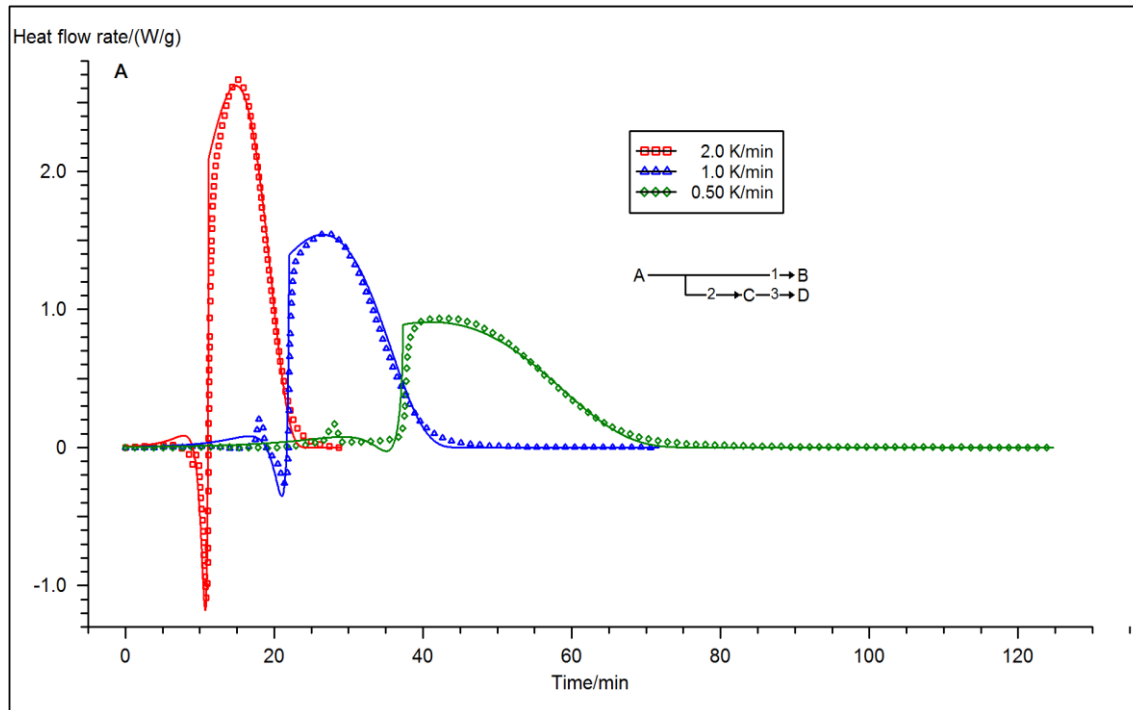


Isothermal

AIBN: different results for different Heating Rates

Moukhina, Thermochemica Acta 621(2015) 25-35



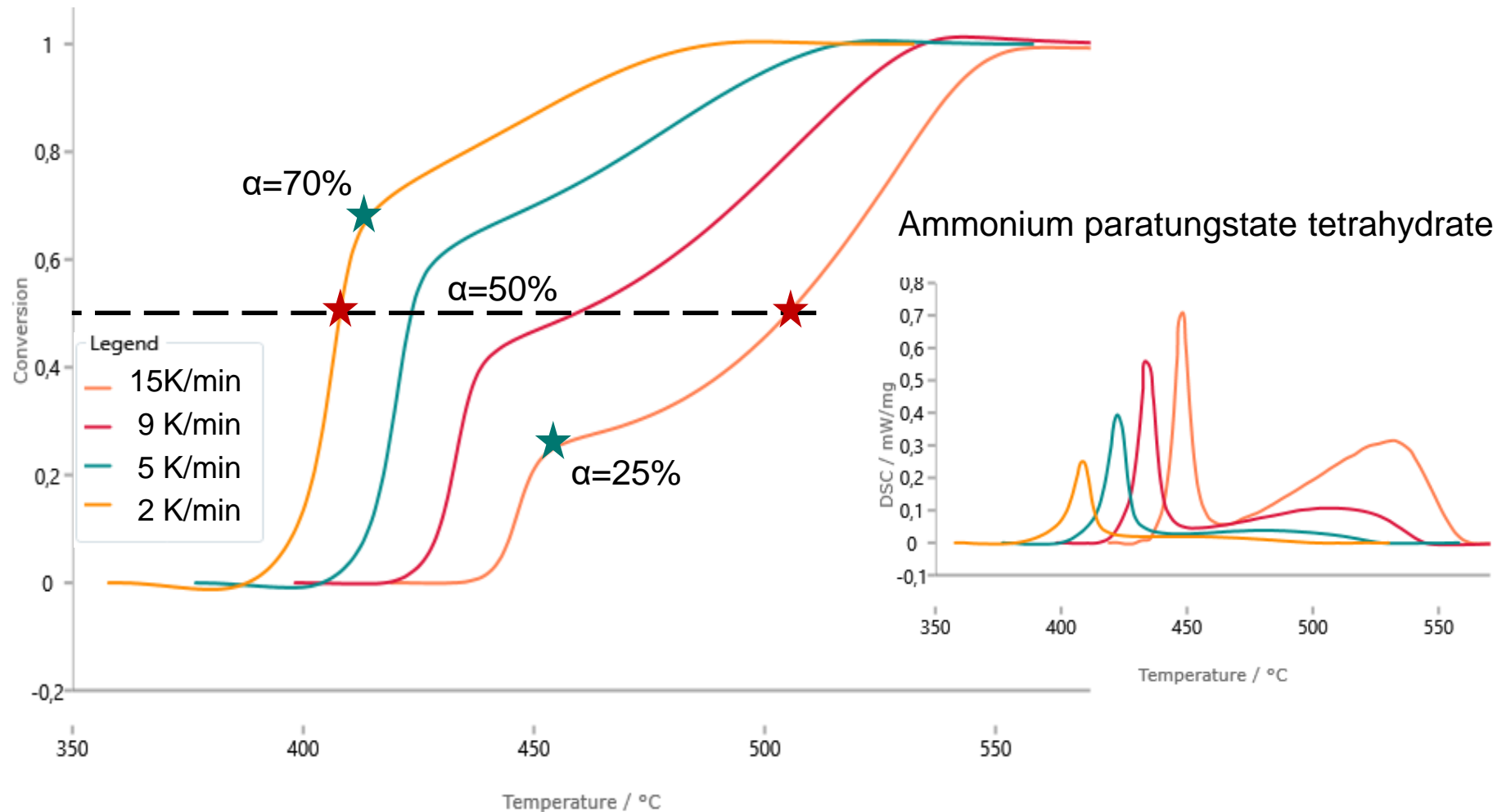


## Decomposition of Azobisisobutyronitrile (AIBN)

Moukhina, Thermochemica Acta 621(2015) 25-35

# When model-free methods do not work?

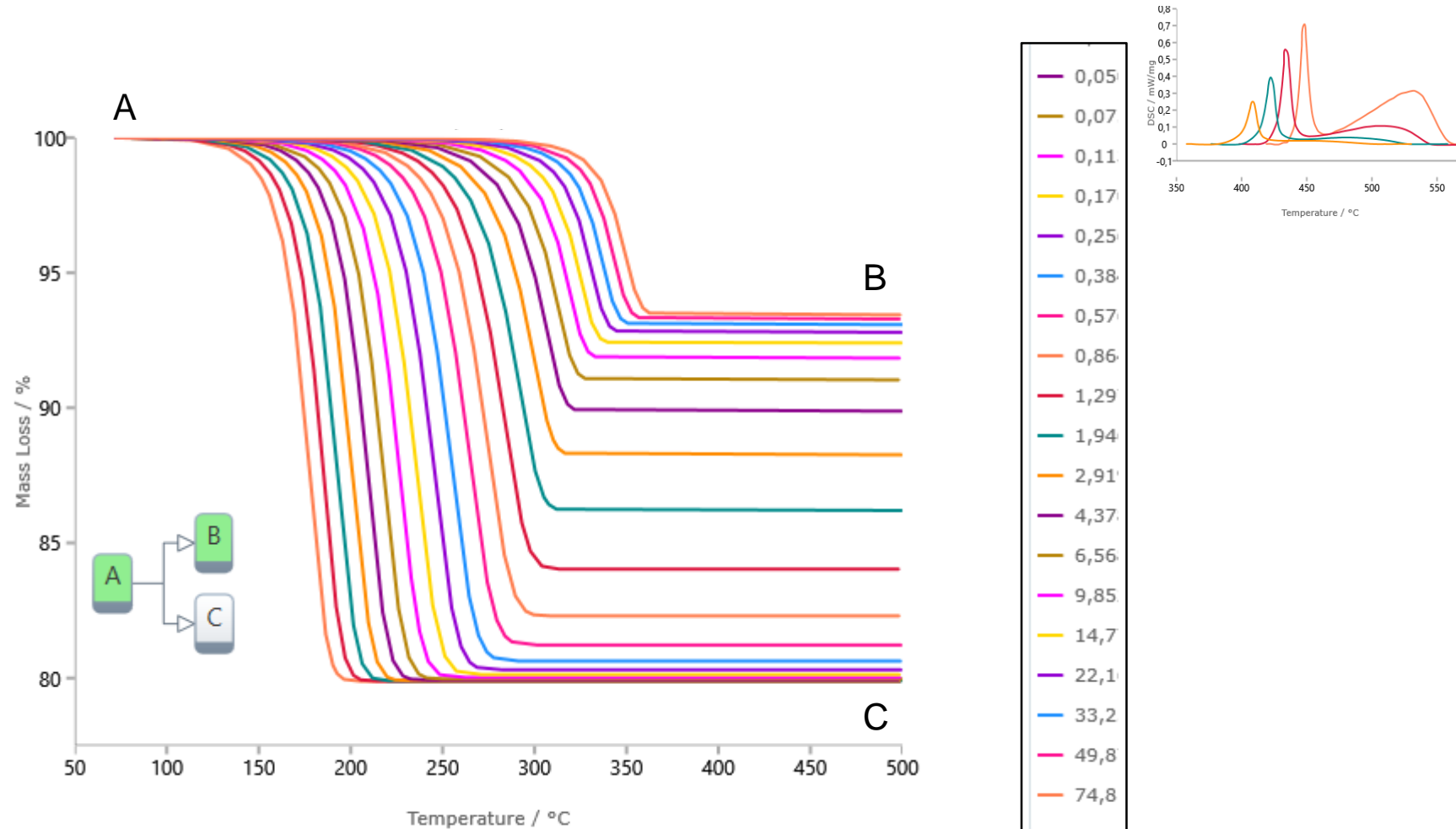
## Example: kinetic mechanism changes at different conversion



Data from Fait, Moukhina, Thermochimica Acta, 637 (2016) 38-50

# When model-free methods do not work?

## Example: competitive steps

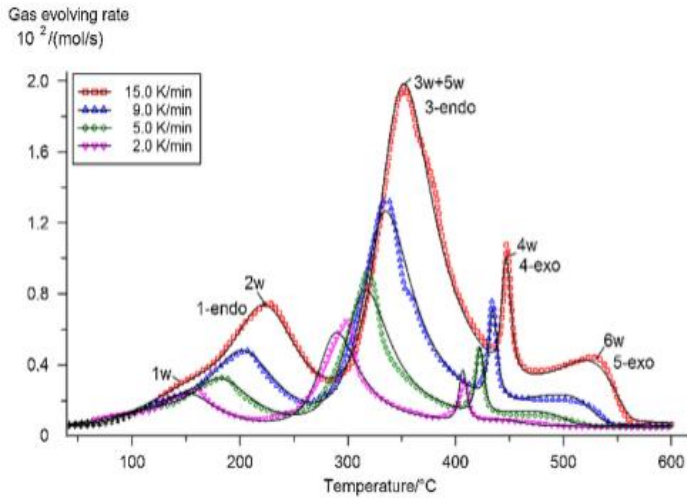


Total effect depends on the heating rate

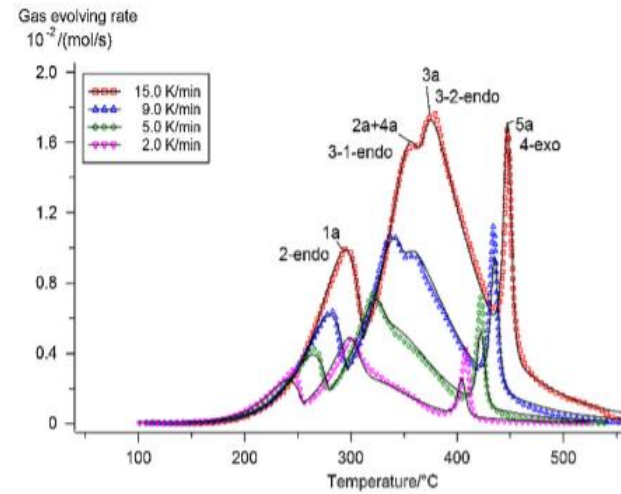


- Modelling
  - unlimited number of models
  - unlimited number of reaction steps
  - individual steps are linked as independent, parallel, competing or following
  - Visual creation of a kinetic model
  - Visual adding, removing or editing of each reaction step.
  - Visual adjustment of position and contribution of each step.
  - Optimization of kinetic parameters for one individual step.
  - Optimization of kinetic parameters for the complete kinetic model.
- Reaction types
  - Reaction of 1st, 2nd and n-th order without autocatalysis
  - Reaction of 1st, 2nd and n-th order with autocatalysis including Prout-Tompkins and Kamal-Sourour reactions
  - 2-/3-dim. phase boundary reactions
  - 1-/2-/3-dim. diffusion (Jander's type and Ginstling-Brounstein)
  - 2-/3-/n-dim. nucleation according to Avrami
  - Curing Reactions with diffusion control (using Di Benedetto model or splines for dependence Tg vs Alpha)
  - Crystallization according to the Nakamura equation using the Hoffman-Lauritzen Theory

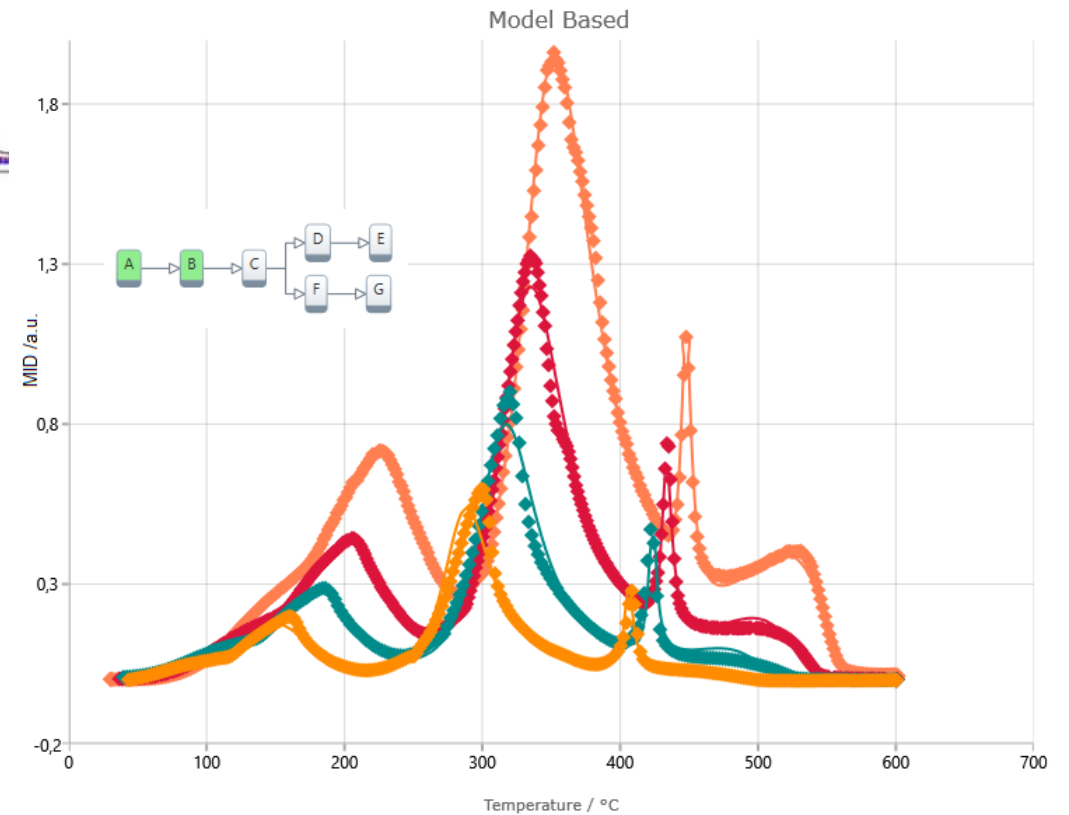
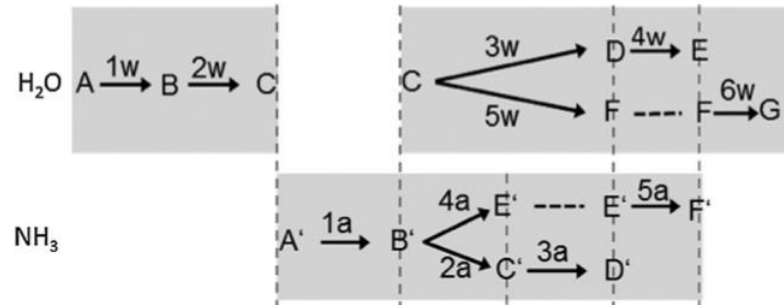
# Model-based analysis: Ammonium paratungstate tetrahydrate, MS decomposition curves



MS curves for water



MS curves for ammonia



M.J.G. Fait, Elena Moukhina, et al. Thermochimica Acta 637 (2016) 38–50

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Predictions

- Isothermal predictions Predictions for several isothermal temperatures
- Isothermal lifetime predictions Predictions for given conversion at several isothermal temperatures
- Dynamic prediction Predictions for several heating rates for reactions or for several cooling rates for crystallization
- Multi-step prediction Prediction for a user-defined sequence of dynamic and isothermal segments with the possibility of export/import of multi-step program to/from text file
- Step-iso prediction Prediction of a step-iso temperature program, representing a stepwise temperature increase
- Modulated predictions Prediction of a modulated temperature program which is the sum of an underlying constant temperature or constant heating and a sinus-shaped temperature oscillation
- Adiabatic prediction Calculation of the adiabatic temperature increase for various initial temperatures.
- TTT diagram Time-Temperature-Transition diagram for reactions with diffusion control.

- Measurement output (signal)
- Conversion
- Conversion rate
- Concentration for each reactant (model-based)
- Reaction rate for each reaction step (model-based)

The simulated values can be presented:

- Curves as a function of time or temperature
- Table with simulated values, time and temperature