

Analyzing & Testing

NETZSCH

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Kinetic Methods for TD24 in Thermal Risk Assessment of Chemical Processes

Webinar
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02/07/2023

1. Introduction. What is necessary to know and why?
2. Definitions
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 - 2.2 Thermal Risk: primary and secondary reactions
 - 2.3 What is TD24? Why it is important?
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1. Introduction.

What is necessary to know and why?



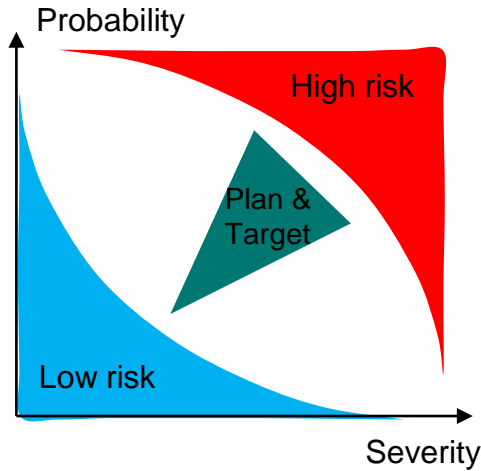
- New materials,
- colors,
- Textiles
- Pharmaceuticals
- Nitration reactions
- Fine chemicals

- Manufacture
- Transportation
- Storage



- Fire
- Explosion
- Economic loss
- **Injuries and deaths**

The core of risk assessment: Severity and probability



$$Risk = Severity * Probability$$

Example assessment criteria for the probability.

Category	Frequency
Frequent	Several times in a week
Moderate	Once or twice a month
Occasional	Several times a year
Remote	Once a year
Unlikely	Once in 10 years
Almost impossible	Once in 100 years or more

Example assessment criteria for the severity.

Category	1. Negligible	2. Marginal	3. Critical	4. Catastrophic
Life/health in company	Injury, ambulant treatment	Injury requiring hospitalization	Injury with long-term disability	Fatality
Business continuity	Not affected	Production stopped over 1 week	Delivery to customers must be interrupted several weeks	Business interruption more than 1 month

- Physical properties :boiling, melting, ...
- Chemical properties: stability, ignition, sensitivity to light, air, water
- Toxicity: toxic and cancirogenic materials
- Ecotoxicity
- Fire and Explosion data: combustion, self-sustaining decomposition
- Chemical interactions: undesired reactions

- Thermal effects
 - Heat of reaction → DSC,ARC
 - Heat capacity → DSC
 - Melting and evaporation enthalpy → DSC
 - Adiabatic temperature rise → DSC, ARC
 - Dependence of reaction rate on temperature → Kinetic analysis:
TMR approximation,
Kinetics Neo
 - Heat removal: cooling
- Pressure effects
 - Gas release
 - Vapor pressure
- Thermal Analysis

$$\text{Risk} = \text{Severity} * \text{Probability}$$

Temperature scale

Time scale

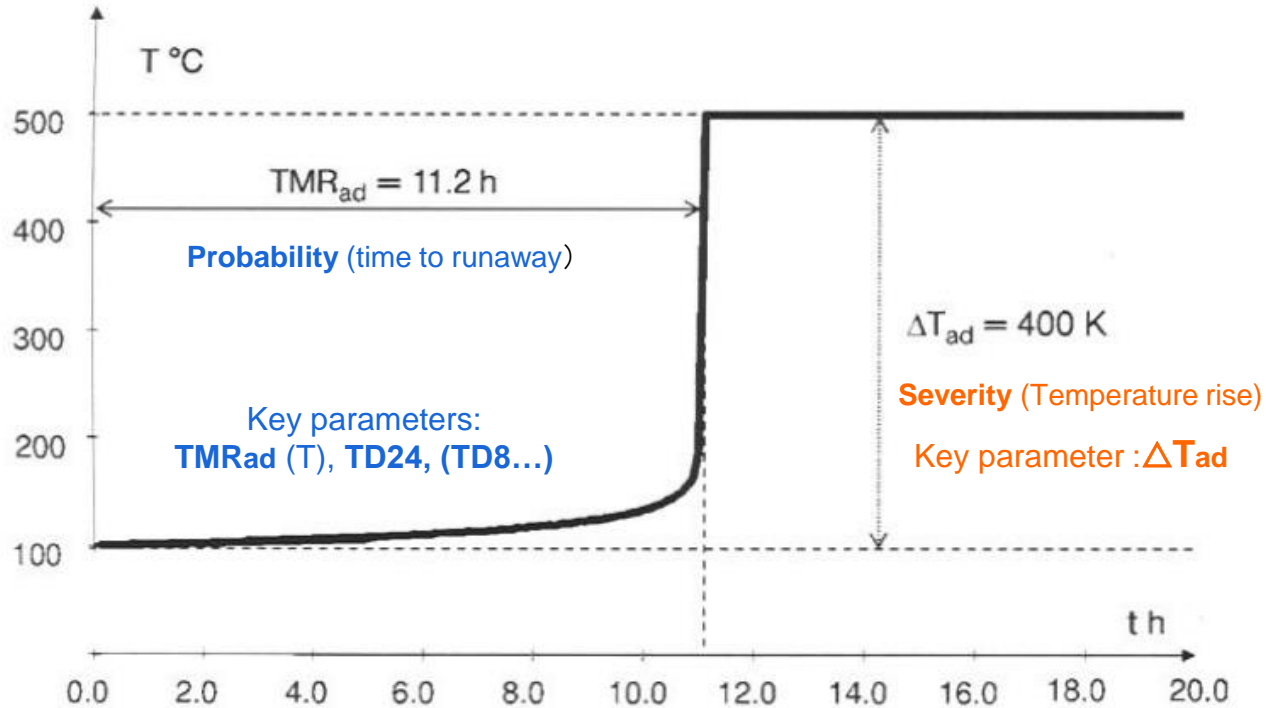
Assesment criteria for severity of a runaway reaction

Simplified	Extended	ΔT_{ad} (K)	Order of magnitude of Q' kJ kg ⁻¹
High	Catastrophic	>400	>800
	Critical	200–400	400–800
Medium	Medium	50–100	100–400
Low	Negligible	<50 and no pressure	<100

Assesment criteria for probability of a runaway reaction

Simplified	Extended	TMR_{ad} (h)
High	Frequent	<1
	Probable	1–8
Medium	Occasional	8–24
Low	Seldom	24–50
	Remote	50–100
	Almost impossible	>100

$$\text{Risk} = \text{Severity} * \text{Probability}$$





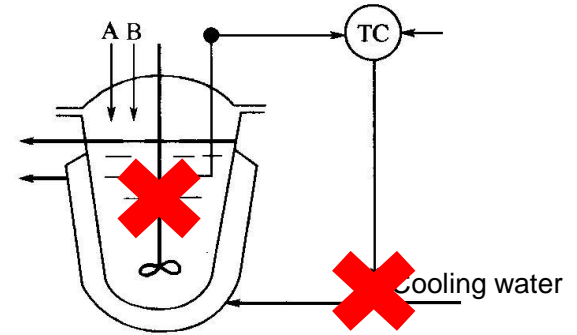
2. Definitions

- a) **Characteristic temperatures of the process:
Tp, MTSR, TMR, MTT**
- b) **Primary and secondary reactions**
- c) **What is TD24? Why it is important?**

■ Normal process :

Heat: **generation** = **removal** + accumulation + loss

➡ Temperature of reaction is under control



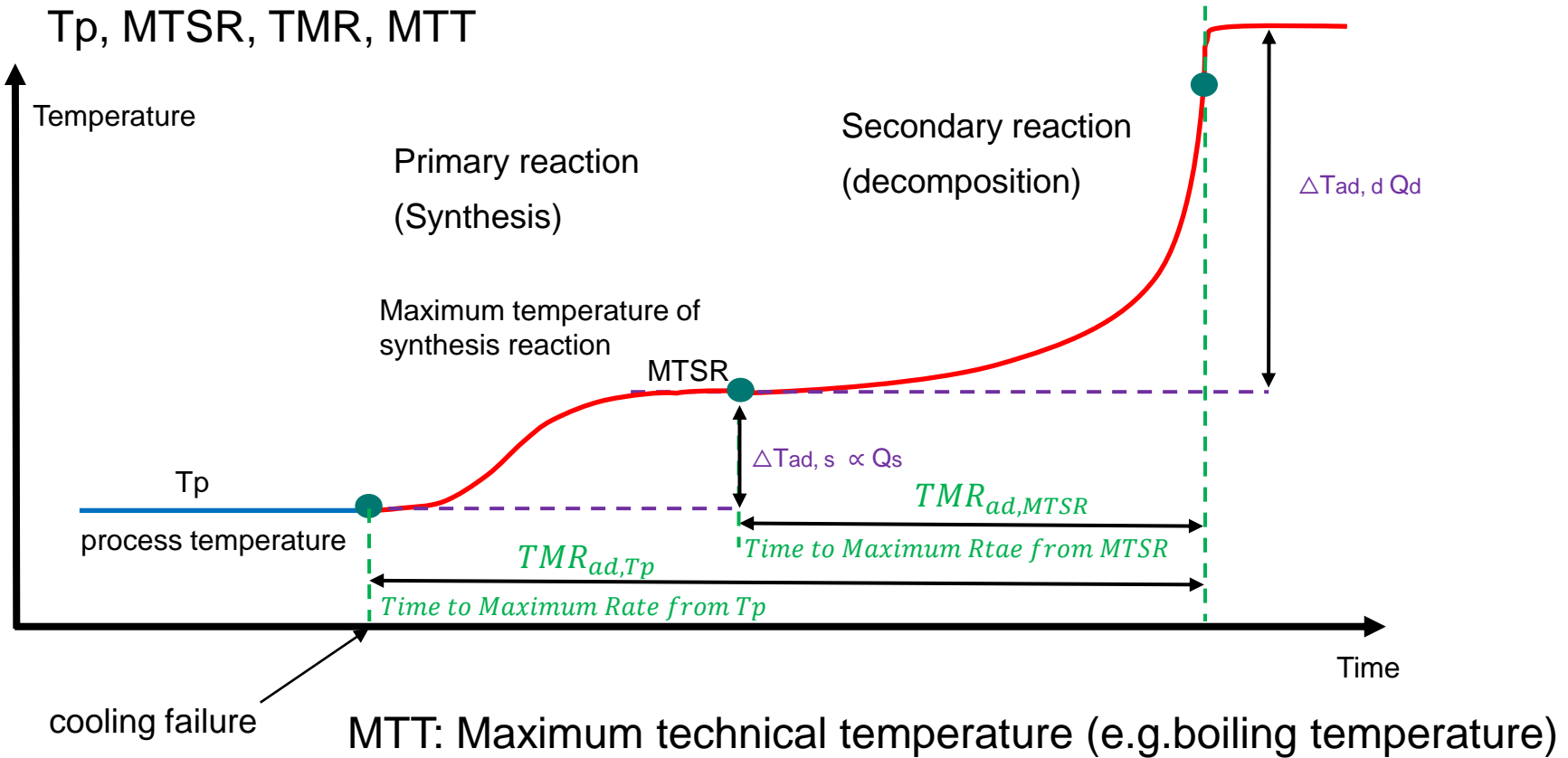
■ Thermal runaway :

Heat: **generation** = ~~removal~~ + accumulation + loss

➡ Temperature rise ➡ Self-accelerating

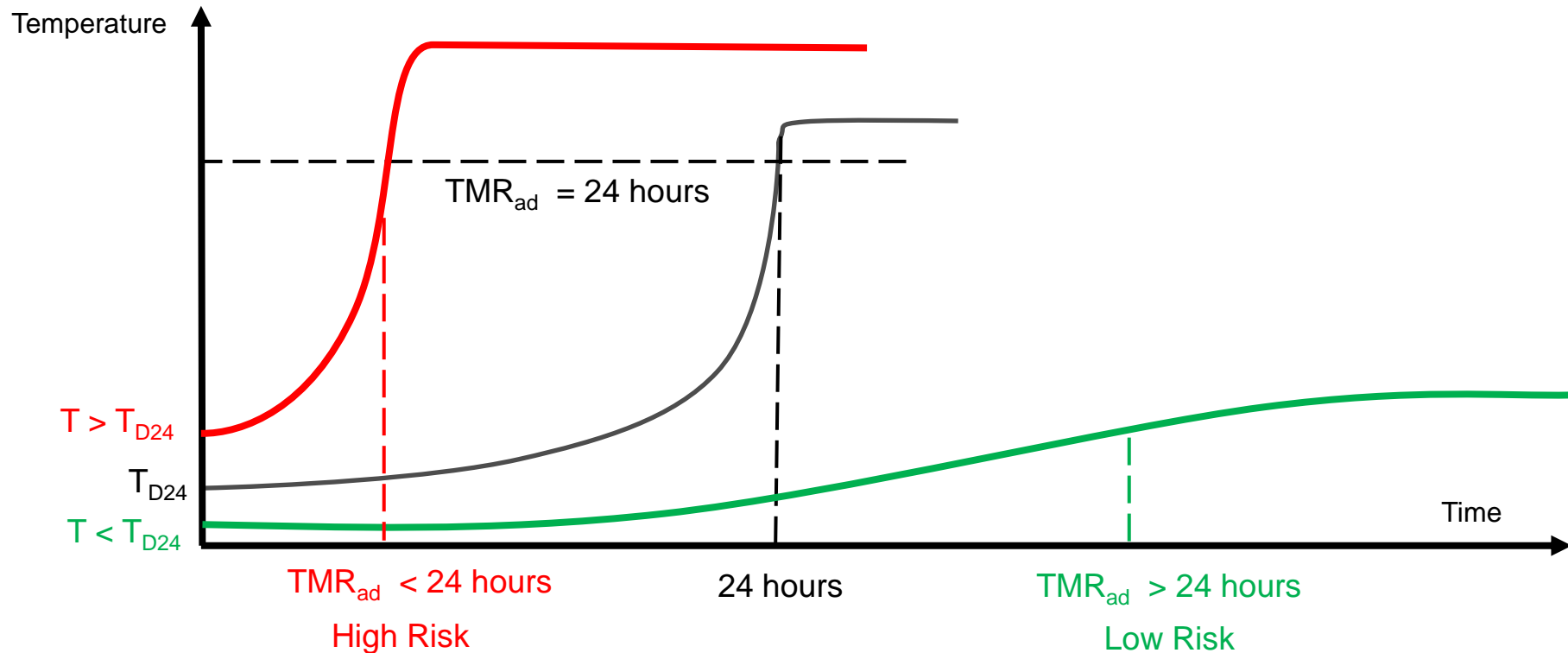


Thermal Risk for cooling failure scenario: primary and secondary reactions

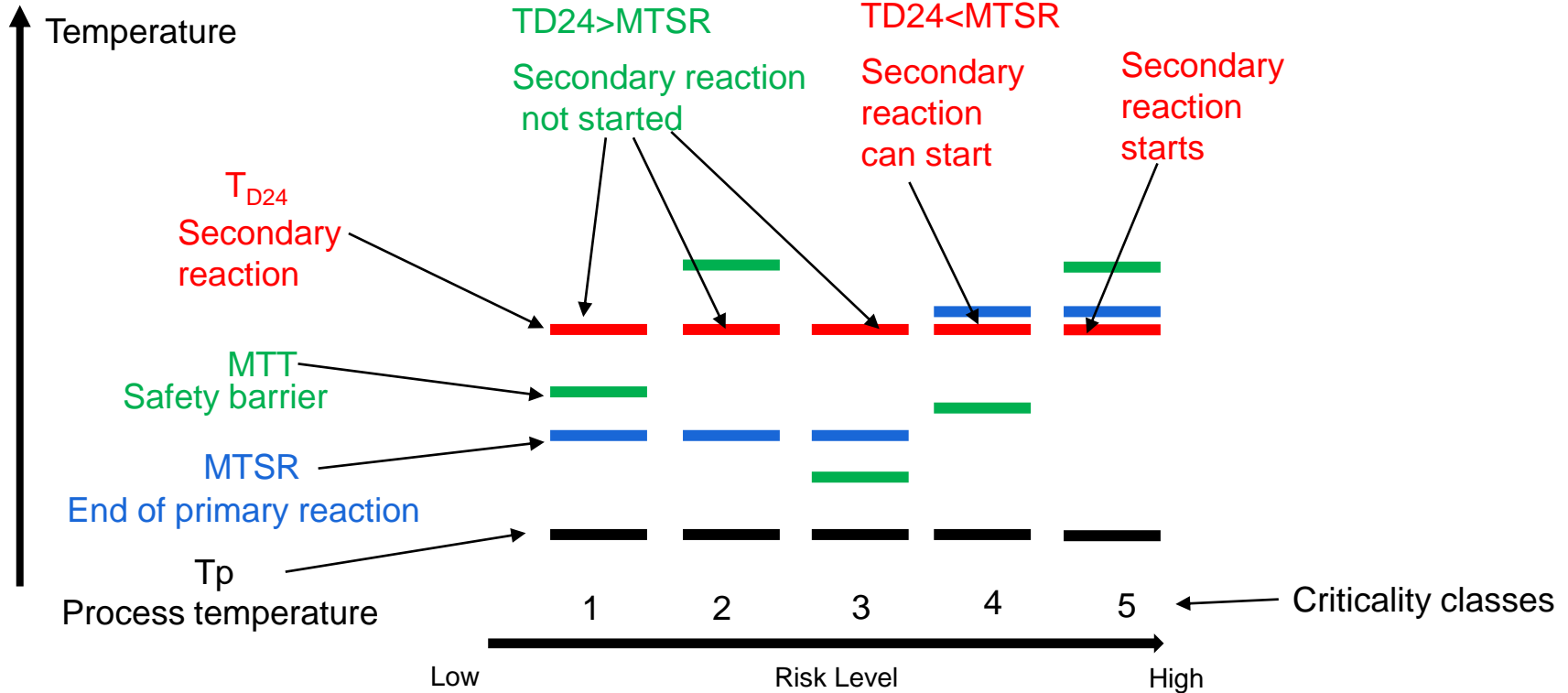


Time To Maximum Rate (TMR) and T_{D24}

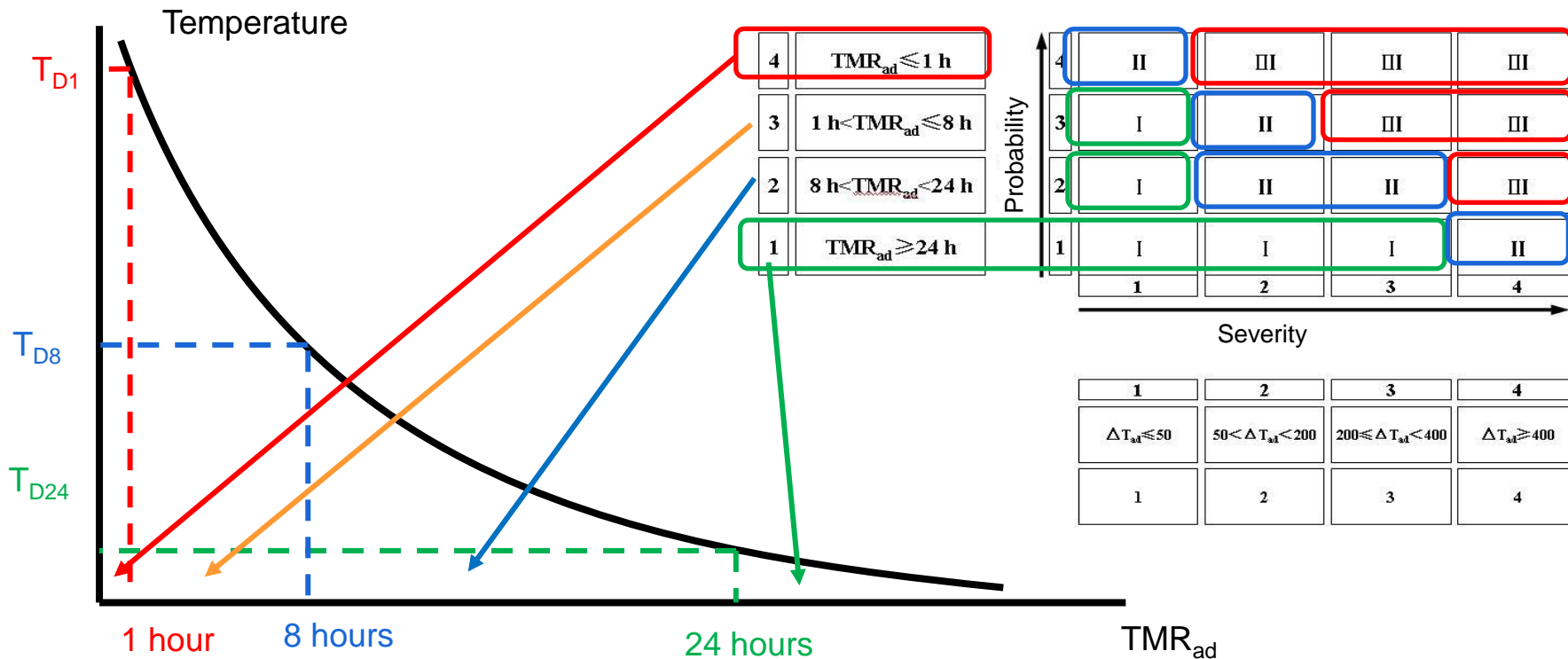
T_{D24} is the **temperature** at which **time to maximum reaction rate** is 24 HOURS.



Some common methods for thermal risk assessment



Why TD24 is important?



TD24 is calculated mostly for secondary/decomposition reaction, but sometimes also for synthesis reaction, depending on the sample type (raw material, or synthesis product) and reaction process.



3. Kinetic Methods of calculation TD24 offered by NETZSCH

- a) Linear TMR Extrapolation**
- b) Non-Linear TMR Extrapolation**
- c) Advances kinetics by Kinetics Neo Software**

Methods for TD24

$$\frac{d\alpha}{dt} = A \cdot f(\alpha) \cdot K(T)$$

Unknown reaction type,
Several reaction steps

For known reaction type

Single-curve

Multi-curve analysis

One ARC experiment

Several experiments
Unknown reactions and steps

Linear TMR

Data: ARC

Approximation:
Zero-order reaction

Non-linear TMR

Data: ARC

Approximation:
n-th order reaction

Kinetics Neo

Data: DSC

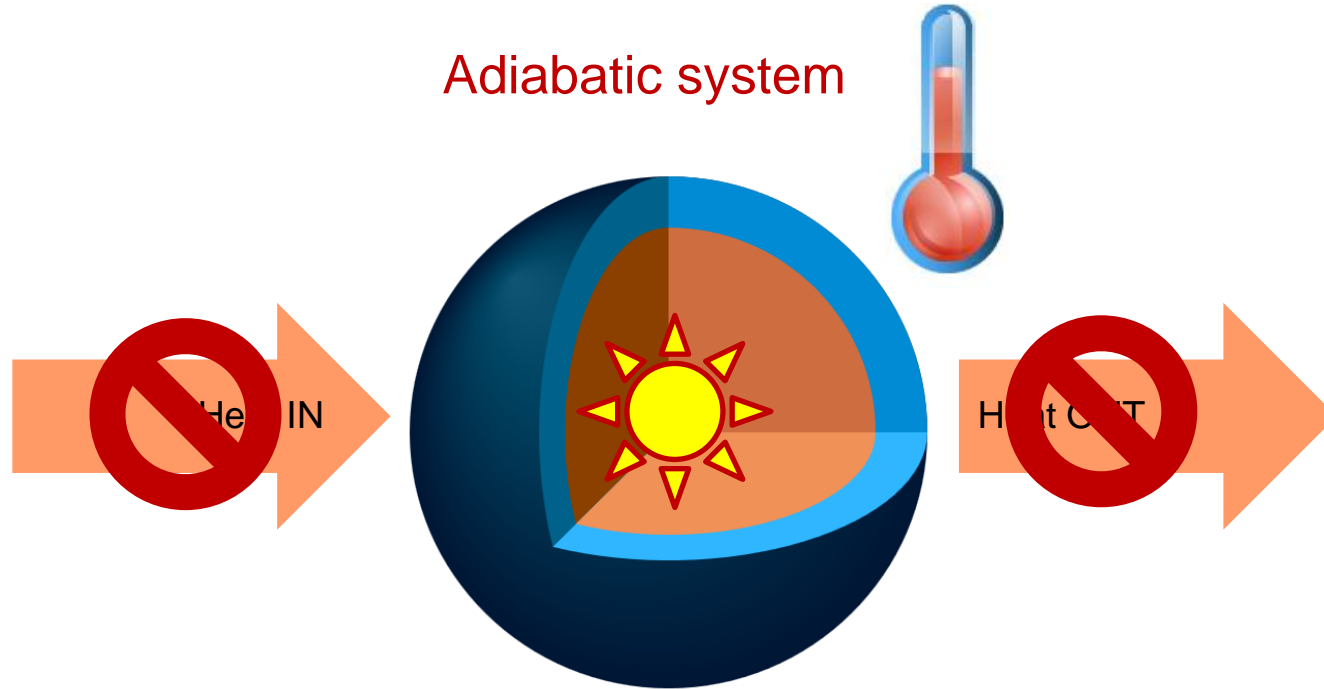
Kinetics Neo

Data: ARC

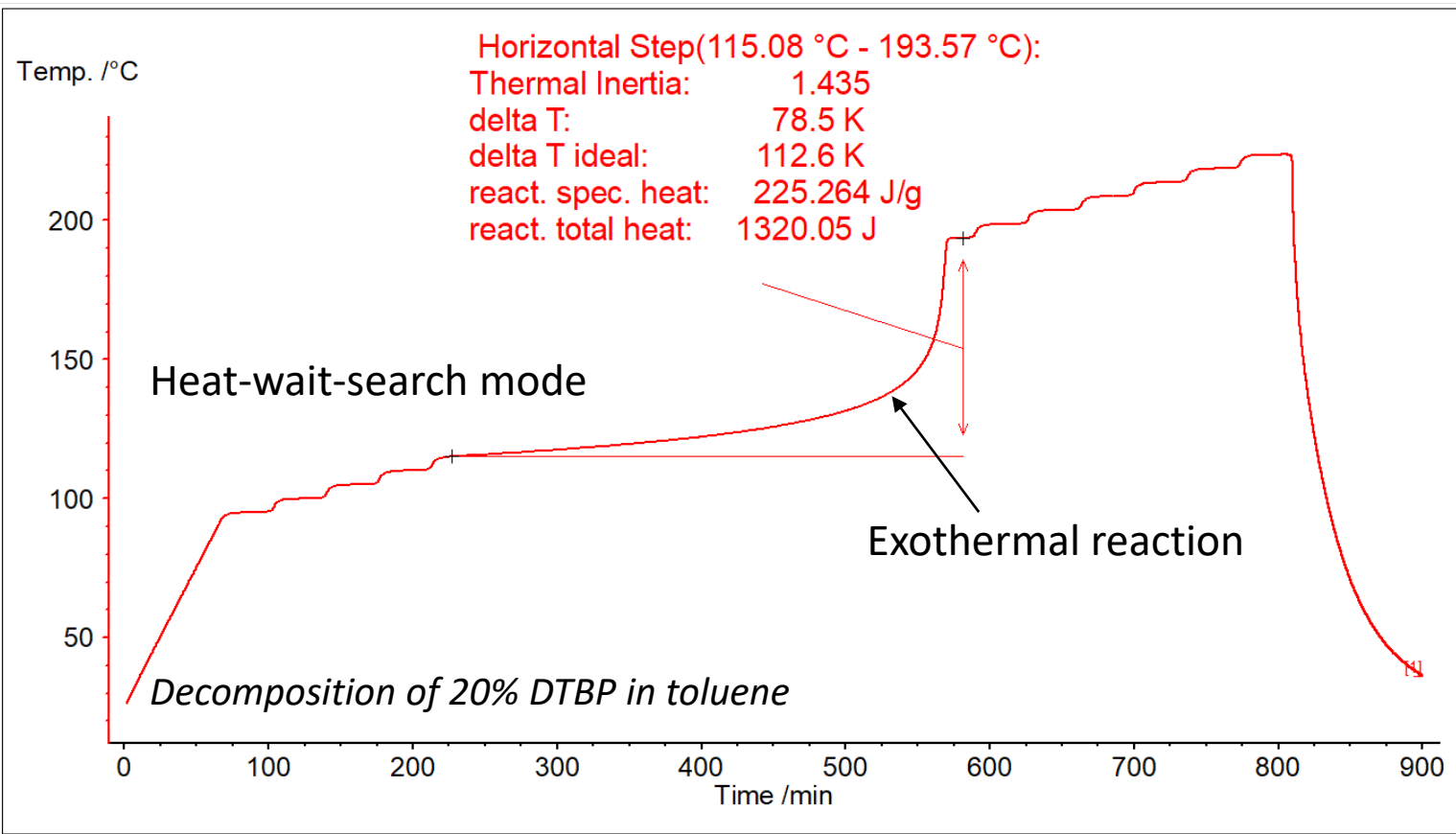


ARC® 244





Temperature increase because of exothermal reaction



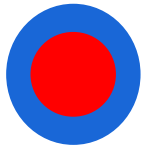
Thermal inertia Φ



Only reactant

Heating of reactant only:

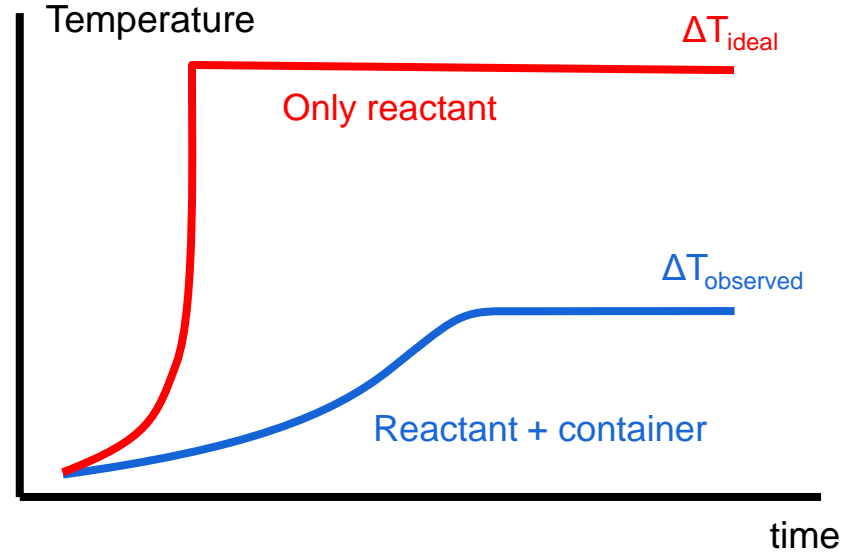
$$Q = m_{\text{sample}} C_{p,\text{sample}} \Delta T_{\text{ideal}}$$



Reactant in container

Heating of reactant with container

$$Q = (m_{\text{sample}} C_{p,\text{sample}} + m_{\text{bomb}} C_{p,\text{bomb}}) \Delta T_{\text{observed}}$$



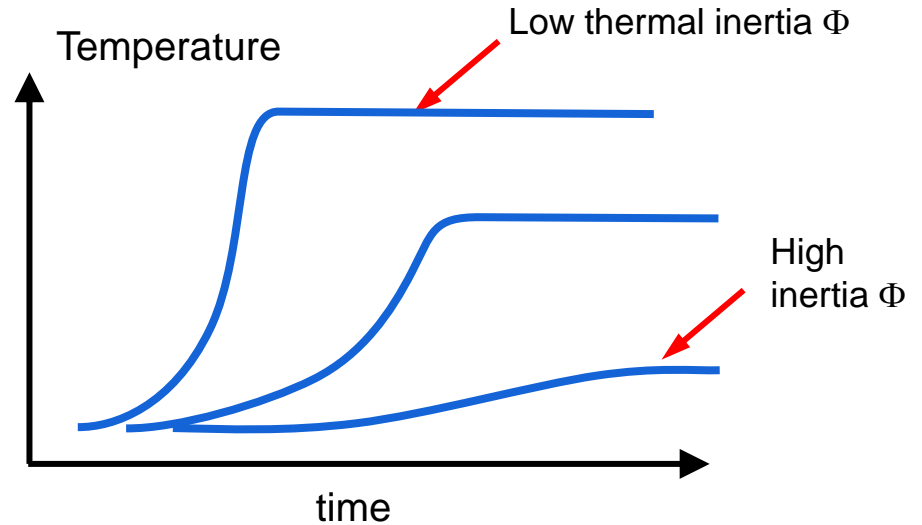
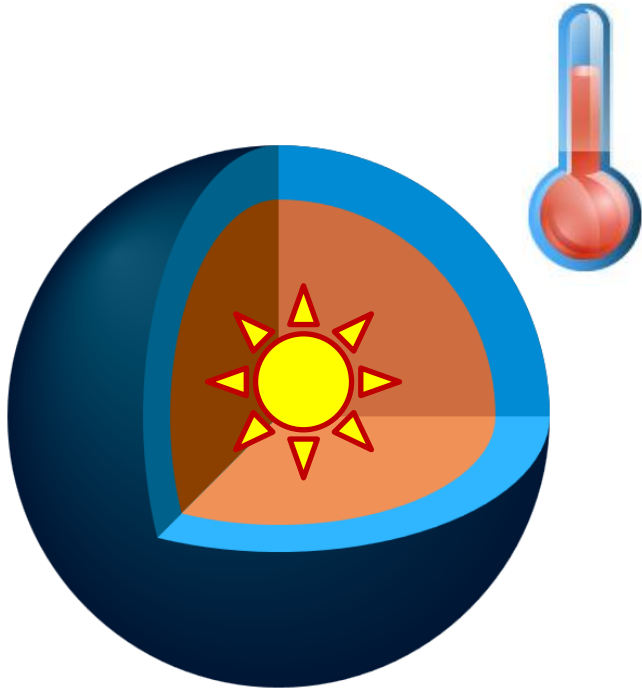
Formula for thermal inertia (Φ -factor) according to ASTM E1981:

$$\Phi = \frac{(m_s \cdot C_{p,s} + m_c \cdot C_{p,c})}{m_s \cdot C_{p,s}}$$

$$\Phi = 1 + \frac{m_c \cdot C_{p,c}}{m_s \cdot C_{p,s}}$$

m_c = mass of the container
 $C_{p,c}$ = heat capacity of the container
 m_s = mass of the sample
 $C_{p,s}$ = heat capacity of the sample

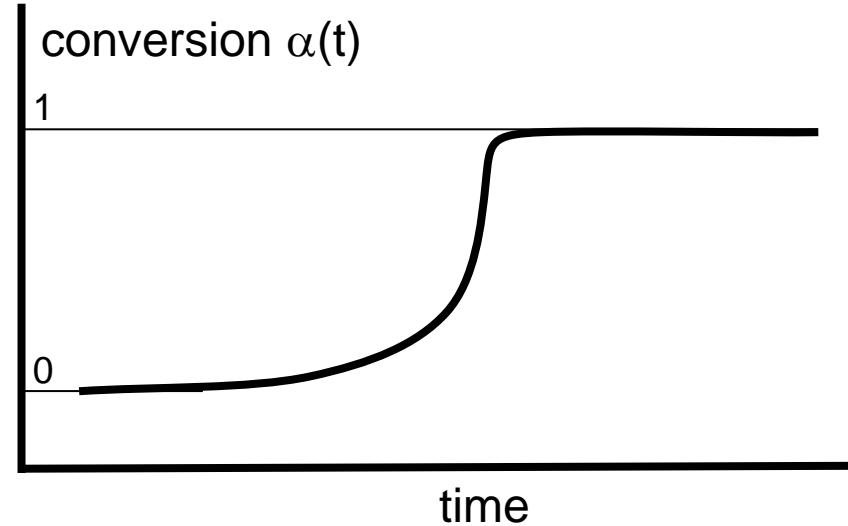
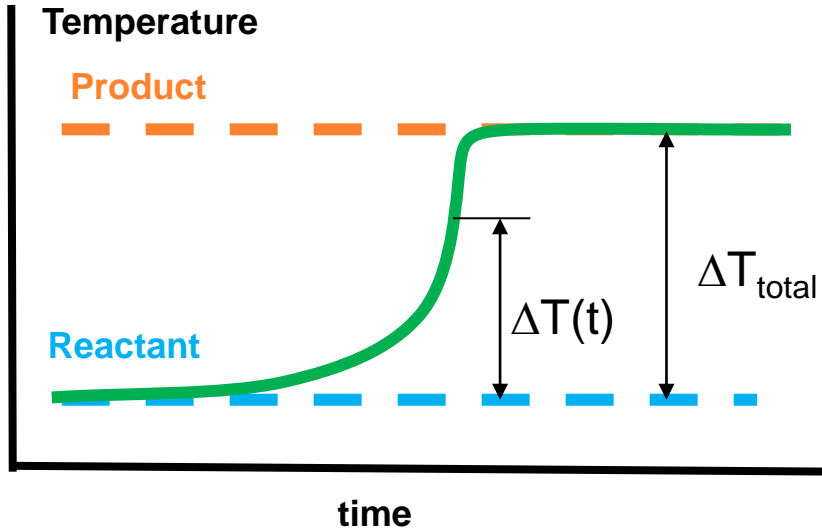
Measurements for kinetic analysis: Accelerating Reaction Calorimetry



Accelerating Reaction Calorimetry: temperature change is measured during self-heating

Degree of conversion $\alpha(t)$ for ARC data (extent of conversion, conversion, extent of reaction)

Commonly denoted by α and defined as the ratio of the partial to total change of a physical property.



$$\alpha(t) = \frac{\Delta T(t)}{\Delta T_{total}}$$

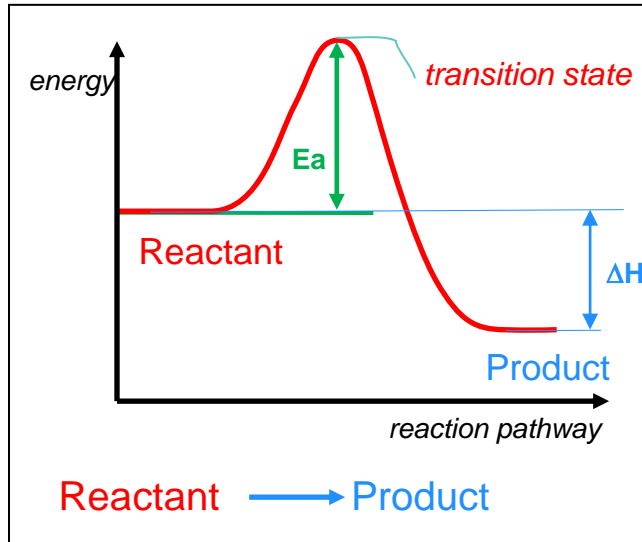
$\alpha=0$

before reaction start

$\alpha=1$

after reaction end

ARC: Conversion is the ratio of the partial temperature increase at given time point to the total temperature increase at the final time point



$$\frac{d\alpha}{dt} = A \cdot f(\alpha) \cdot K(T)$$

Arrhenius equation (1889) for reaction rate:

$$\frac{d\alpha}{dt} = A \cdot f(\alpha) \cdot \exp(-E_a/RT)$$

Pre-exponential factor [1/s]

Reaction type: (nth order, autocatalysis, nucleation)

Activation energy [kJ/mol]

As temperature rises, the reaction rate increases exponentially!

Heat balance:

$$Cp \cdot \Phi \cdot \frac{dT}{dt} = \Delta H \cdot A \cdot f(\alpha) \cdot \text{Exp} \left[\frac{-Ea}{RT} \right]$$

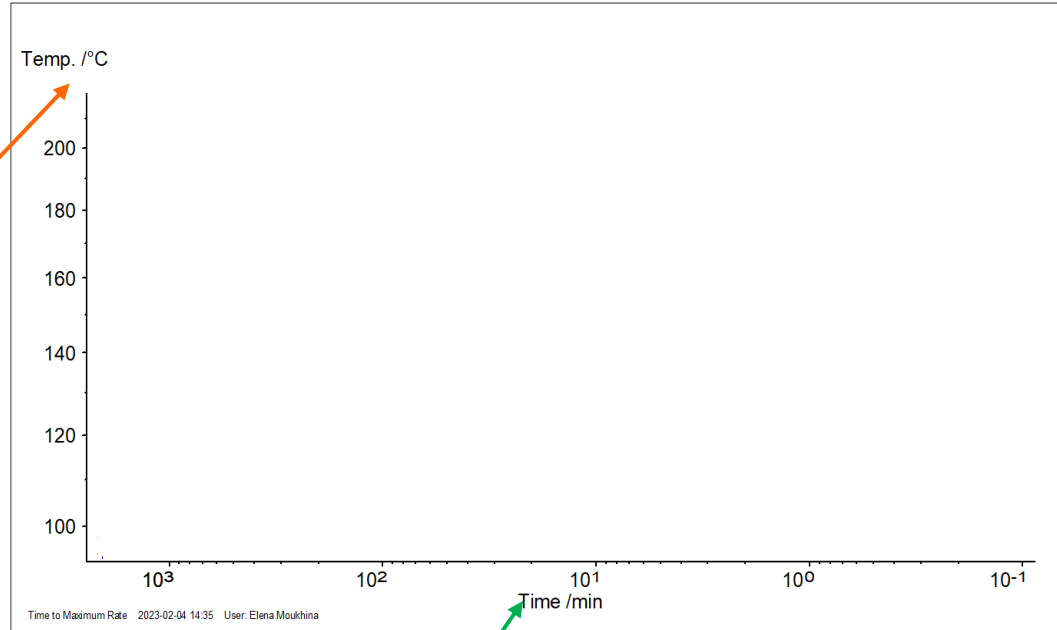
Linear approximation

Zero-order reaction
 $f(\alpha)=1$

$$\log(TMR) = \frac{Ea}{R} \frac{1}{T} + Const + \log \Phi$$

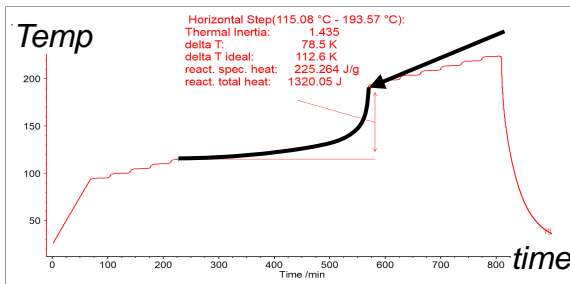


$-1/T$



TMR in logarithmic scale

Experimental data



$\Phi > 1$

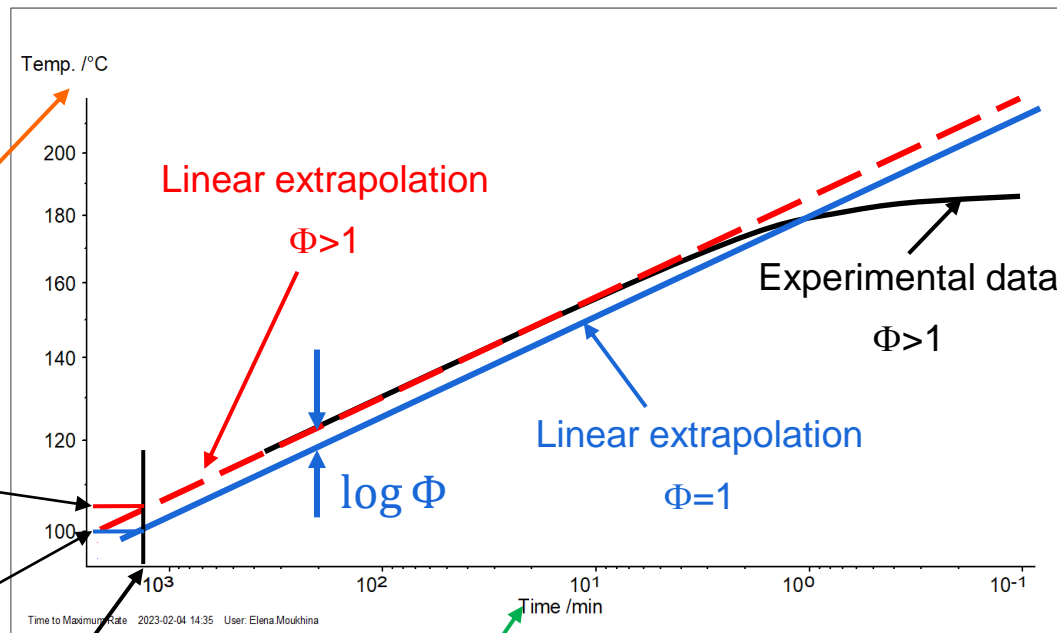
$-1/T$

$$\log(TMR) = \frac{Ea}{R} \frac{1}{T} + Const + \log \Phi$$

TD24=101.0°C

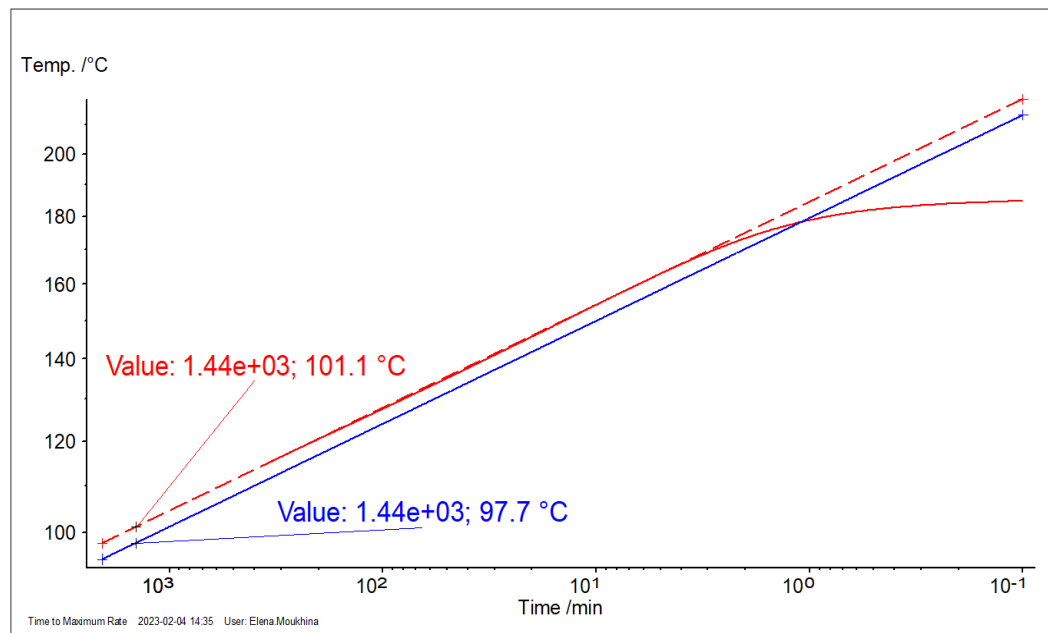
TD24=97.7°C

24h=1440 min



TMR in logarithmic scale

$$\log(TMR) = \frac{Ea}{R} \frac{1}{T} + Const + \log \Phi$$



NETZSCH Unique feature: Non-Linear TMR extrapolation for decomposition

Measured curve for Φ_1 has temperature step ΔT_1
and the following equation

$$\left(\frac{dT_1}{dt}\right)_{\Phi_1} = \Delta T_1 \cdot A(\alpha_1) \cdot f(\alpha_1) \cdot \exp\left(\frac{-E(\alpha_1)}{RT_1}\right)$$

We would like to recalculate to the new Φ_2
with temperature step ΔT_2 :

$$\left(\frac{dT_2}{dt}\right)_{\Phi_2} = \Delta T_2 \cdot A(\alpha_2) \cdot f(\alpha_2) \cdot \exp\left(\frac{-E(\alpha_2)}{RT_2}\right)$$

Recalculation of the measured temperature curve at Φ_1 to Φ_2 at the same conversion value:

$$\left(\frac{dT_2}{dt}\right)_{\Phi_2} = \left(\frac{dT_1}{dt}\right)_{\Phi_1} \cdot \frac{\Phi_1}{\Phi_2} \cdot \exp\left(\frac{-E(\alpha)}{R} \left(\frac{1}{T_2} - \frac{1}{T_1}\right)\right)$$

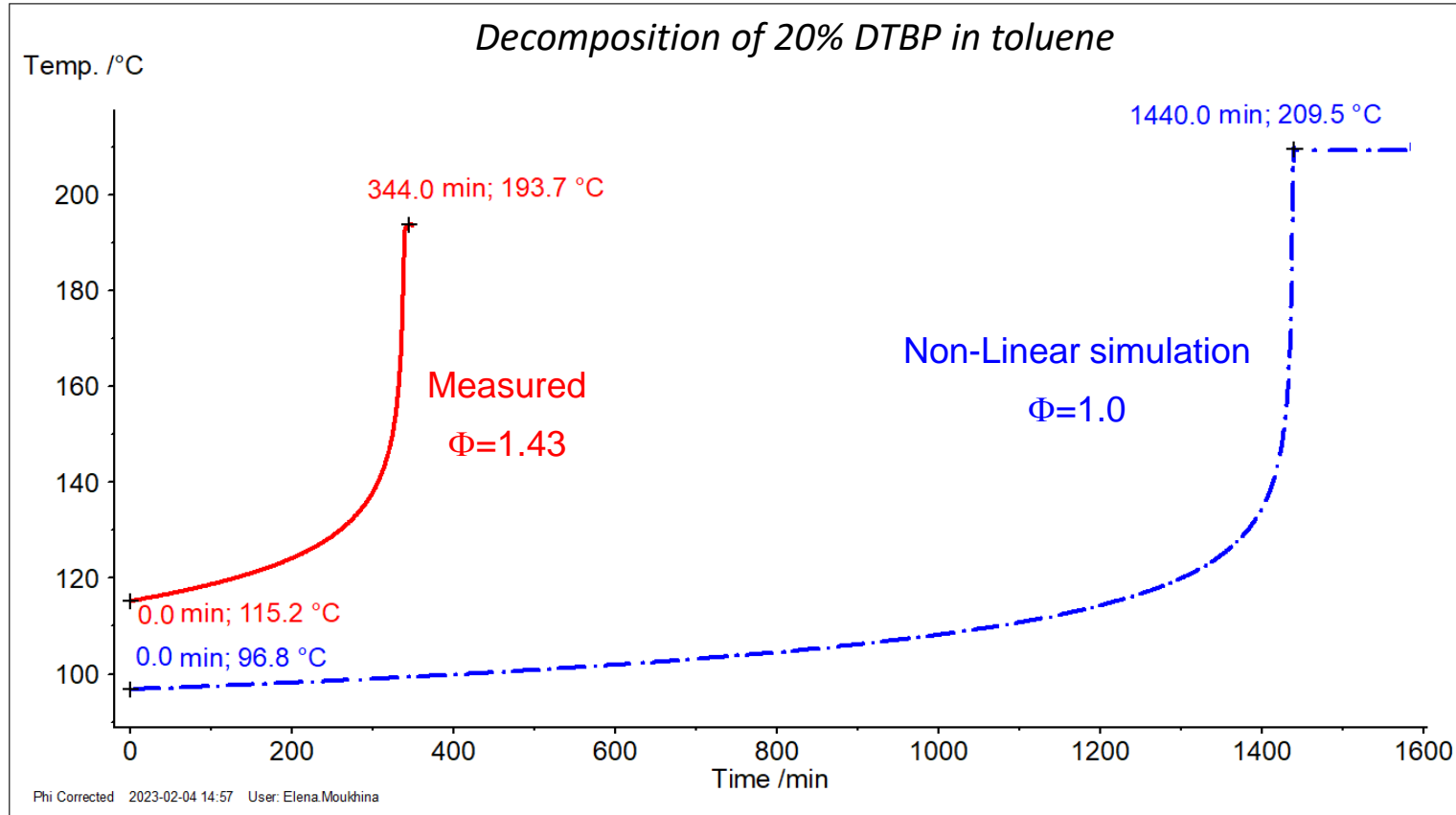
Isoconversional method is used, where the points of the same conversion are taken into account.

Main assumption: activation energy is the same for whole process.

Reaction type and pre-exponent are not important for this isoconversional method.

This method ensures the accuracy for whole range and makes prediction possible.

Unique feature: Non-Linear TMR extrapolation for decomposition



Linear TMR approximation:

- It's based on zero-order simplification which is only valid for low-conversion regions, so the line on high-conversion region makes no sense.
- Some minor items are discarded during mathematical deduction, so the result is not so accurate.

Non-linear TMR approximation:

- The assumption for activation energy: E_a is constant for the whole process.
- The assumption of process begin as the n-th order reaction is used only for obtaining E_a from the first few points.
- No simplification for reaction type, result is more accurate.

$$\frac{d\alpha}{dt} = A \cdot f(\alpha) \cdot K(T)$$

Unknown reaction type,
Several reaction steps

Multi-curve analysis

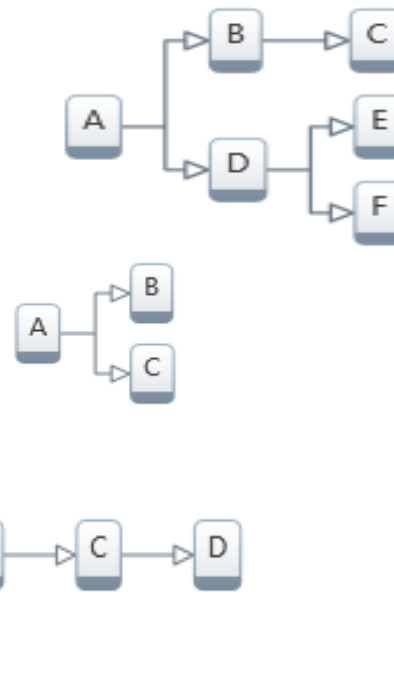
Several experiments
Unknown reactions and steps

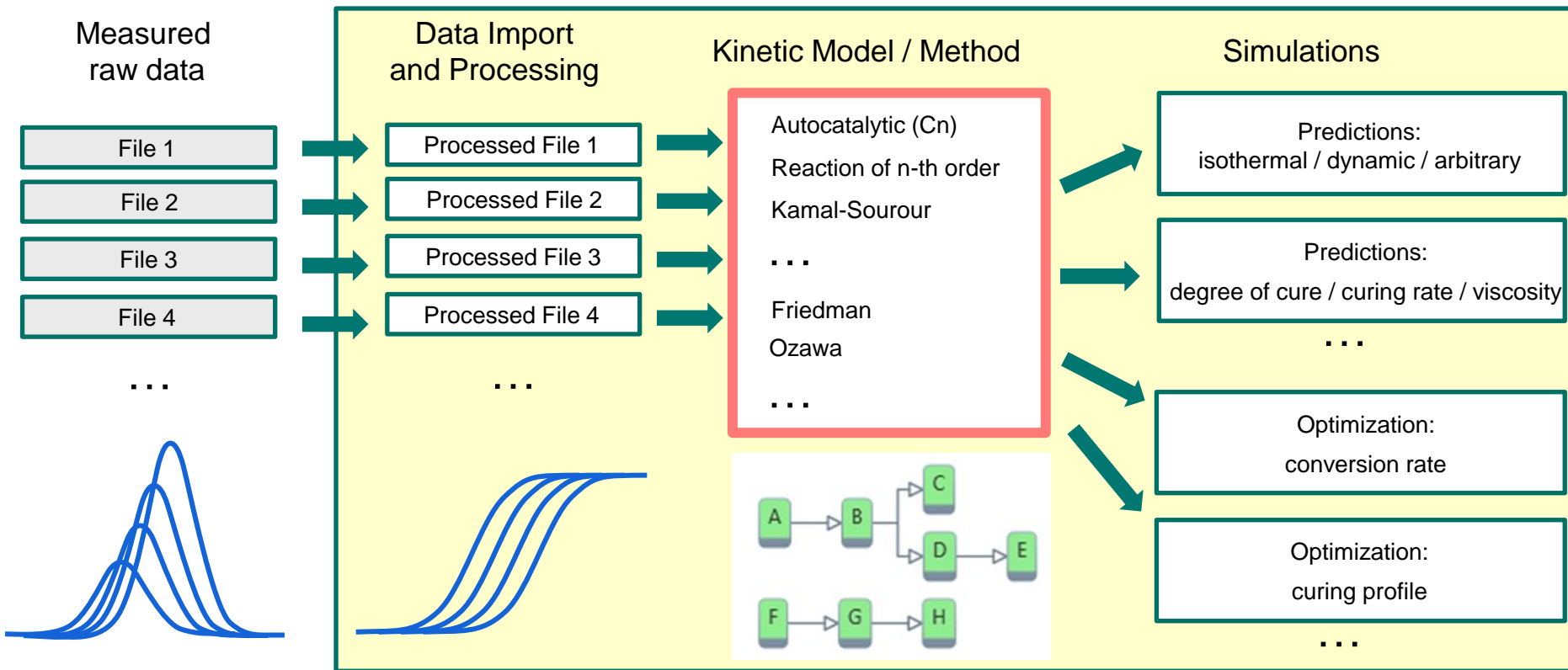
Kinetics Neo

Data: DSC

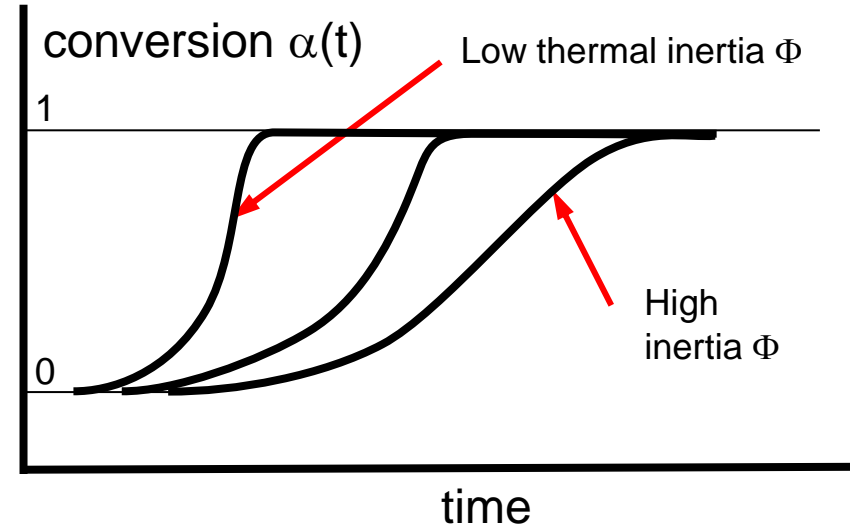
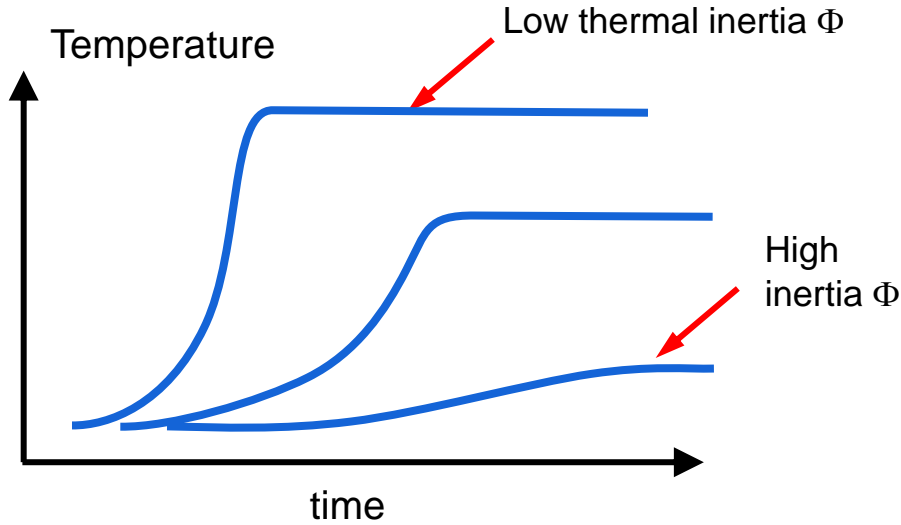
Kinetics Neo

Data: ARC





Degree of conversion for kinetic analysis: Accelerating Reaction Calorimetry

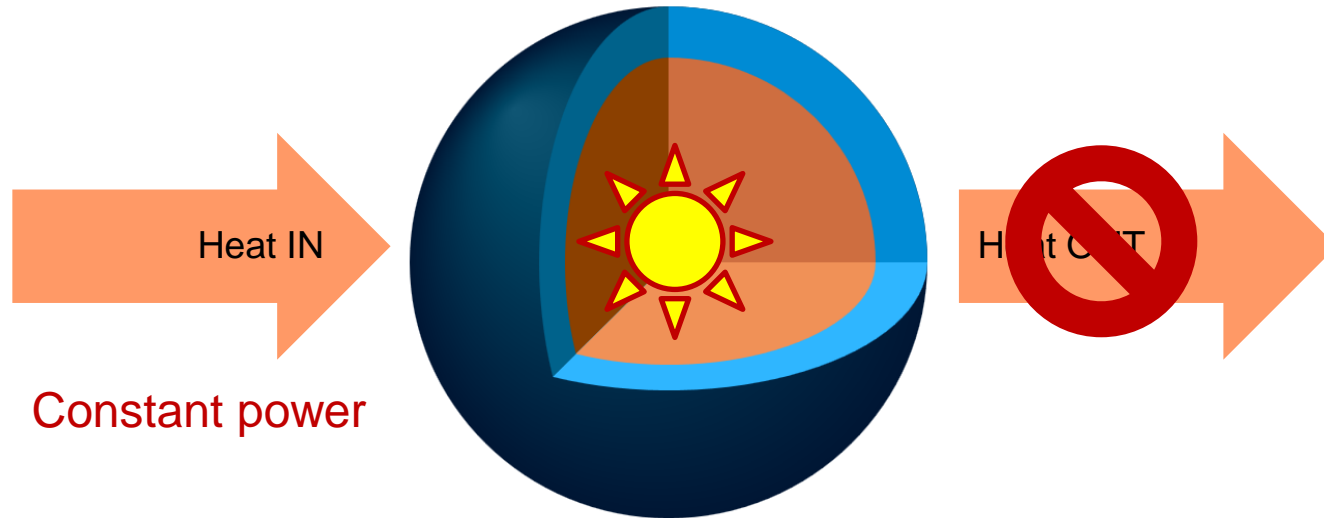


How to change Φ ?

For unknown reaction the ratio between reactant mass and container mass should be different

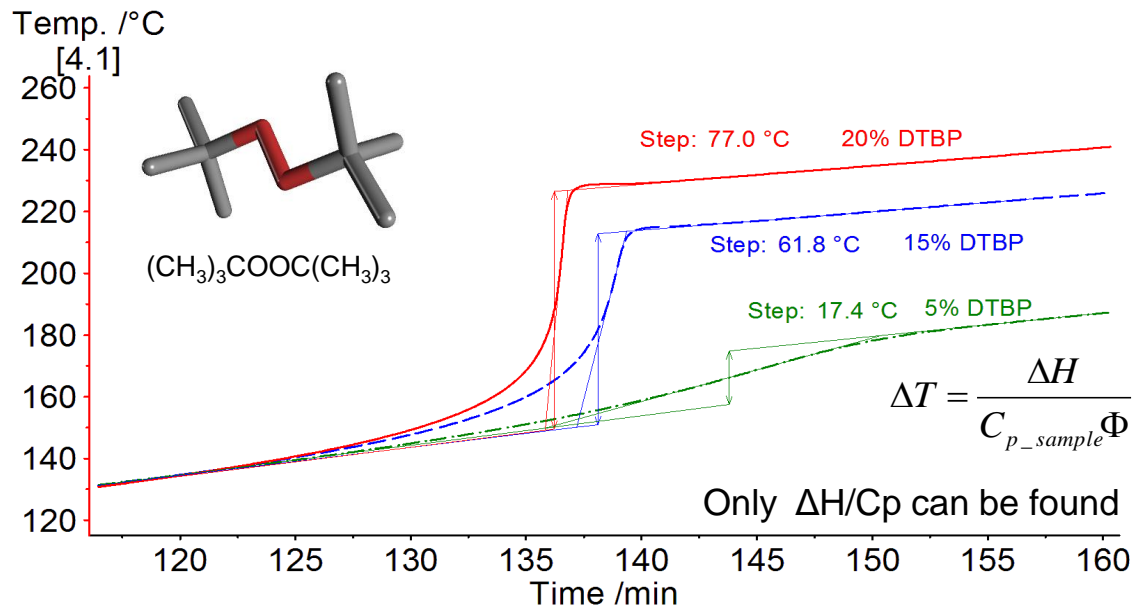
Only for first-order reaction type the solution with solvent can be measured. Solvent increases thermal inertia

Adiabatic system with constant power input



Temperature increase because of exothermal reaction and constant power input

Reaction causes the step on temperature curve

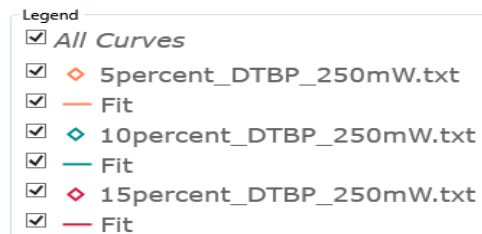
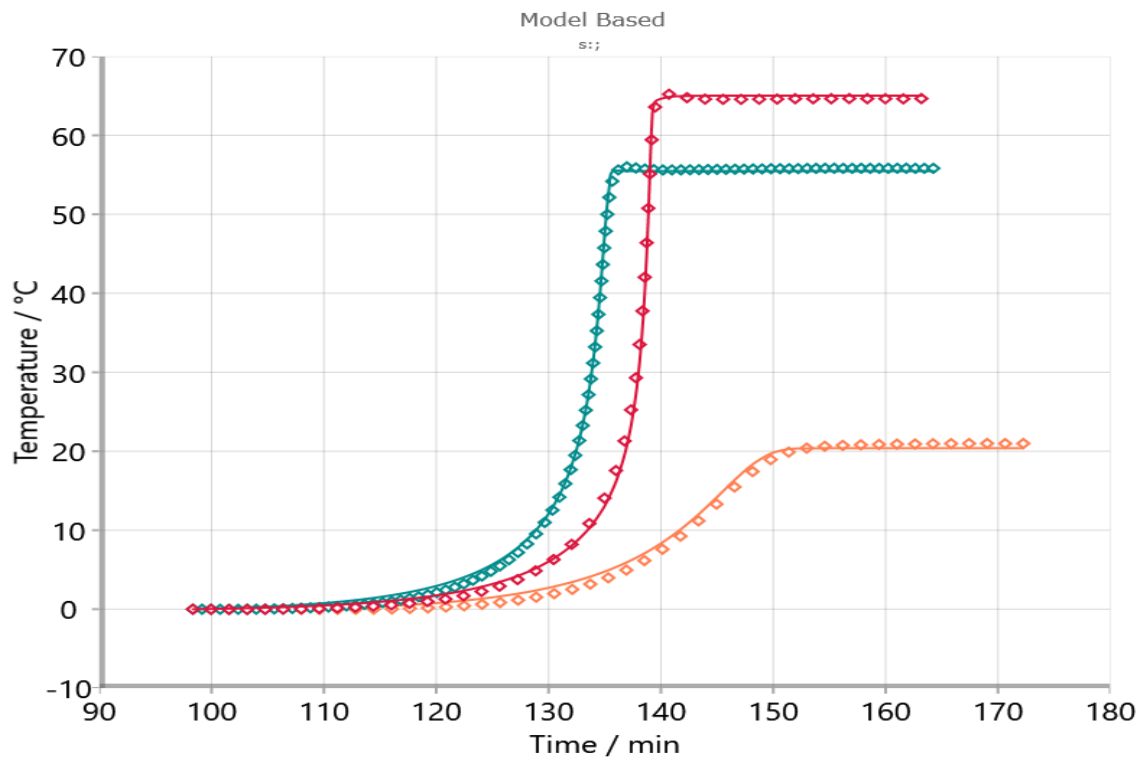


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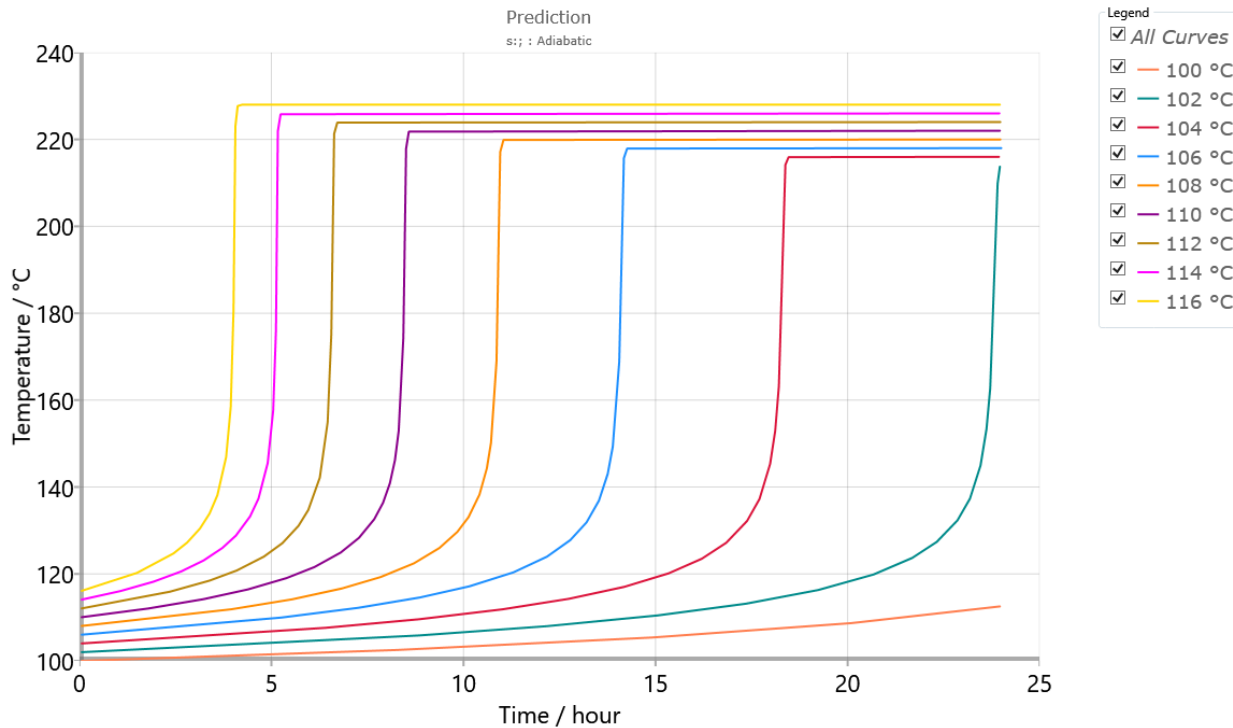
Temperature rise with different concentrations of di-tert-butyl peroxid (DTBP) in toluene

Acceleration rate calorimeter ARC 254 in VaryPhi mode with the constant underlying power 250mW.

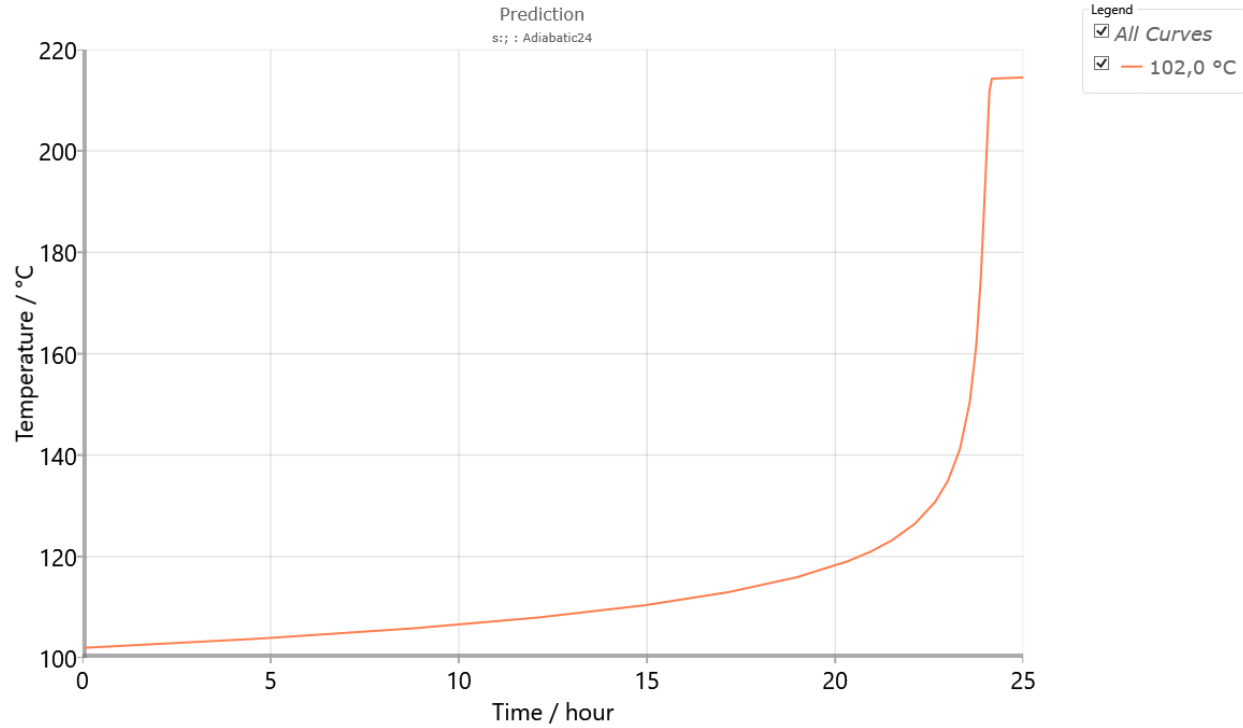
One kinetic model for all three experiments

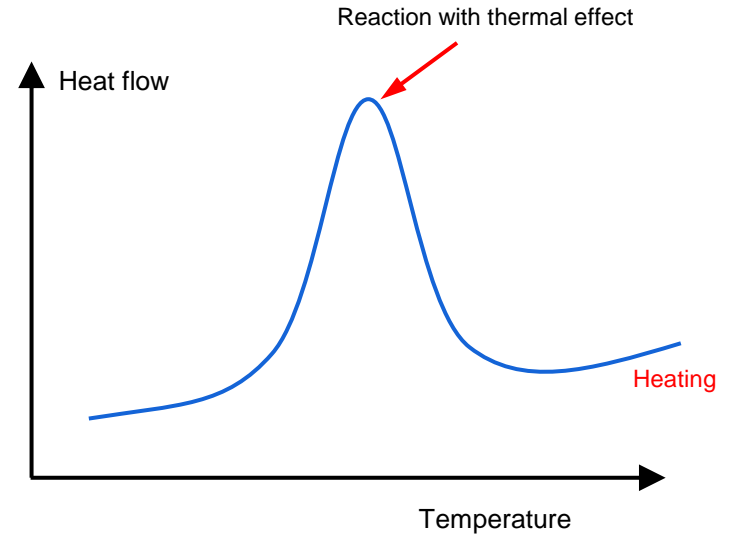
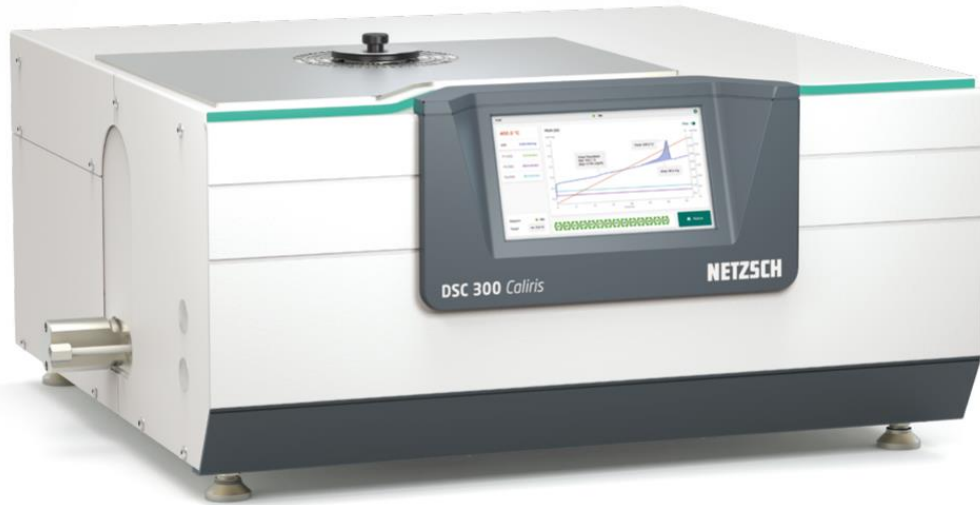


Simulation of adiabatic self-heating at different temperatures for $\Phi=1.0$

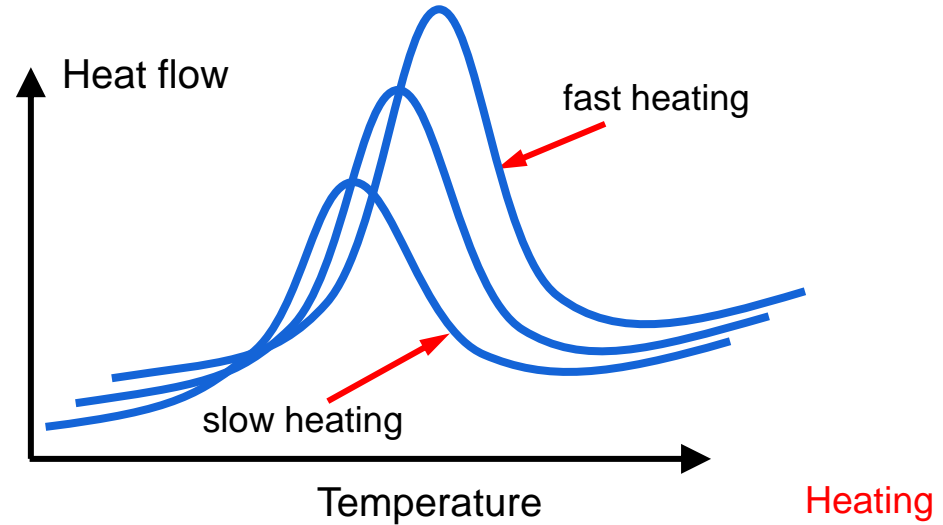


Calculation of T_{D24} for $\Phi=1.0$ and simulation of adiabatic self-heating at this temperature

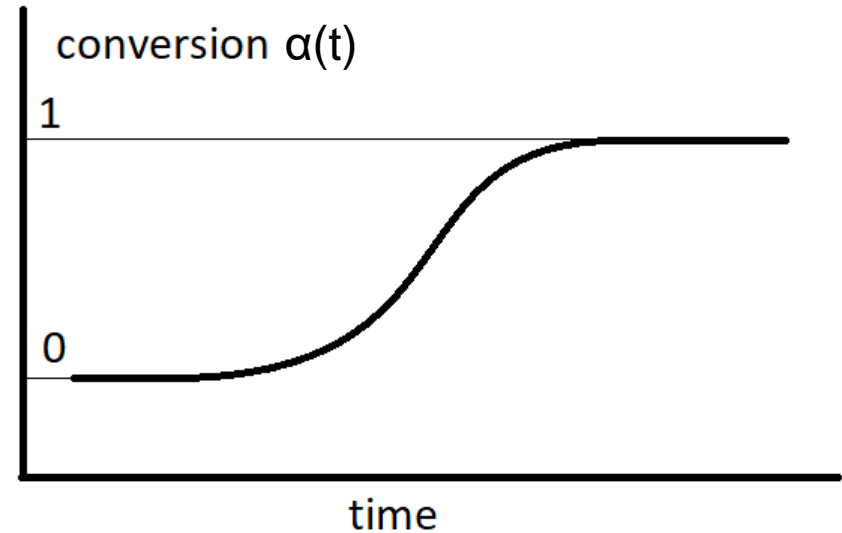
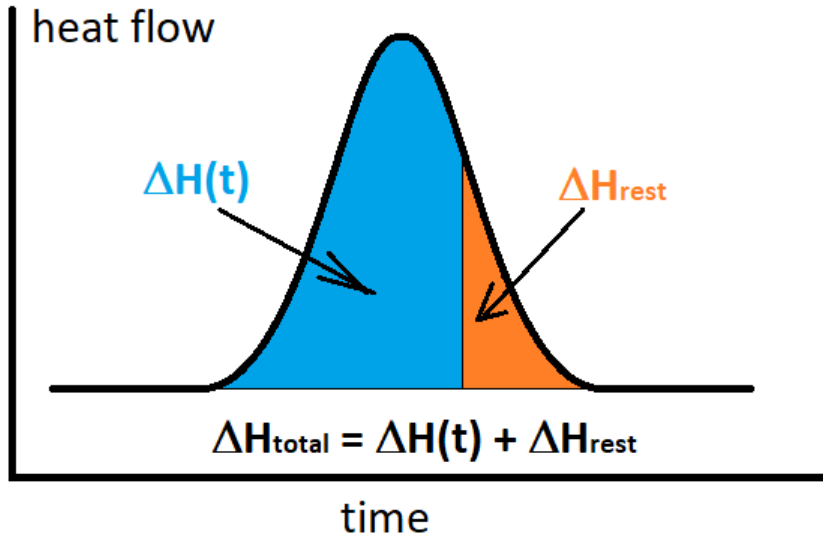




Measurements for kinetic analysis: Differential scanning calorimetry



Differential scanning calorimetry: heat flow is measured during temperature



$$\alpha(t) = \frac{\Delta H(t)}{\Delta H_{total}}$$

DSC: Conversion is the ratio of the partial enthalpy change at given time point to the total enthalpy change at the final time point

Arrhenius equation

$$\frac{d\alpha}{dt} = A \cdot f(\alpha) \cdot \exp\left(\frac{-E_A}{RT}\right)$$

Reaction of **n-th order** is typical for decomposition

$$F_n \quad \frac{d\alpha}{dt} = A \cdot (1 - \alpha)^n \cdot \exp\left(\frac{-E_a}{RT}\right)$$

Chemical process is **generally** described by Arrhenius equation:

$$\frac{d\alpha}{dt} = A \cdot f(\alpha) \cdot \exp\left(\frac{-E_A}{RT}\right)$$

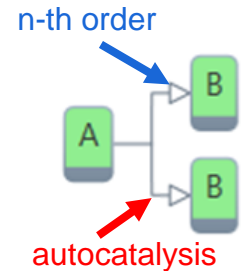
Bna – autocatalytical reaction of Prout-Tompkins

$$\frac{d\alpha}{dt} = A \cdot (1 - \alpha)^n \cdot \exp\left(\frac{-E_a}{RT}\right) \cdot \alpha^m$$



Curing can be described by the equation **Kamal-Sourour** for autocatalytic reaction:

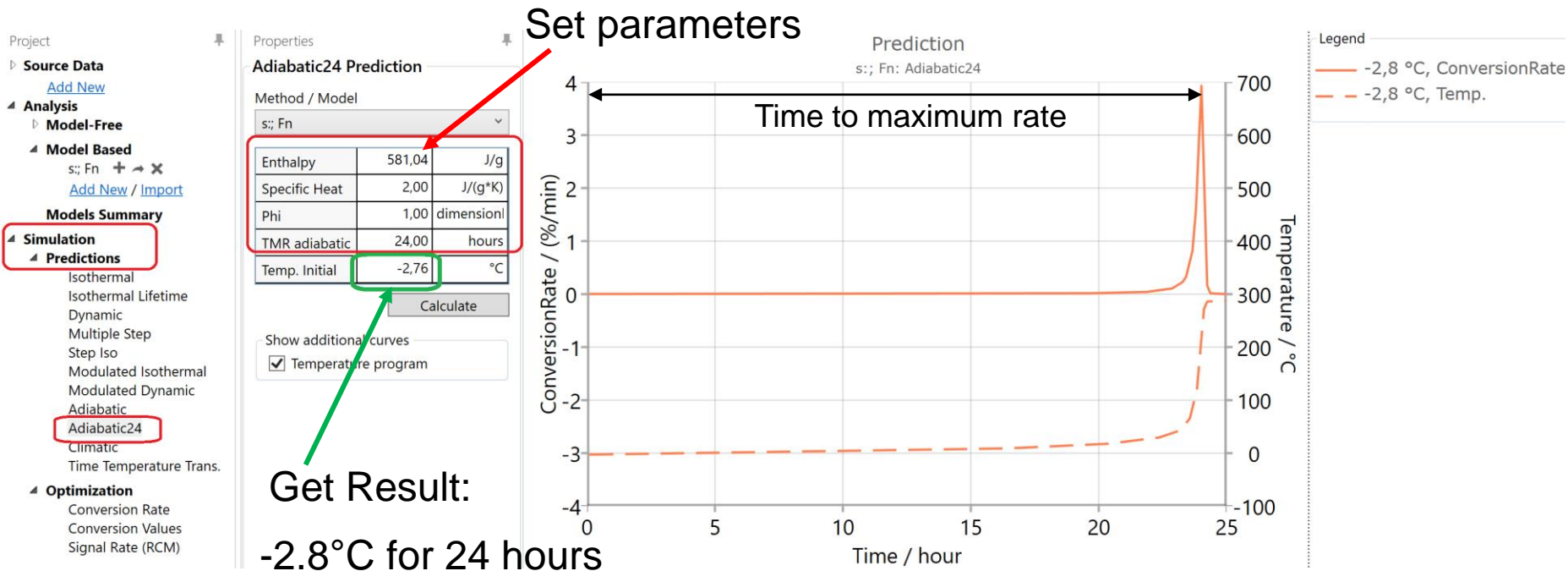
$$\frac{d\alpha}{dt} = \underbrace{A \cdot (1 - \alpha)^n \cdot \exp\left(\frac{-E_{a1}}{RT}\right)}_{\text{n-th order}} + \underbrace{A \cdot K \cdot (1 - \alpha)^n \cdot \alpha^m \cdot \exp\left(\frac{-E_{a2}}{RT}\right)}_{\text{autocatalysis}}$$



This **equation** with its parameters A , E_{a1} , n , E_{a2} , K , m , is the **kinetic model**.

Cyclopentadiene:

What is the initial temperature for TMR=24 hours for Phi=1.0?



■ Cyclopentadiene

- Can polymerise, but its main danger lies in its propensity to dimerise by the Diels-Alder reaction. This reaction takes place at a temperature starting at 0-40°C, under pressure. If the dimerisation is not controlled, the storage equipments' temperature and pressure rise very quickly, which leads to their destruction. Storage temperatures of -80°C have been recommended.

"The conversion occurs in hours at room temperature, but the monomer can be stored for days at -20 °C"

Hönicke, Dieter; Födisch, Ringo; Claus, Peter; Olson, Michael. "Cyclopentadiene and Cyclopentene". *Ullmann's Encyclopedia of Industrial Chemistry*. Weinheim: Wiley-VCH.

Methods for TD24

$$\frac{d\alpha}{dt} = A \cdot f(\alpha) \cdot K(T)$$

Unknown reaction type,
Several reaction steps

For known reaction type

Single-curve

Multi-curve analysis

One ARC experiment

Several experiments
Unknown reactions and steps

Linear TMR

Data: ARC

Approximation:
Zero-order reaction

Non-linear TMR

Data: ARC

Approximation:
n-th order reaction

Kinetics Neo

Data: DSC

Kinetics Neo

Data: ARC

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