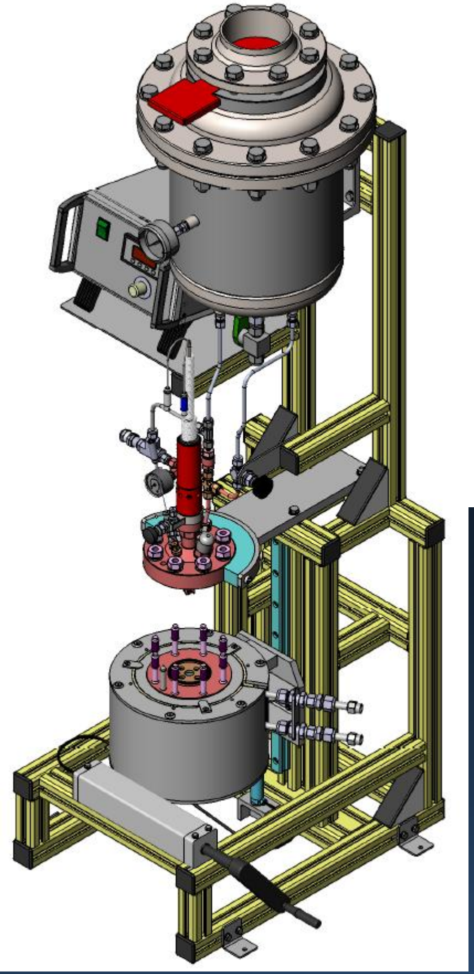
Reaction Calorimetry User Forum 2025

«High-phi-factor” calorimetry for safety analysis



Prof. Dr. Andreas Zogg & Luca Moschen

andreas.zogg@fhnw.ch

https://www.fhnw.ch/de/personen/andreas-zogg/

Fachhochschule Nordwestschweiz

28.10.2025

University of Applied Sciences and Arts Northwestern Switzerland (FHNW)


Business


Life Sciences


Engineering


Architecture Construction Geomatics

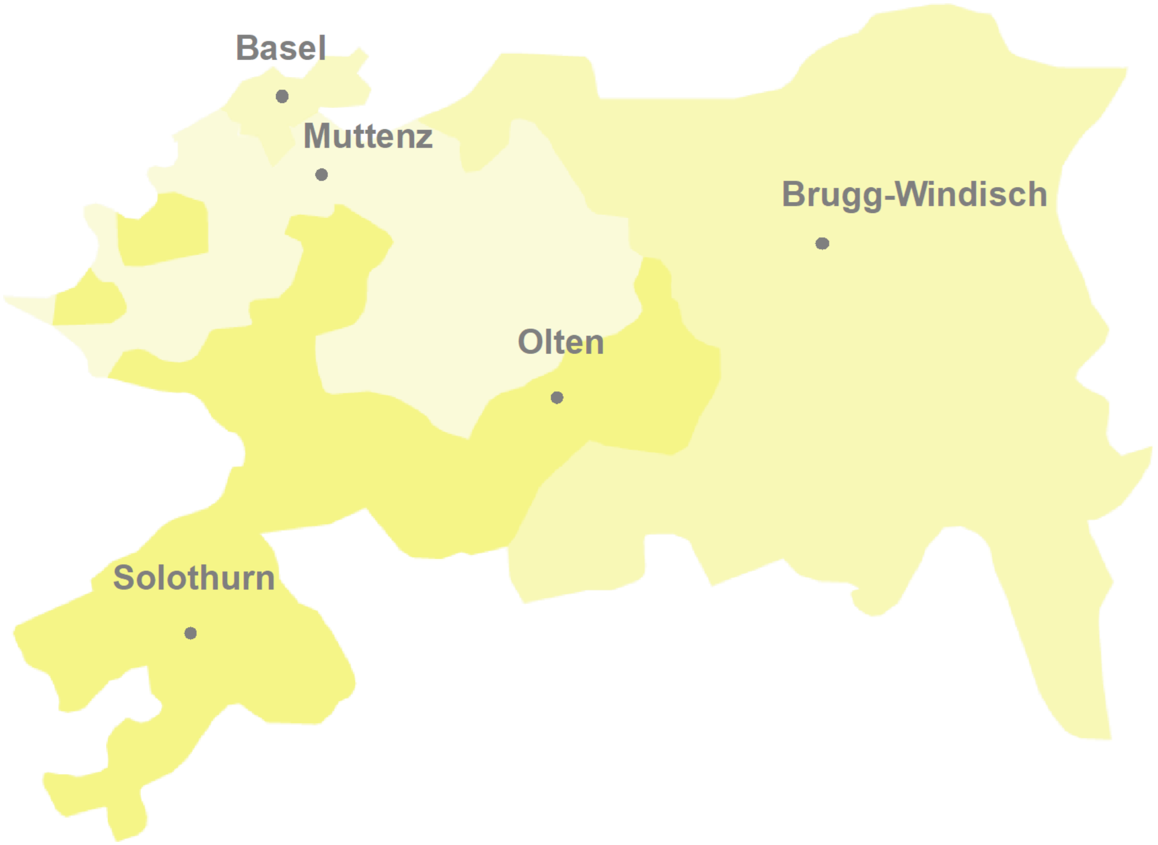

Applied Psychology


Social Work


Teacher Education


Art


Music



School of Life Sciences (HLS)

800 Students
300 Employees

5000 + 1200 m² Lab space
200 Applied research projects

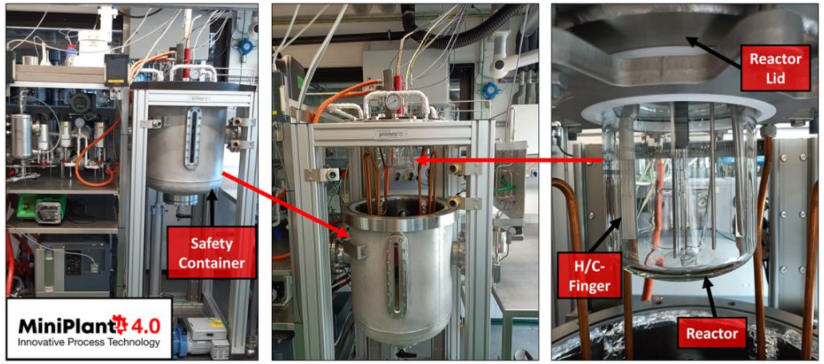
Process Technology Centres



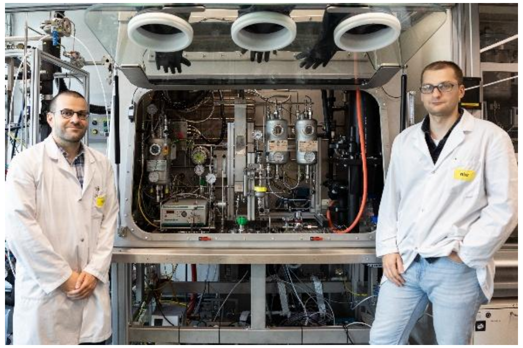








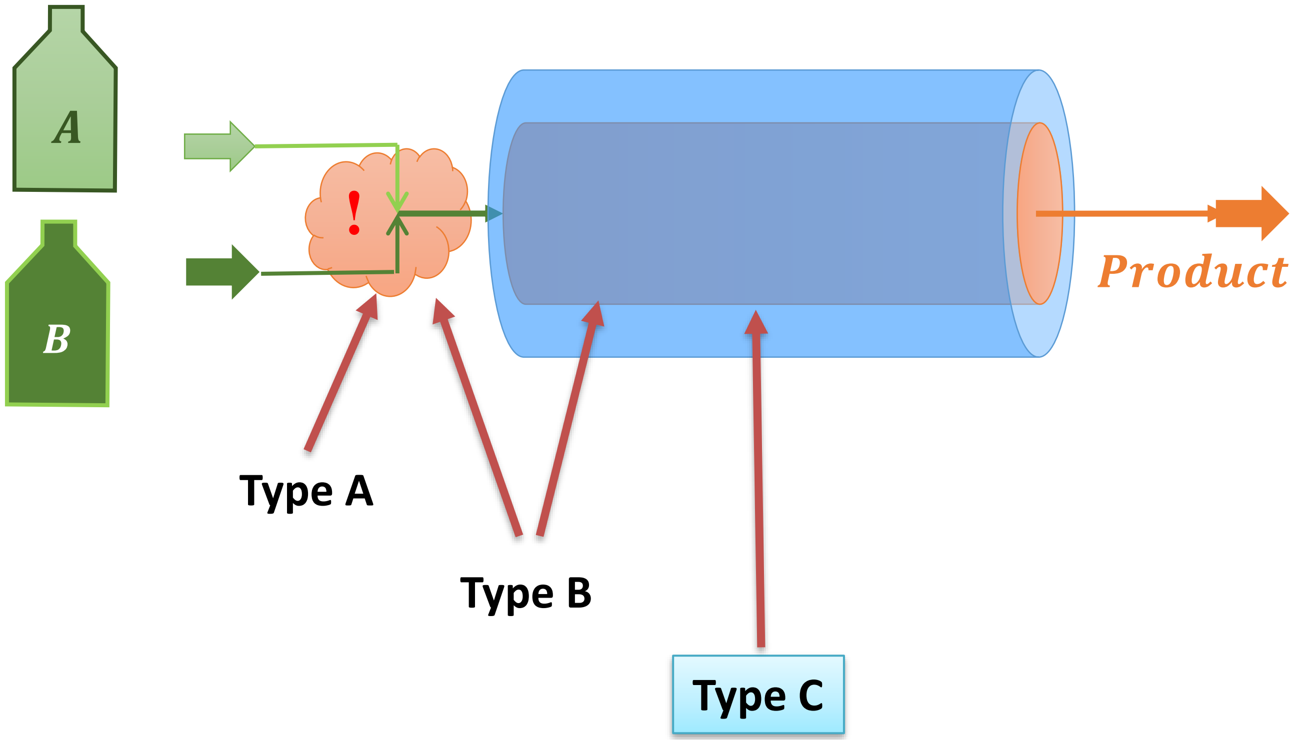



Content

1. Introduction
    - Target application: Scale-Up of hazardous chemical reactions
    - “DSC-Workflow”
    - Limitations of the “DSC-Workflow”
2. “High-phi-factor” calorimeter
    - Requirements and specifications
    - Laboratory safety aspects
3. Application example: Polymerization of vinyl-acetate
    - Initial DSC measurements
    - Calibration and results of the “high-phi-factor” calorimeter
4. Summary
5. Outlook

1. Scale-Up of hazardous chemical reactions
Focus: Continuous reactors



Type A reaction
- very fast (< 1s)
- take place mainly in the mixing zone and are controlled by the mixing process
- Normally < 0 °C.

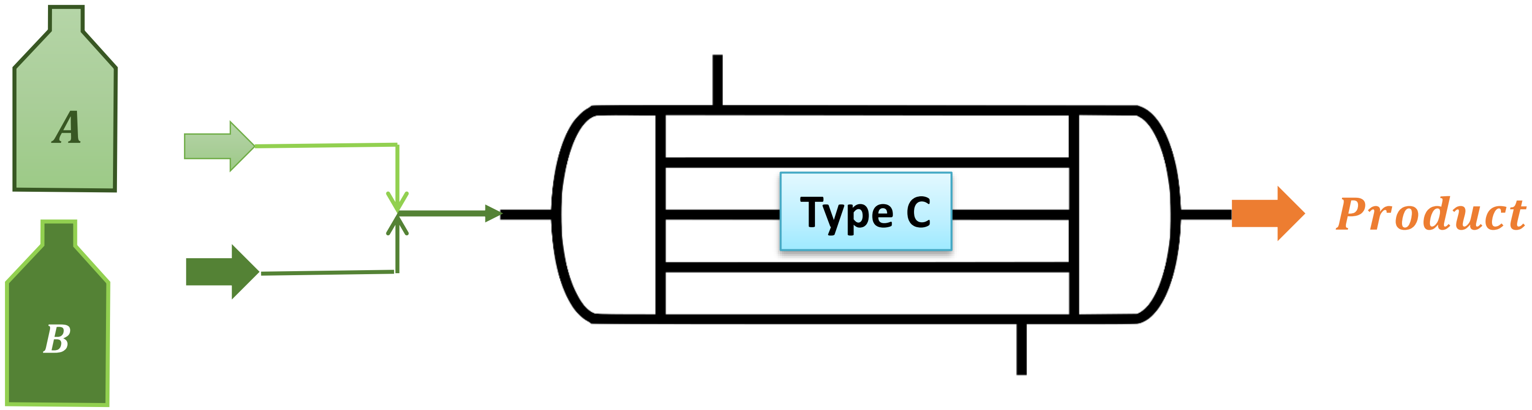
Type B reaction
- Rapid (1s … 10 min)
- predominantly kinetically controlled
- Challenge: Control of the heat flow!

Type C reaction
- Slow (> 10 min)
- Would suit batch/semi batch processes

D. M. Roberge et al., *Chem. Eng. Technol.* **2005**, 28 (3), 318-323

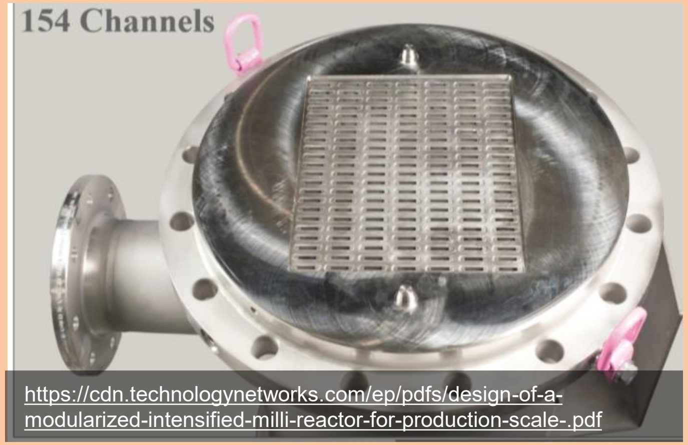
➔ **Focus for this presentation: Type C Reactions**
➔ A continuous process would lead to a safety or quality advantage.

1. Scale-Up of hazardous chemical reactions
Focus: Continuous reactors



Reaction in the tube

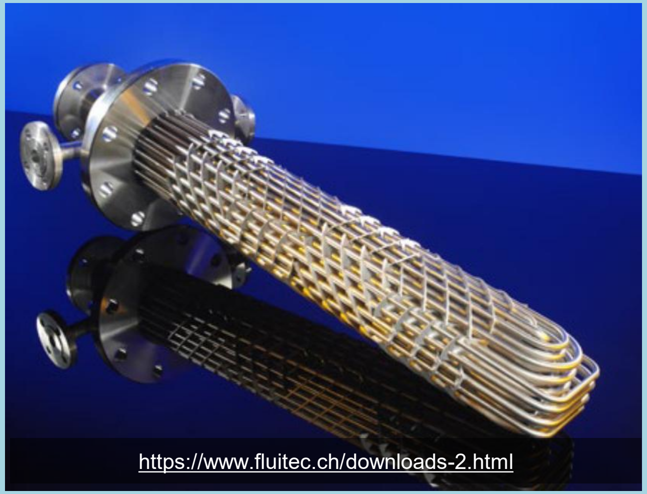

https://www.sulzer.com/en/shared/products/multitube-heat-exchanger-smxl



https://cdn.technologynetworks.com/ep/pdfs/design-of-a-modularized-intensified-milli-reactor-for-production-scale-.pdf

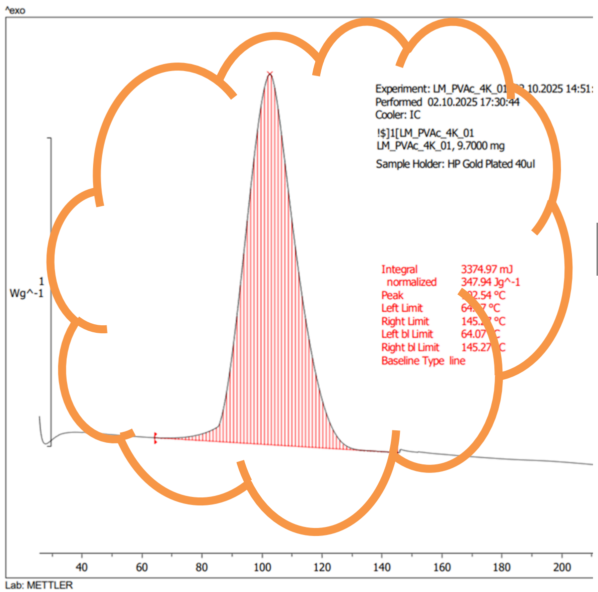
Reaction in the shell

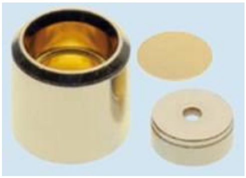

https://www.sulzer.com/-/media/files/products/separation-technology/brochures/english/heat_exhanger_smr_e10843_en_web.pdf


https://www.fluitec.ch/downloads-2.html

1: Scale-Up of hazardous chemical reactions
Thermokinetic reaction models based on DSC data

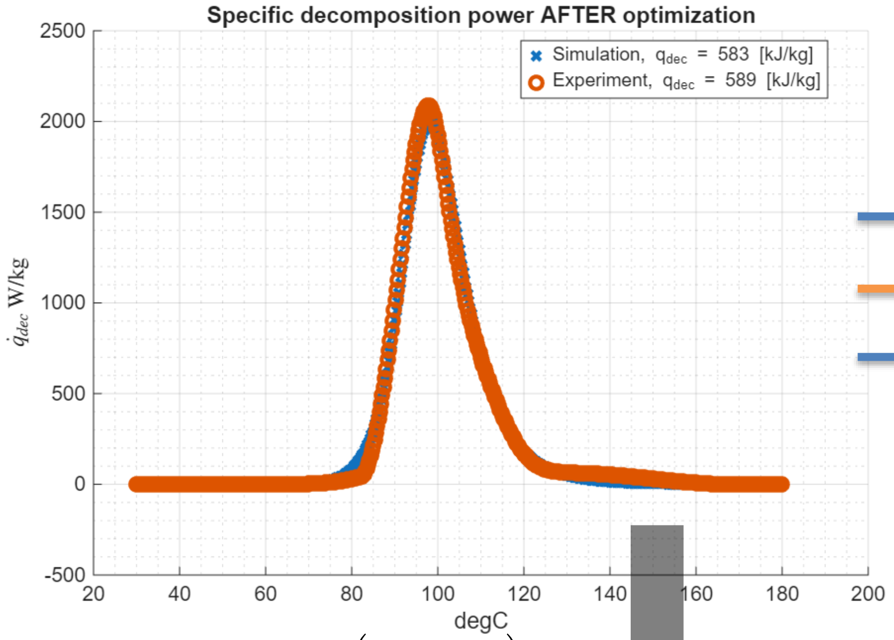
“DSC”-Workflow





Investigated Reaction

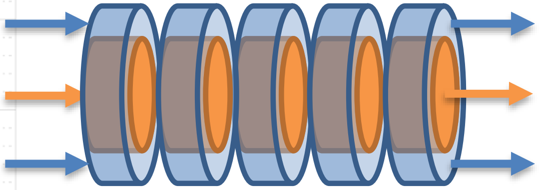
Thermokinetic Reaction Model
Eg. n’th order or Benito Perez



$$r = k_0 \cdot C_A^n \cdot e^{\left(\frac{EA}{R}\cdot\left(\frac{1}{T_0}-\frac{1}{T}\right)\right)}$$

$$r = k_1 \cdot e^{\left(\frac{EA_1}{R}\cdot\left(\frac{1}{T_0}-\frac{1}{T}\right)\right)} \cdot C_A + k_2 \cdot e^{\left(\frac{EA_2}{R}\cdot\left(\frac{1}{T_0}-\frac{1}{T}\right)\right)} \cdot C_A \cdot C_{Prod}$$

simulate behavior in Scale-Up



Reactor Model
Eg. non isothermal tanks in series model

Reactor Properties
Eg. Heat transfer, flow pattern.

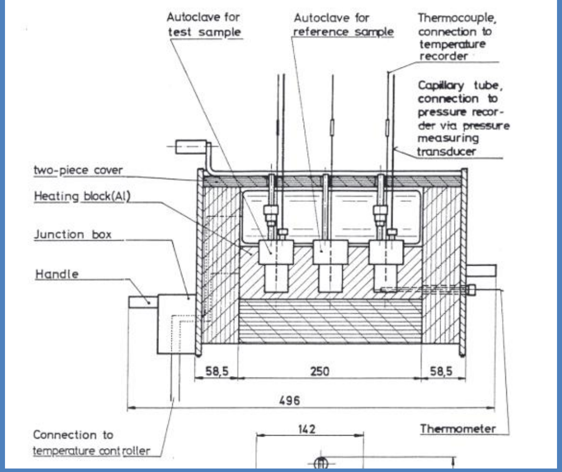
1: Scale-Up of hazardous chemical reactions Limitations of the "DSC-Workflow"

- Due to practical reasons, it is often not feasible to get a **representative mixture** of the reactants into the DSC crucible to observe the desired reaction. E.g. **volatile reactants**, **suspensions** etc.
- Is a small sample of a few mg **representative** for the bulk material?
- The **mixing** of the reactants might not be representative for the later application.
- Does the **surface** of the crucible have a non representative catalytic effect on the thermal signal?
- There is no information about the **pressure** and the potential formation of **gaseous side products**.
- Is the **T(t) ramp** representative for the later application?

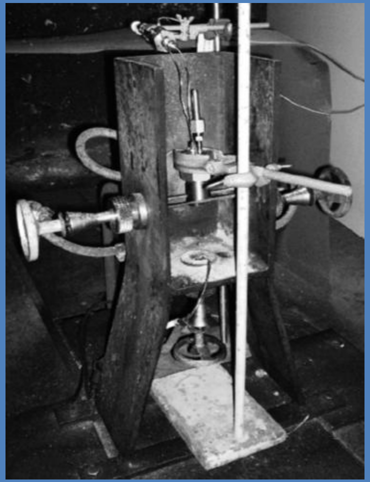
2. Requirements: Larger sample, pressure measurement, agitation

Mini autoclaves without agitator, with pressure measurement

https://www.systag.ch/wp-content/uploads/2020/01/Thermisches_Sicherheits_Kalorimeter_flexy tsc_deutsch.pdf

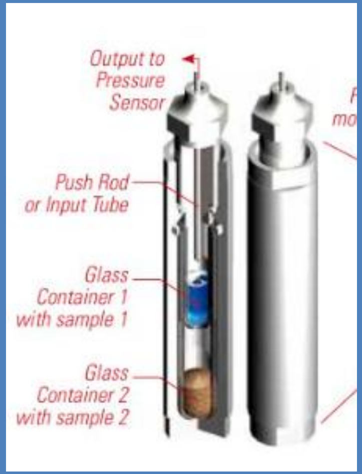


Whitmore, M. W. & Baker, G. P. Investigation of the use of a closed pressure vessel test for estimating condensed phase explosive properties of organic compounds. *Journal of Loss Prevention in the Process Industries* **12**, 207–216 (1999).



Knorr, A. *et al.* A closed pressure vessel test (CPVT) screen for explosive properties of energetic organic compounds. *Journal of Loss Prevention in the Process Industries* **20**, 1–6 (2007).

https://www.omnicaltech.com/dsc.html



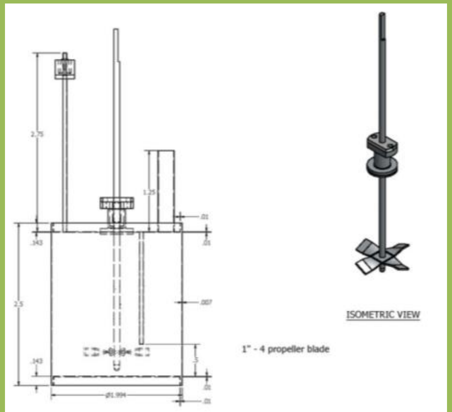
https://pdf.medicalexpo.com/pdf/setaram-instrumentation/c80/112816-175387.html

Reactors for low phi-calorimeters

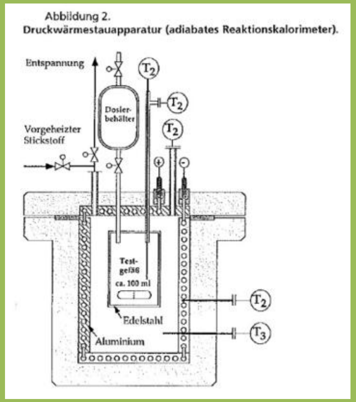
https://www.arcspares.com/products/arc-bombs

https://store.fauske.com/

Agitators

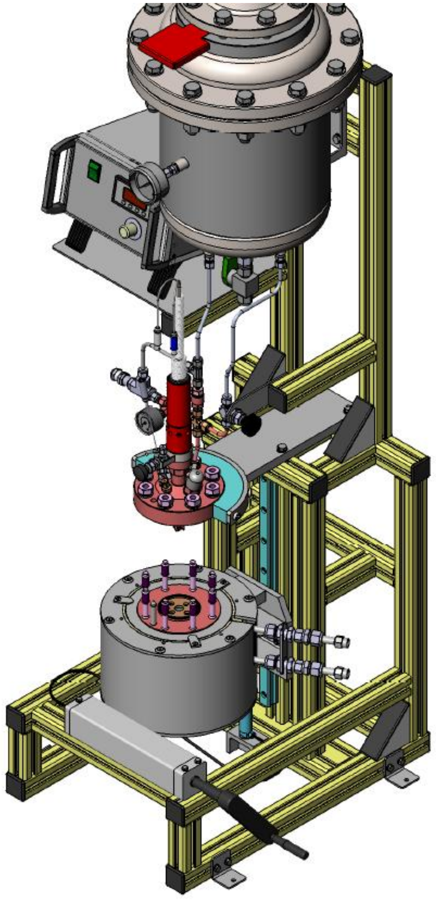


https://pdf.medicalexpo.com/pdf/setaram-instrumentation/c80/112816-175387.html

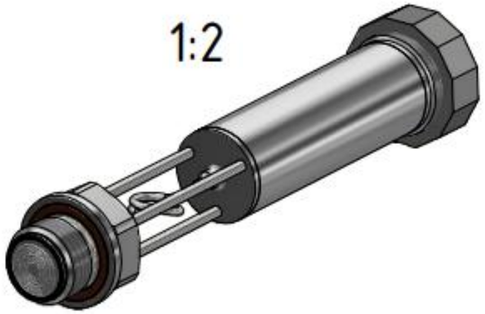


J. Schmidt, F. Westphal, CIT, 69, 776, 1997 (BASF & Hoechst AG)

2. Specifications of the “high-phi-factor” calorimeter



Max. 300 bar
Max. 250 °C
Hastelloy® C-22, 2.4602
Reactor volume: 125 ml
Blow-Down-Tank: -1/+6 bar, 20 L, open via safety valve, N_2.
Calibration heater
Pressure transmitter:
0 … 300 bar, 20 … 300 °C (no capillary!)



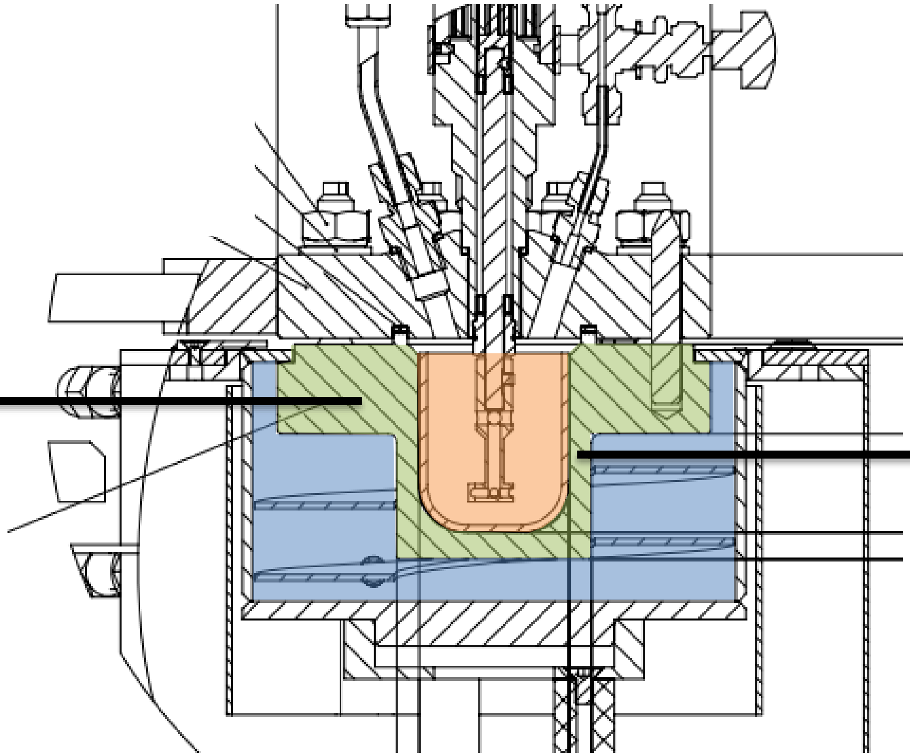
Originally designed for the measurements of explosion in the gas phase under reaction conditions:

1) Zogg et al., Kontinuierliche Ethoxylierung, Pharma Forum **25.04.2024**, FHNW-Muttenz, https://irf.fhnw.ch/handle/11654/45972
Jan Skula, Master-Thesis FHNW-HLS, F. Hoffmann – La Roche, **2017. 2)** Leonhardt et al., Chem. Ing. Tech. **2017**, 89, No. 4, 432–439

2. Specifications of the "high-phi-factor" calorimeter

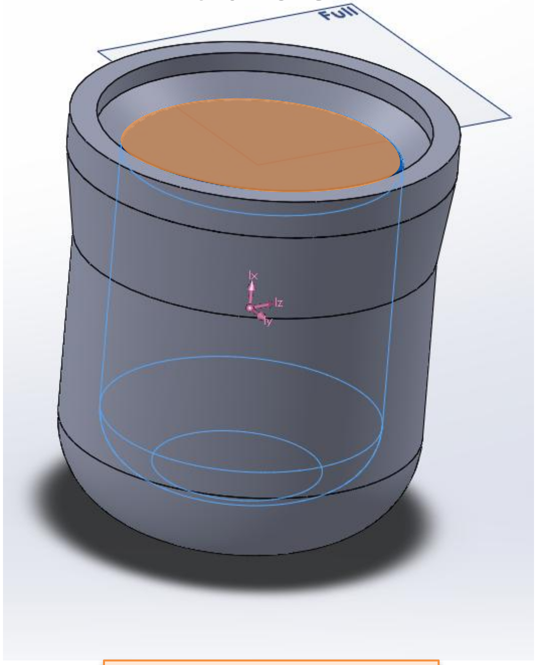
Mass of the reactor wall m_{RW} relevant for the phi-factor

m_{RW} = 4.4 kg



V_J = 1.1 Liter

Reactor volume V_R and thickness of the reactor wall s_{RW} relevant for the heat transfer



V_R = 125 ml

s_{RW} = 7 mm

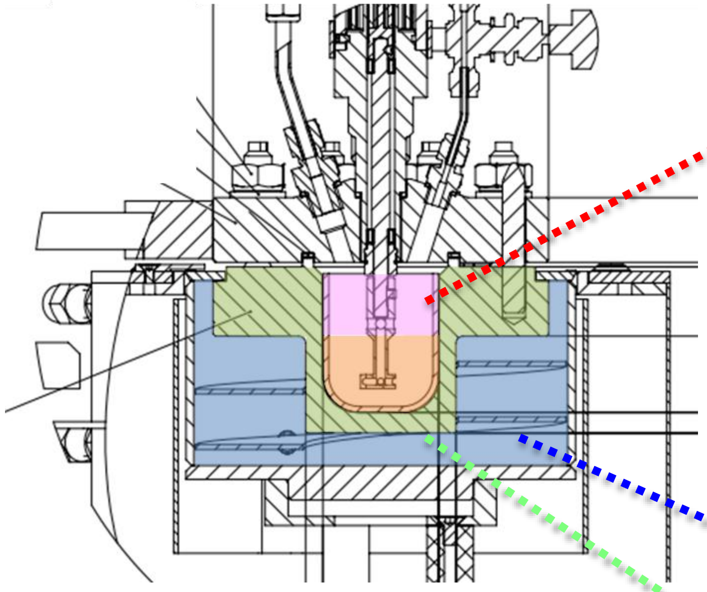
2. Laboratory safety aspects of the "high-phi-factor" calorimeter

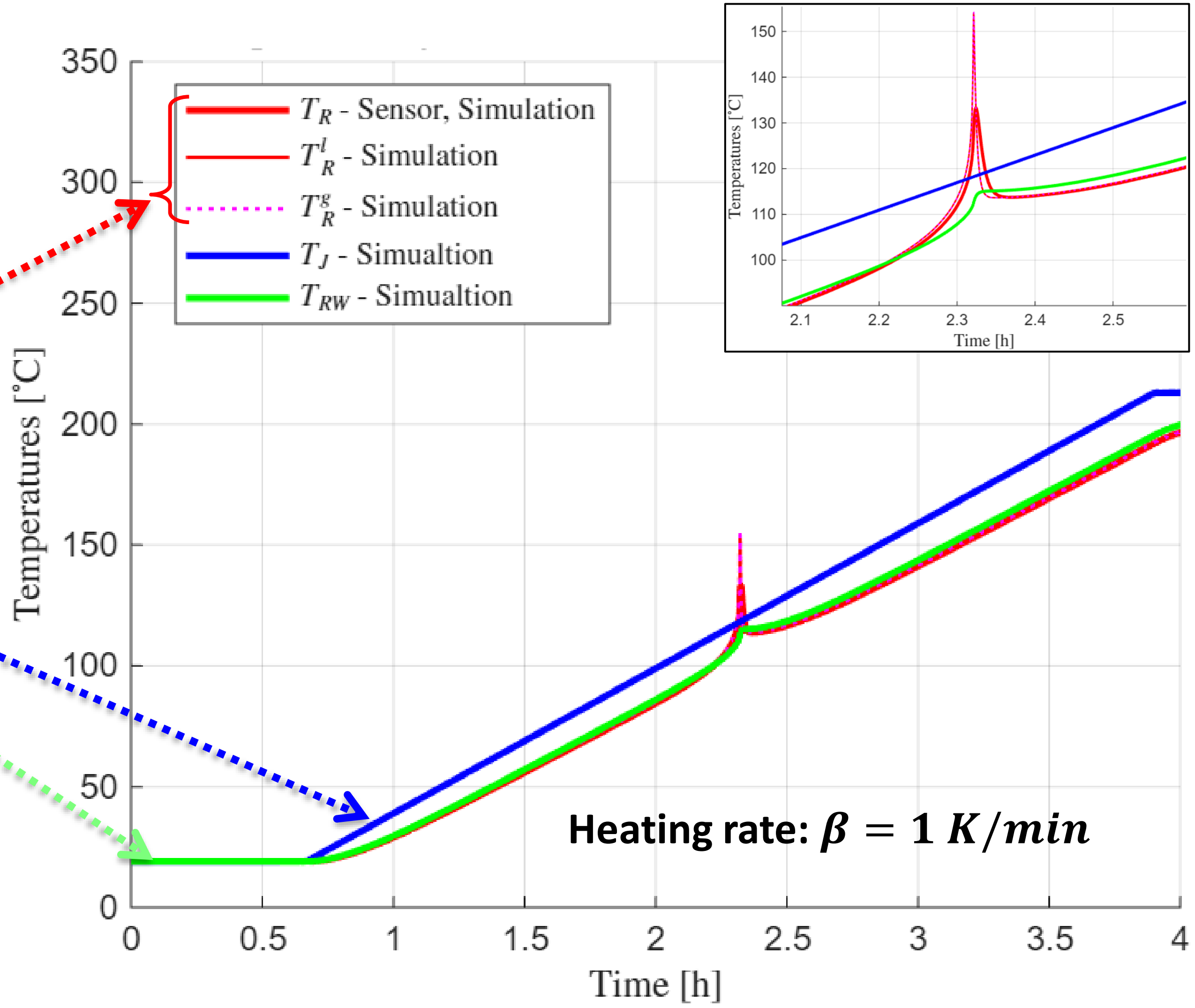
		«high-phi-factor» calorimeter	DSC	«low-phi-factor» calorimeter	16 m^3 vessel
Reactor wall	m_{RW}	4.4 kg	1.4 g	35 g	5700 kg
	cp_{RW}	414 kJ/kg	414 kJ/kg	414 kJ/kg	414 kJ/kg
Reaction mass	m_{RM}	55 g	5 mg	80 g	16 t
	cp_{RM}	2000 kJ/kg	2000 kJ/kg	2000 kJ/kg	2000 kJ/kg
phi-factor	ϕ	**18**	**59**	**1.1**	**1.1**
Adiabatic temperature rise (example)	ΔT_{ad}	**250**	**250**	**250**	**250**
Adiabatic temperature rise phi-corrected	$\Delta T_{"exp"}$	**13** !	**4**	**230**	**230**

The advantage of a «high-phi-factor» calorimeter is that the thermal mass of the reactor wall can act as a cooling source.

but …

2. Laboratory safety aspects of the “high-phi-factor” calorimeter – Simulation





$\Delta T_{"exp"} \approx 40\ K$ ✓

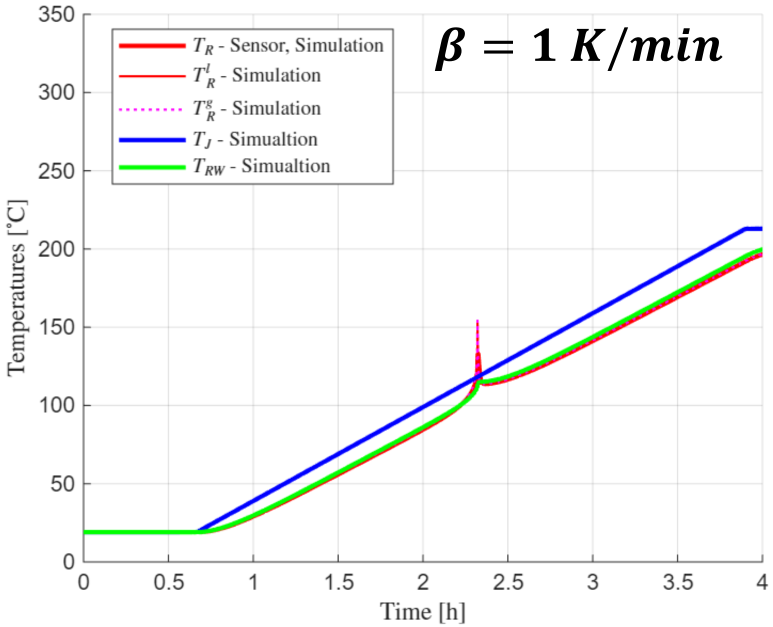
Cooling within a few minutes expected ✓
➔ Triggering of potential decomposition reactions unlikely

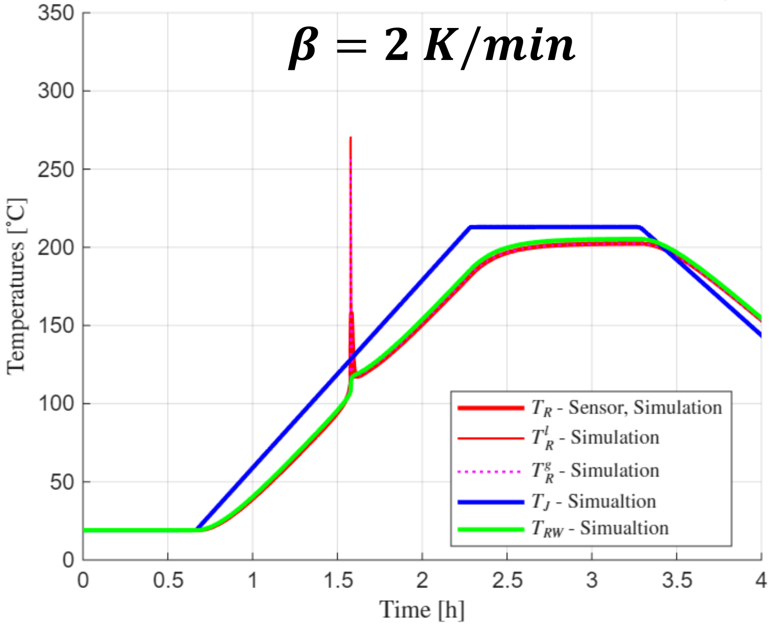
n’th order reaction
$EA = 180\ kJ/mol$

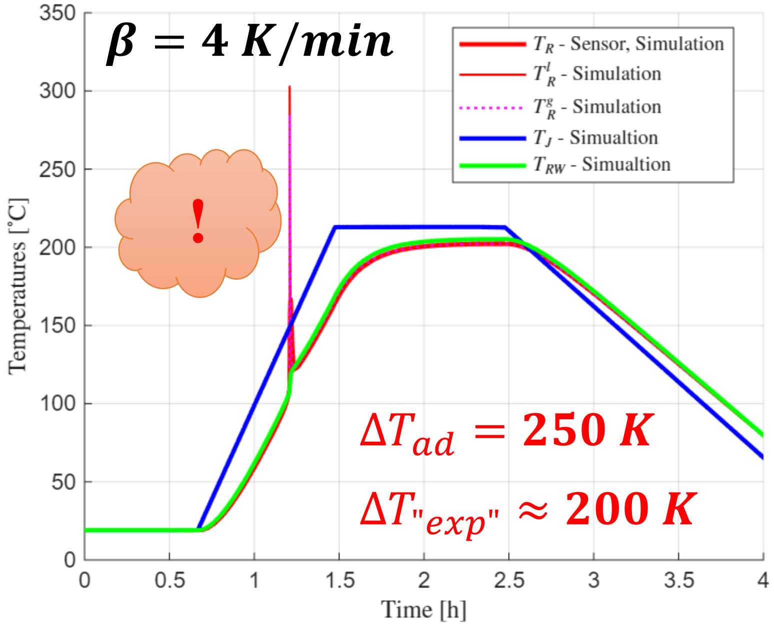
$\Delta T_{ad} = 250\ K$

Overall heat transfer coefficient: $k_{RJ} = 300 \frac{W}{m^2 \cdot K}$

2. Laboratory safety aspects of the "high-phi-factor" calorimeter – Simulation

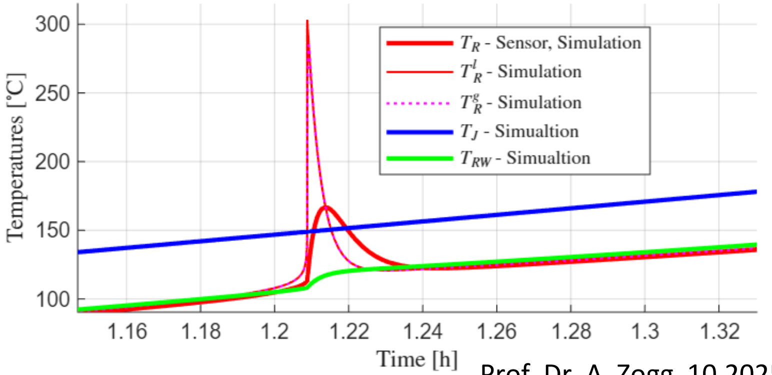




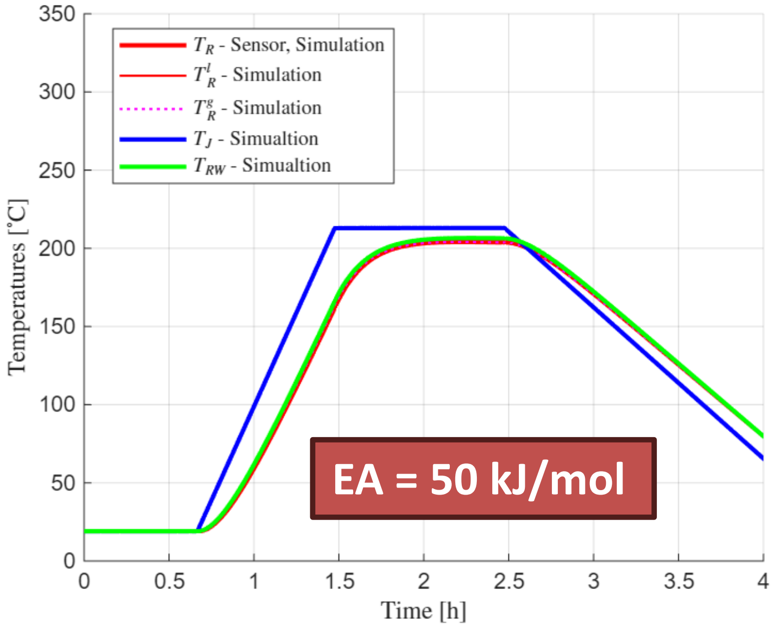


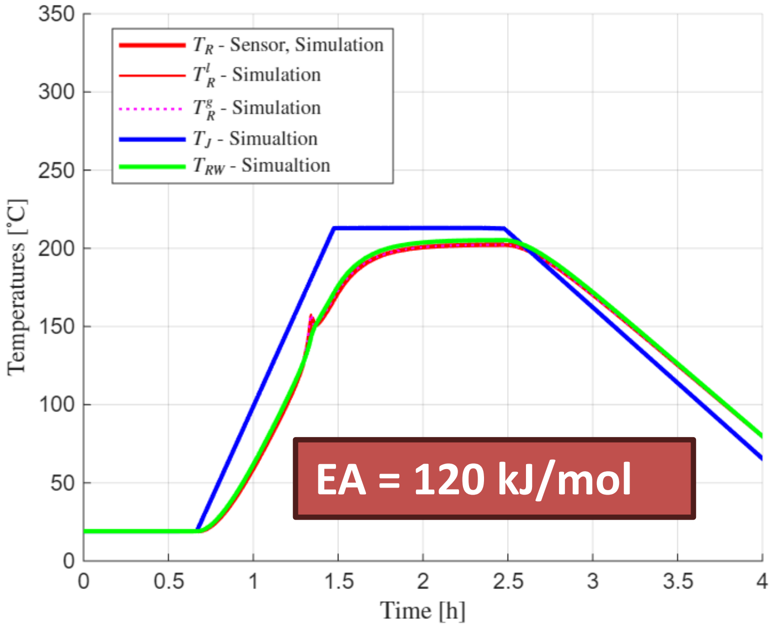
Measures and considerations for laboratory safety:

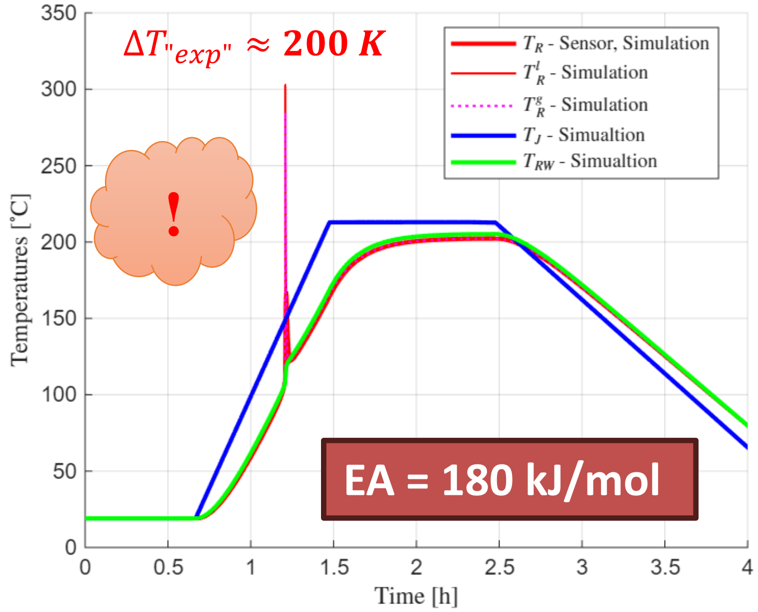
1) **Simulate** the experiment before measuring!
2) Start with a **low temperature** ramp and verify the reaction model afterwards!
3) Be **careful** with high heating rates.
4) The **temperature peak cannot be measured** (time constant of the sensor)!
5) Could the short temperature peak trigger a **decomposition** reaction?
6) Does the **rupture disk / pressure sensor** withstand the **pressure-peak?**



2. Laboratory safety aspects of the "high-phi-factor" calorimeter – Simulation



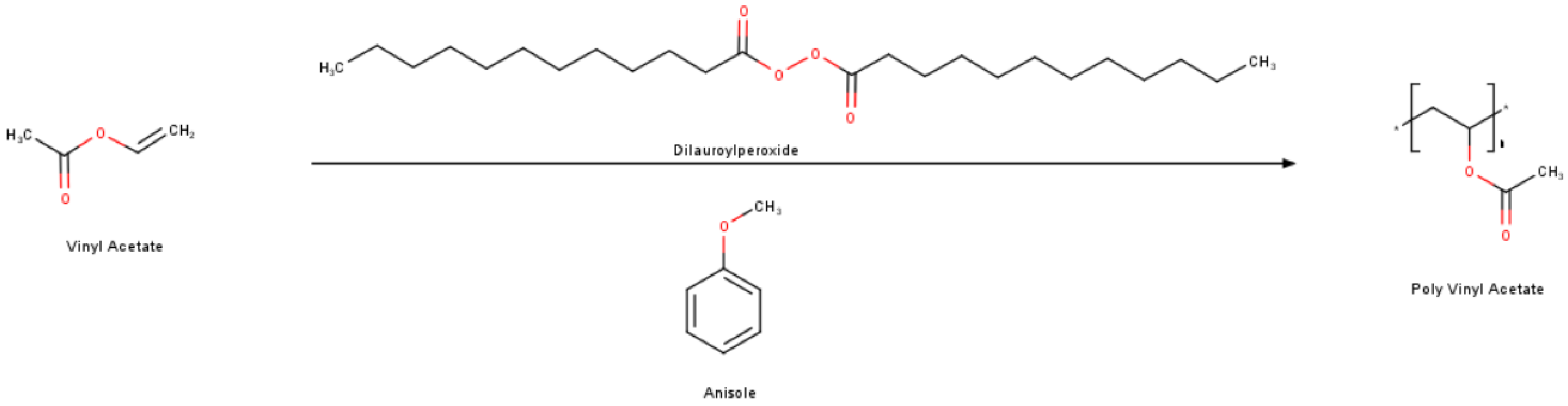




➔ A low activation energy in the model is not "conservative", **conservative reaction models have a high activation** energy.

➔ Important for Scale-Up: Reaction models with wrong activation energies can be detected!

3. Application example: Polymerization of vinyl-acetate



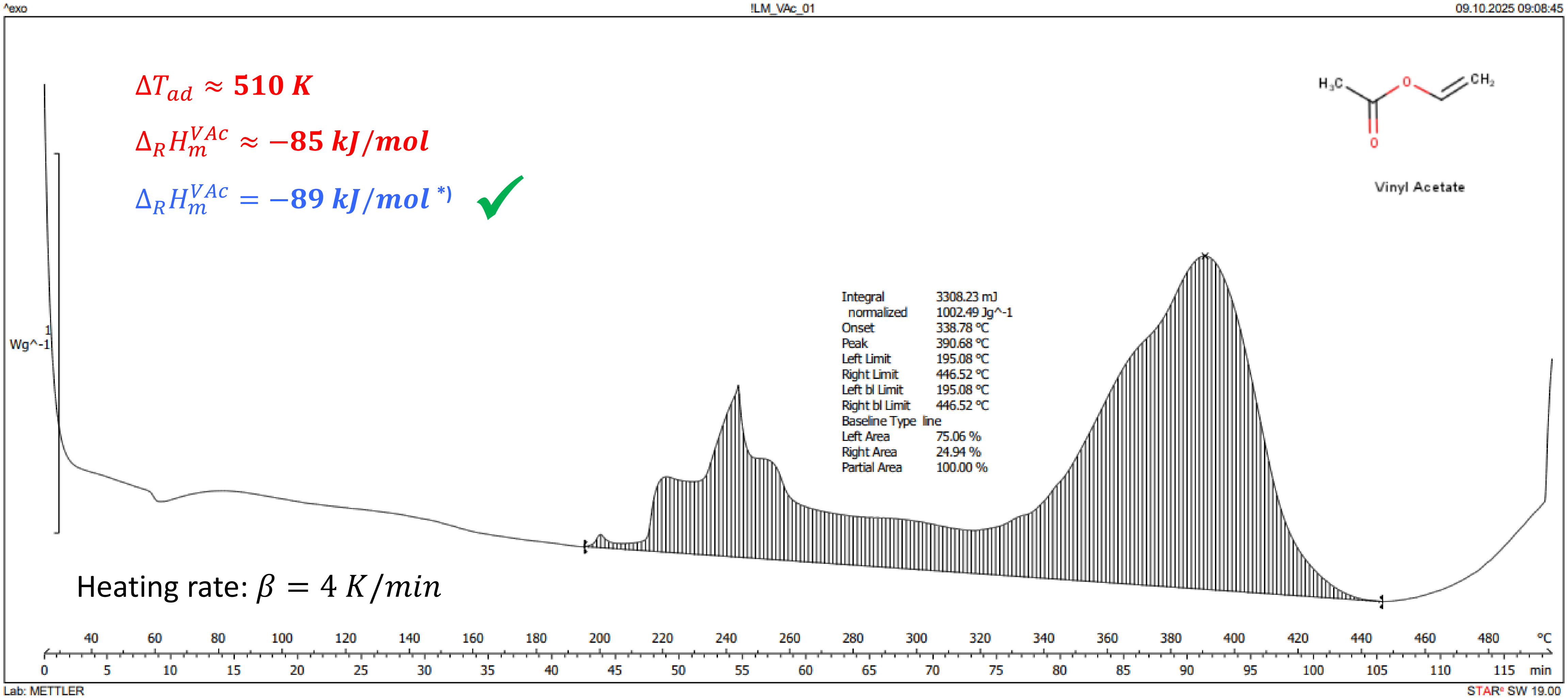
Gustin, J.-L. & Laganier, F. Understanding Vinyl Acetate Polymerization Accidents. *Org. Process Res. Dev.* **9**, 962–975 (2005).

3. Polymerization of pure Vinyl Acetate by DSC

$\Delta T_{ad} \approx 510\ K$

$\Delta_R H_m^{VAc} \approx -85\ kJ/mol$

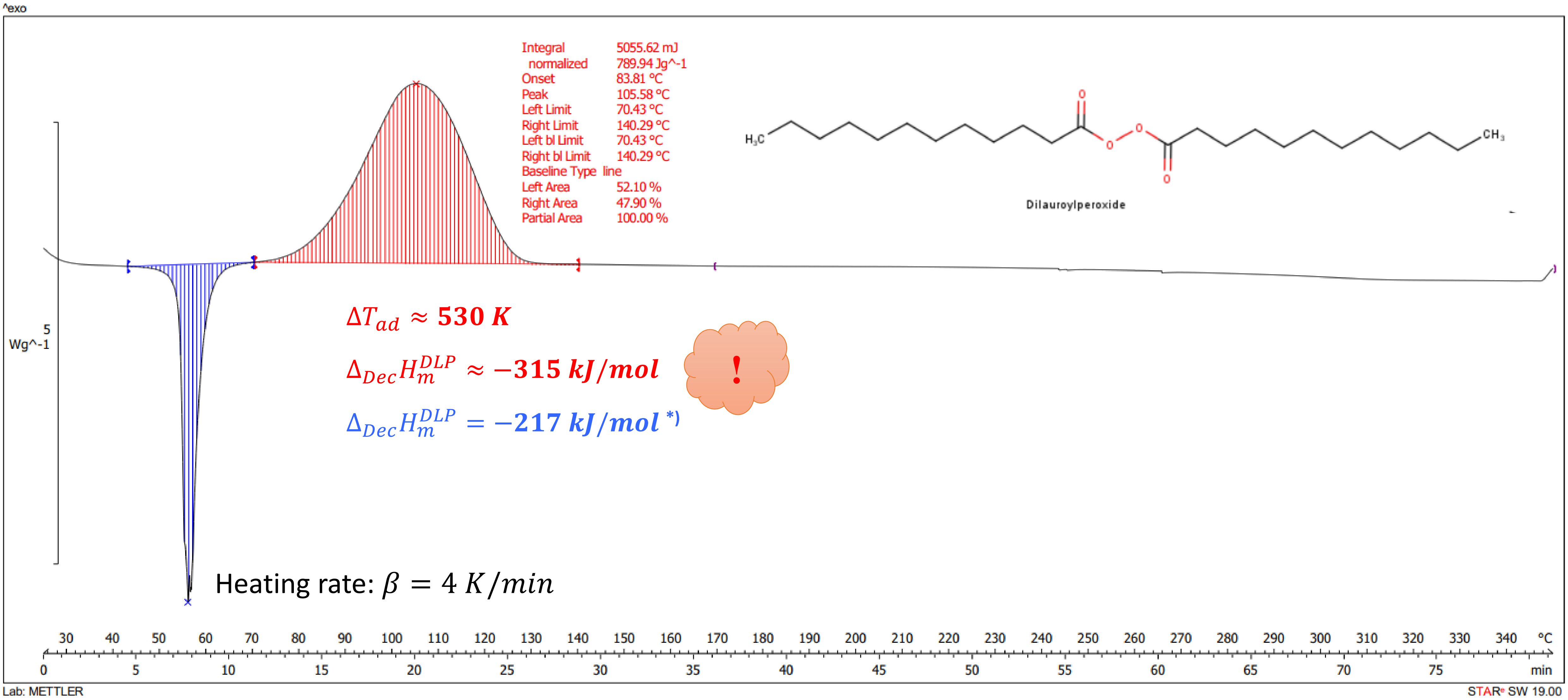
$\Delta_R H_m^{VAc} = -89\ kJ/mol$ *) ✓



Heating rate: $\beta = 4\ K/min$

*) Roberts, D. E. Heats of polymerization - a summary of published values and their relation to structure. J. RES. NATL. BUR. STAN. 44, 221 (1950).

3. Decomposition of pure dilauroyl peroxide by DSC



$\Delta T_{ad} \approx \mathbf{530\ K}$

$\Delta_{Dec}H_m^{DLP} \approx \mathbf{-315\ kJ/mol}$

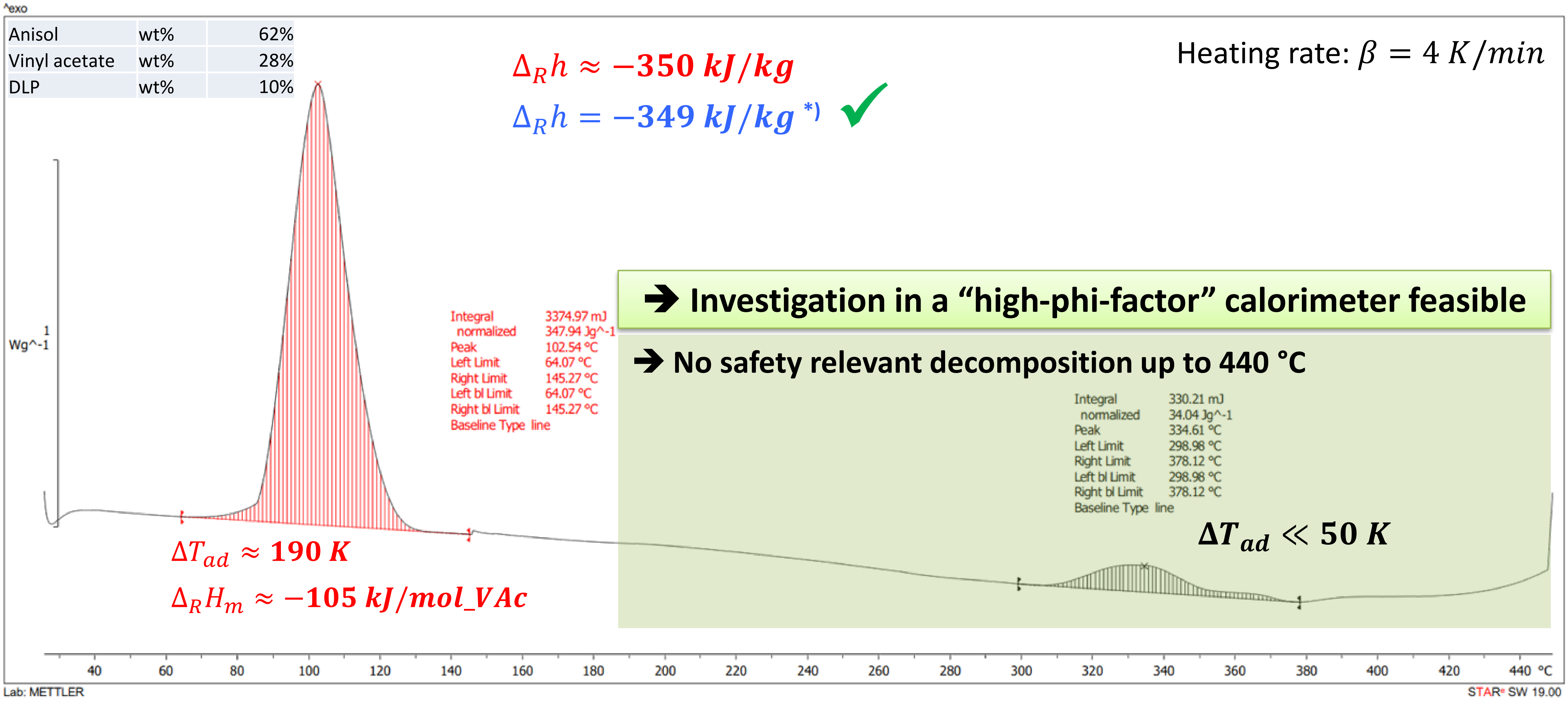
!

$\Delta_{Dec}H_m^{DLP} = \mathbf{-217\ kJ/mol}$ *)

Heating rate: $\beta = 4\ K/min$

*) Zang, N., et al. Thermal stability of lauroyl peroxide by isoconversional kinetics evaluation and finite element analysis. Journal of the Taiwan Institute of Chemical Engineers 45, 461–467 (2014).

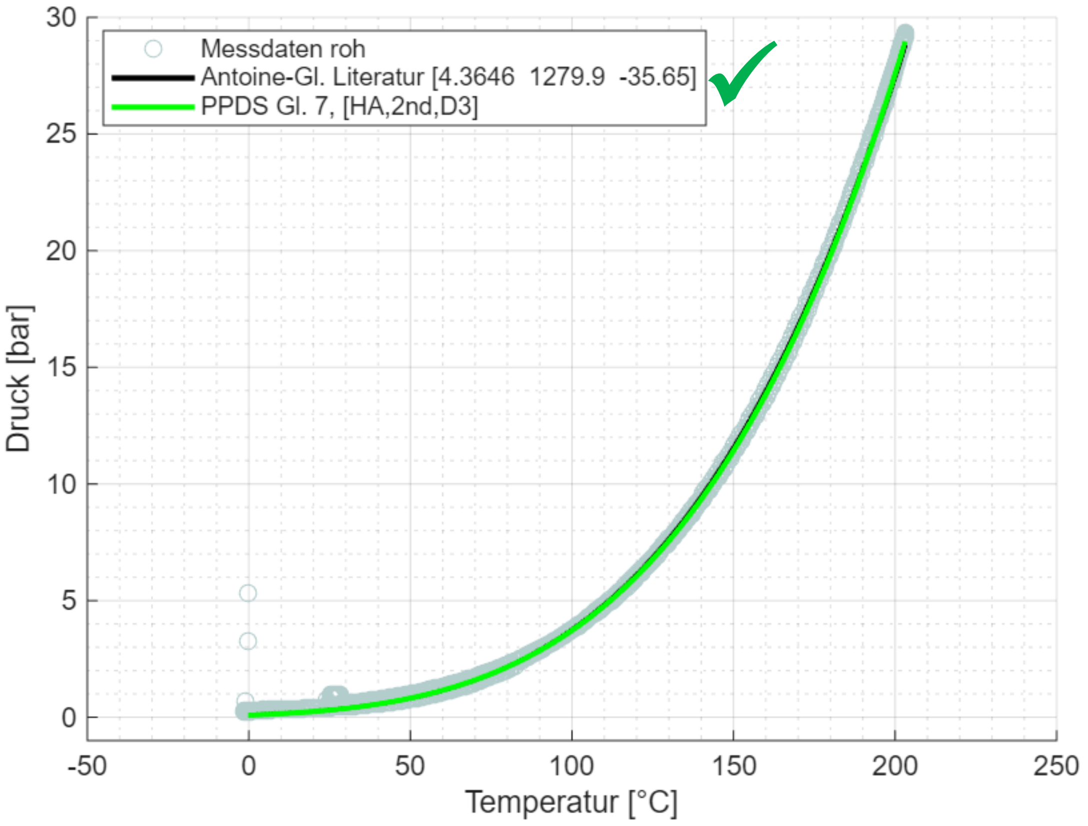
3. Polymerization of Vinyl Acetate in Anisole by DSC

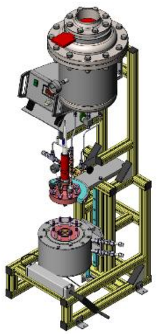


*) Calculated based on literature values of the pure reaction and decomposition enthalpies: $\Delta_R H_m^{VAc} = -89\ kJ/mol$ & $\Delta_{Dec} H_m^{DLP} = -217\ kJ/mol$

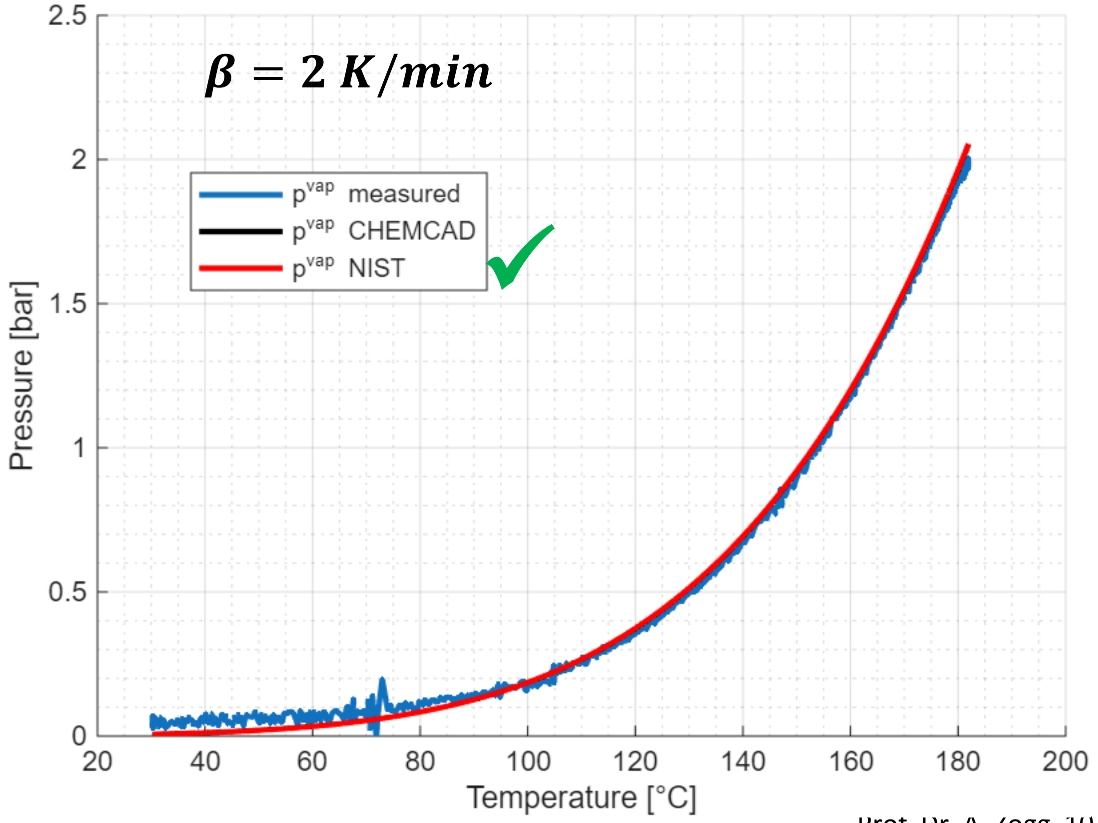
3. Calibration of the “high-phi-factor” calorimeter & measurement of the baseline

Calibration of the p and T sensor:
Vapor pressure of pure Acetone





Measurement of the baseline:
Pure solvent = Anisole

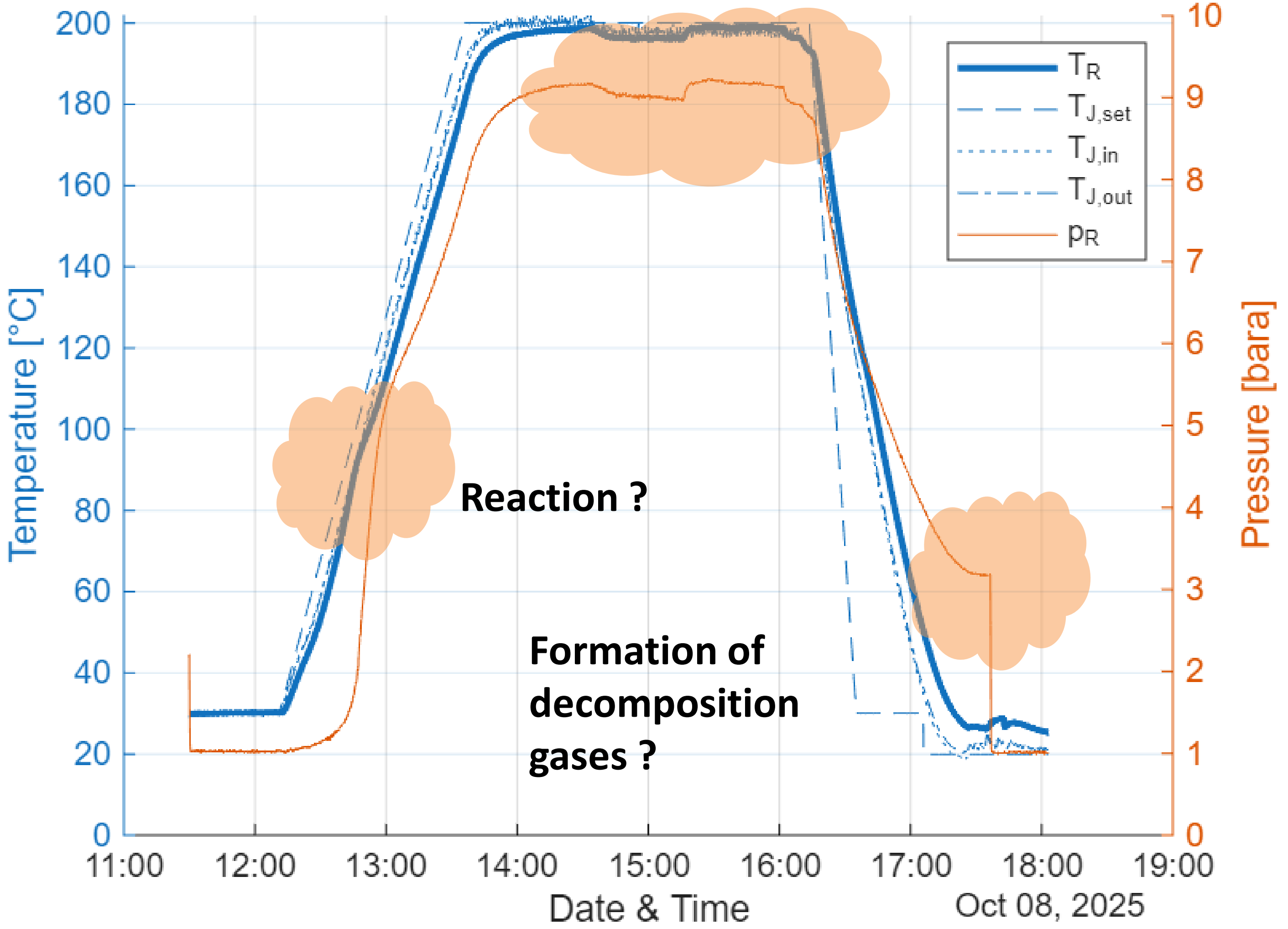


3. Polymerization of Vinyl Acetate in Anisole in the "high-phi-factor" calorimeter

$\boldsymbol{\beta = 2\ K/min}$

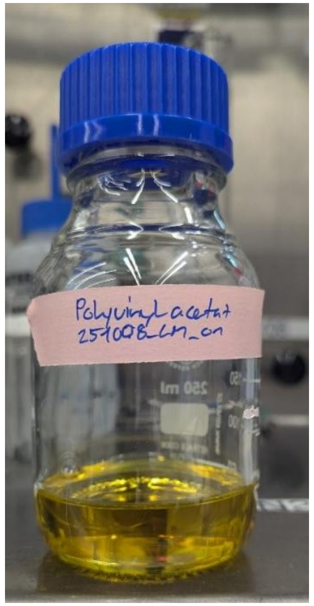
$\Delta T_{ad} \approx \mathbf{130\ K}$

Anisol	wt%	70%
Vinyl acetate	wt%	20%
DLP	wt%	10%

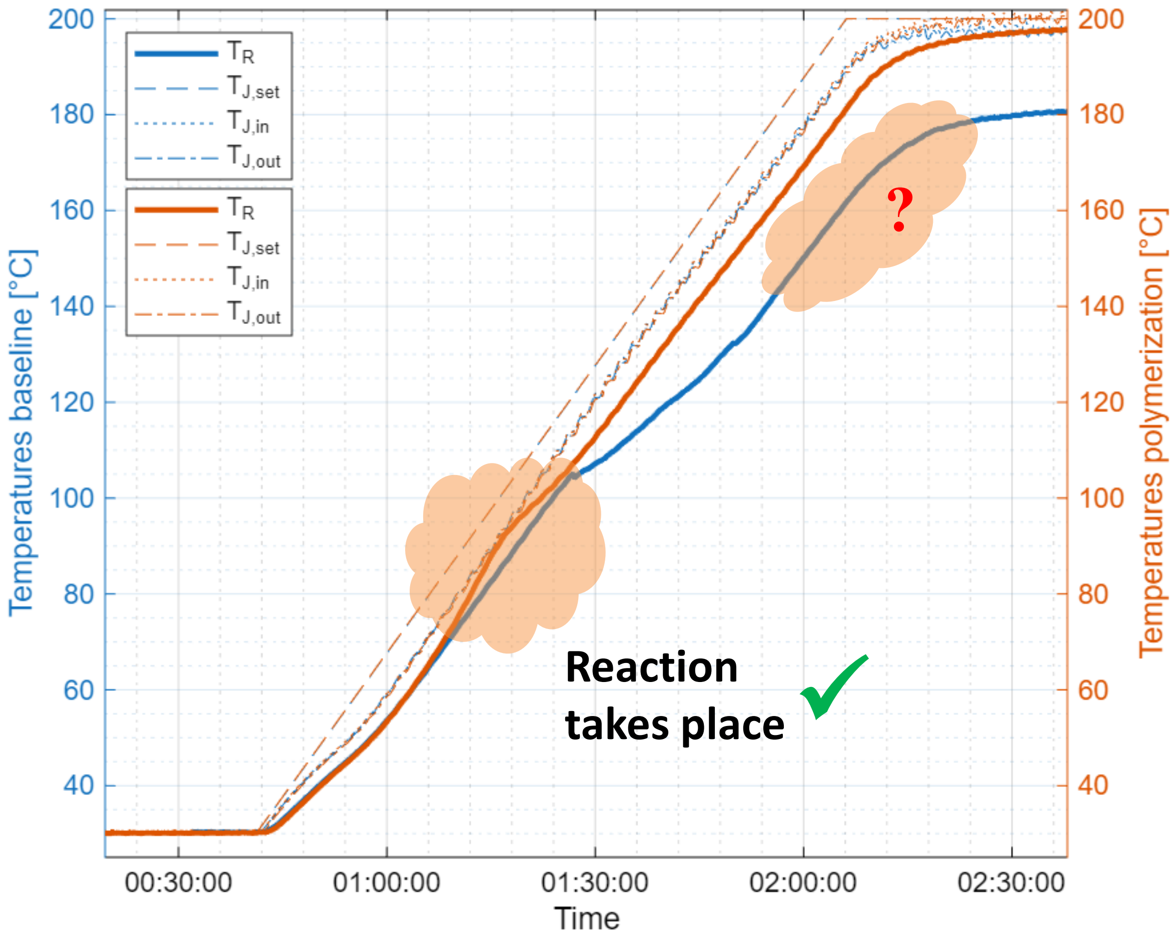


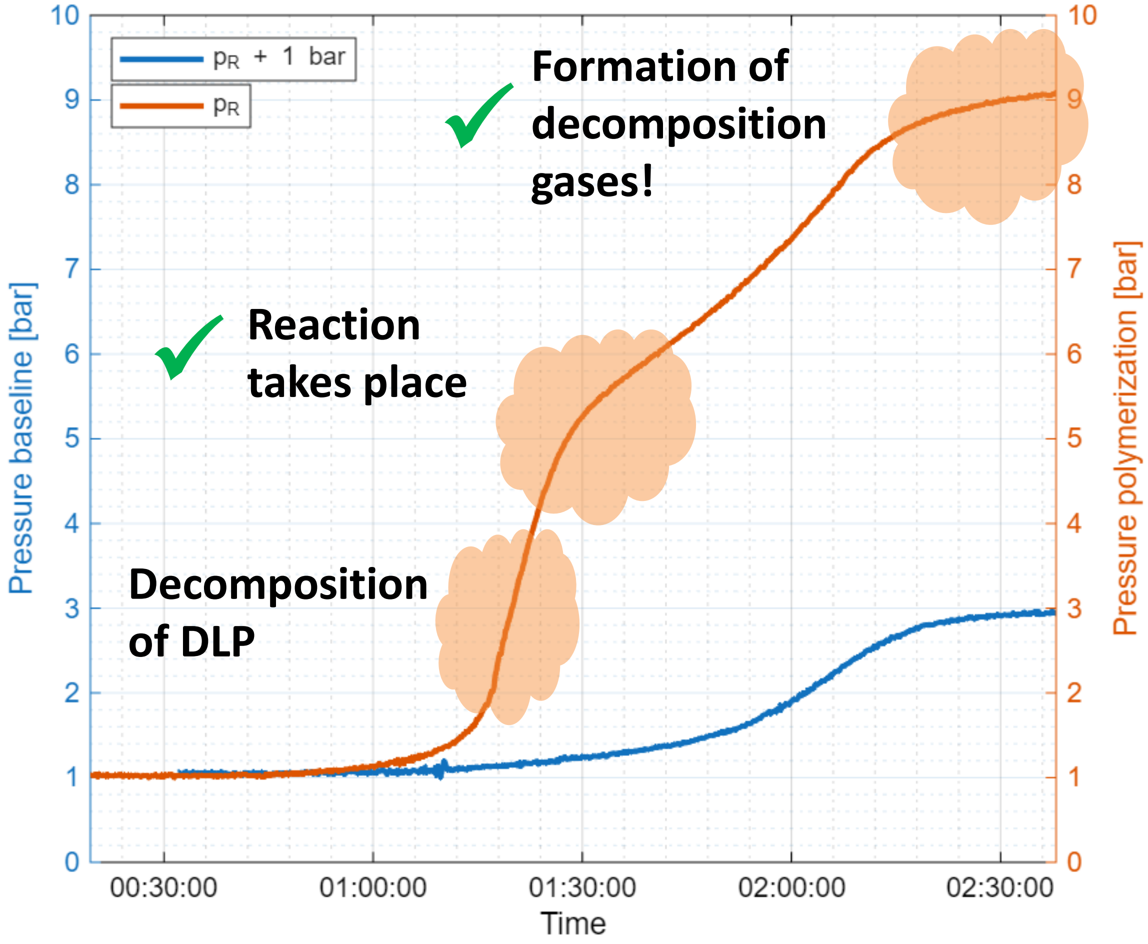
Calibration of the overall heat transfer coefficient:

$$k_{RJ} \approx 700\,\frac{W}{m^2 \cdot K}$$



3. Polymerization of Vinyl Acetate in Anisole in the "high-phi-factor" calorimeter – overlay with baseline

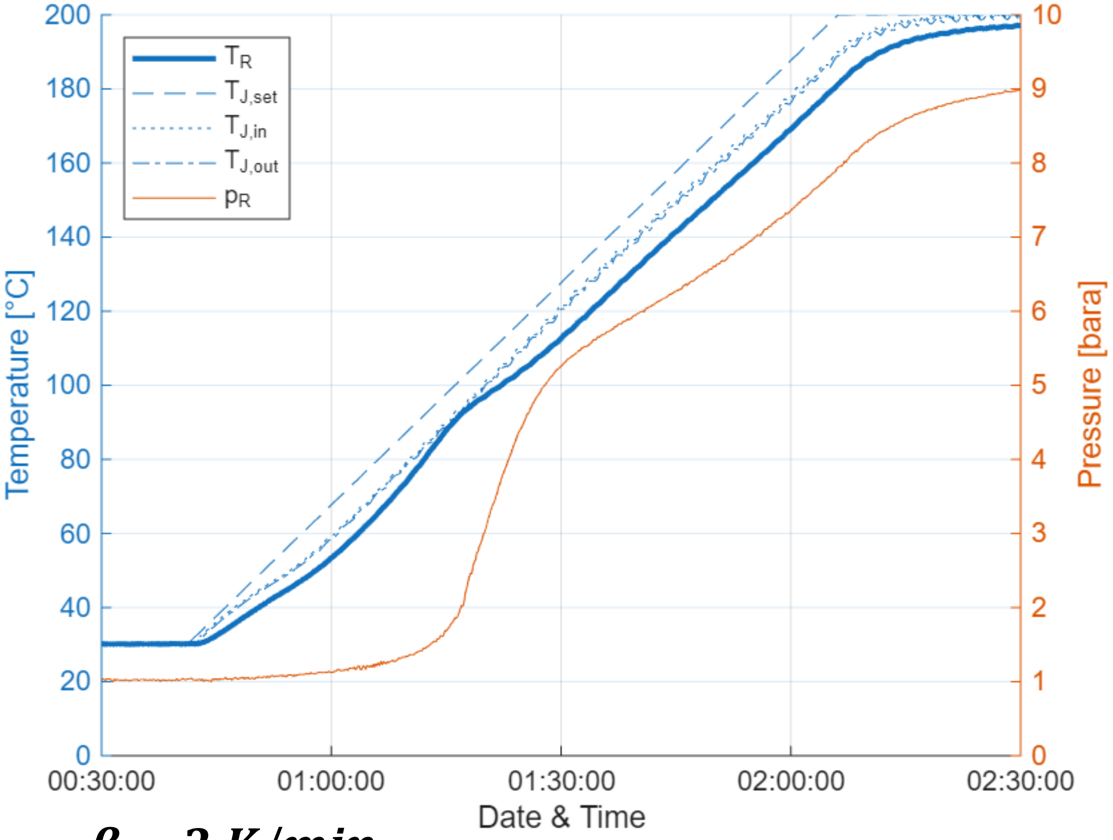




3. Polymerization of Vinyl Acetate in Anisole in the "high-phi-factor" calorimeter

Anisol	wt%	70%
Vinyl acetate	**wt%**	**20%**
DLP	wt%	10%

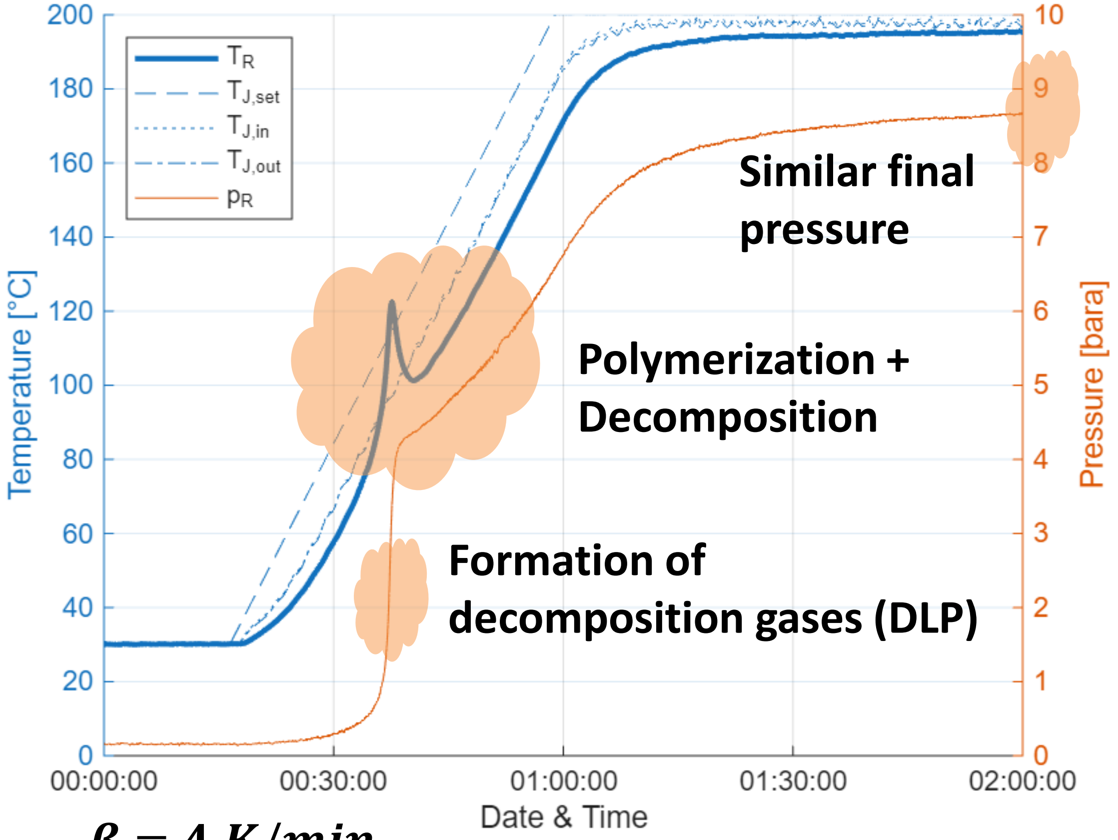
$\Delta T_{ad} \approx \mathbf{130\ K}$



$\boldsymbol{\beta = 2\ K/min}$

Anisol	wt%	60%
Vinyl acetate	**wt%**	**30%**
DLP	wt%	10%

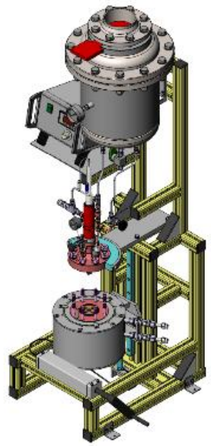
$\Delta T_{ad} \approx \mathbf{200\ K}$



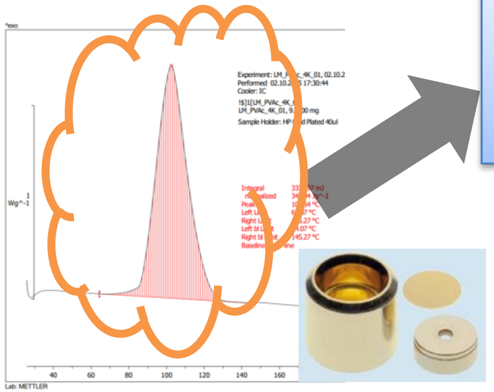
$\boldsymbol{\beta = 4\ K/min}$

4. Summary: Scale-Up of hazardous chemical reactions

“High-phi-factor” calorimetry workflow



Reactor Properties
Dynamic: Baseline
Steady State: Heat transfer coefficient



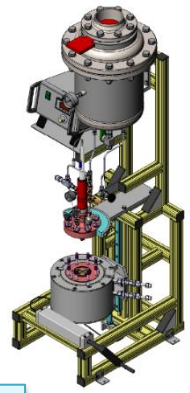
Thermokinetic Reaction Model
Eg. n’th order, Benito Perez

$$r = k_0 \cdot C_A^n \cdot e^{\left(\frac{EA}{R}\cdot\left(\frac{1}{T_0}-\frac{1}{T}\right)\right)}$$

Reactor Model

Reaction model
(gas formation & reaction power)
VLE model
Heat Flow Model

refine Reactor Model



***simulate* Experiment**

***perform* Experiment**

Scale-Up

Outlook

- Repeat **baseline** measurements with anisole (2 K/min and 4 K/min)
- Optimized **temperature** sensor with **smaller time constant**.
- Separate **temperature** sensor for the **gas phase**.
- Derive dedicated first principles correlation equations for the **heat transfer coefficient**.
- **Pseudo adiabatic** measurements with pressure relief.
- Perform a classical reaction similar to Tian et al. [1)]
- **Validate** the reactor model in a **pilot scale** continuous reactor.

[1)] Tian, Y. M. Lanz, P. Hoehn, X. Wang, J. Wiss, Ch. Heuberger, J.L. Schmuck, · X. Jiang, J. Wang, · Y. Ding.
Application-based calibration method for calorimeter FlexyTSC SEDEX. *J Therm Anal Calorim* **150**, 6117–6125 (2025).

Thanks a lot

Luca Moschen
scientific assistant

Michael Teger
system engineer

Corina Constantin
scientific assistant

Benedikt Brönnimann
scientific assistant

This Zahnd
scientific assistant

Christoph Hasler,
senior technician
retired