Storage Stability of Reactive Substances

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Aachen

Markus Gödde, BASF Process Safety - Group Research
Johannes Schröder, BASF Safety Assessment & Testing

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Typical issues in the storage of reactive substances

- Quality of the product (degradation by slow reaction)
- Thermal safety – Runaway in the storage tank due to insufficient heat dissipation
- Gas formation and creeping pressure build-up in closed containers
- Explosive conversion after <u>local</u> decomposition
- Influence of contamination on stability

Bürrig Explosion, Leverkusen

Source: rp-online.de

Waste storage tank after thermal explosion

- In July 2021, an explosion occurred in a waste tank
- thermal runaway
- 7 fatalities, 31 injured
- Improper energy balance, unexpected high reactivity

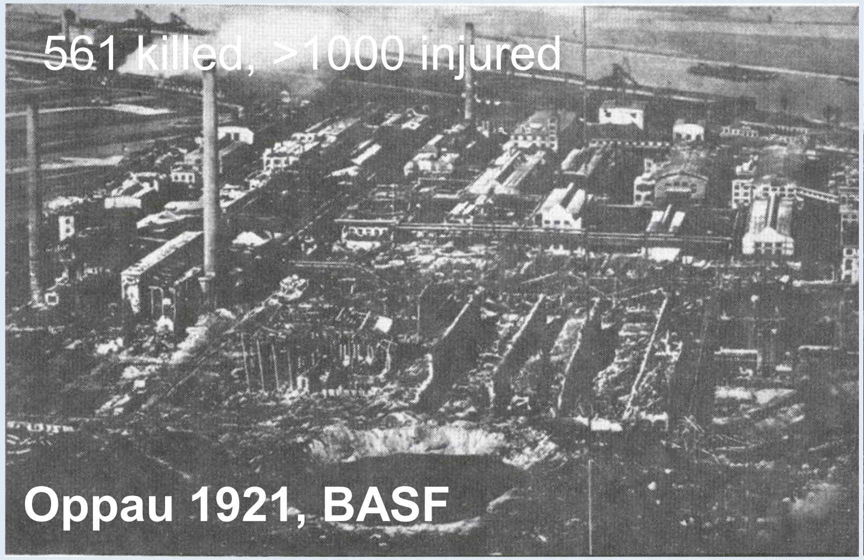
MS Flaminia Event

Source: Wikipedia

The damaged container ship MSC Flaminia on its way to Wilhelmshaven off Wangerooge, 9 September 2012

- In July 2012, an explosion occurred on a voyage from Charleston to Antwerp in the Atlantic Ocean
- Runaway of divinylbenzene
- 3 fatalities, 2 seriously injured
- Improper storage/loss of stabilization

Explosives Properties (Ammonium Nitrate)



- Mass Explosion after local initiation
- Local sensitization through contamination (hypothesis)
- Underestimated sensitivity
- Strong initiation stimulus

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Self-heating, Mannheim, 2022

- Self-heating of Hydrosulfite through air ingress
- 17 injured
- **Cause:**
  Damaged packaging, access to humid air

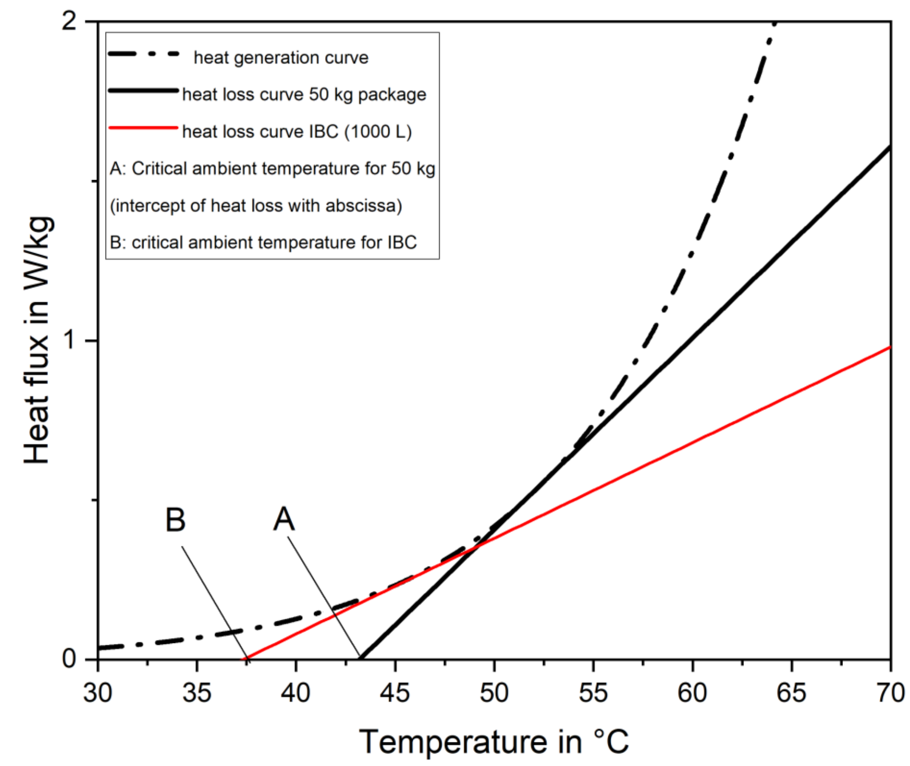
Source: Mannheim 2022, Source SWR

Basic concepts for the safe storage of reactive substances

- → Storage temperature below the critical heat production rate i.e. heat production can always be dissipated from the tank/container
- → Assessment of heat generation and specific heat loss

If this is not possible:

- → Safe limitation of the storage period well below the induction time (usually inhibited or autocatalytic material systems), PIT concept
- → Assessment of inhibition time (PIT) and storage time



Experimental challenges

Assessment of large storage containers

Container type	Volume in m³	Specific heat Loss in mW/kg K	value c_p of 2 J/gK Half-time of Cooling in h	Critical heat flux in W/kg*
Drum	0,06	60	6,4	0,192
IBC	1	30	12,8	0,096
Tank	3,4	18	21,3	0,057
Tankcontainer	20	10	38,5	0,031
Insulated tank container	20	1,7	226,5	0,005
Storage tank (non-insulated)	100	6	64	0,019
Storage tank (insulated)	100	1	385	0,003

*applies to activation energy of 100kJ/mol, 50°C

- Heat dissipation to ambient air via convection (5 W/m²K), low heat generation rates can lead to thermal explosion
- Direct measurement of critical heat fluxes for larger storage quantities, a very high sensitivity is required
- For large quantities it must be extrapolated

Measurement	Sensitivity in W/kg
DSC	5-20
Adiabatic	0,05 - 2
Calvet	0,1
TAM	0,001

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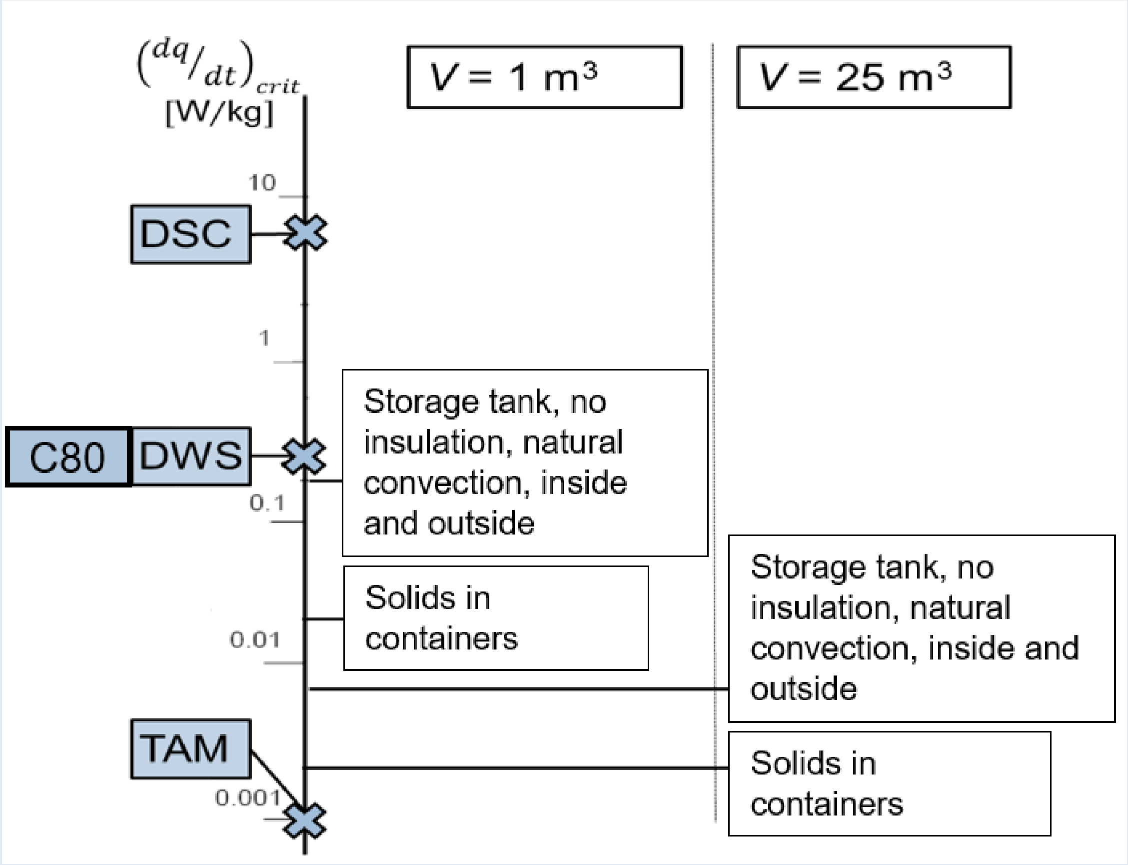
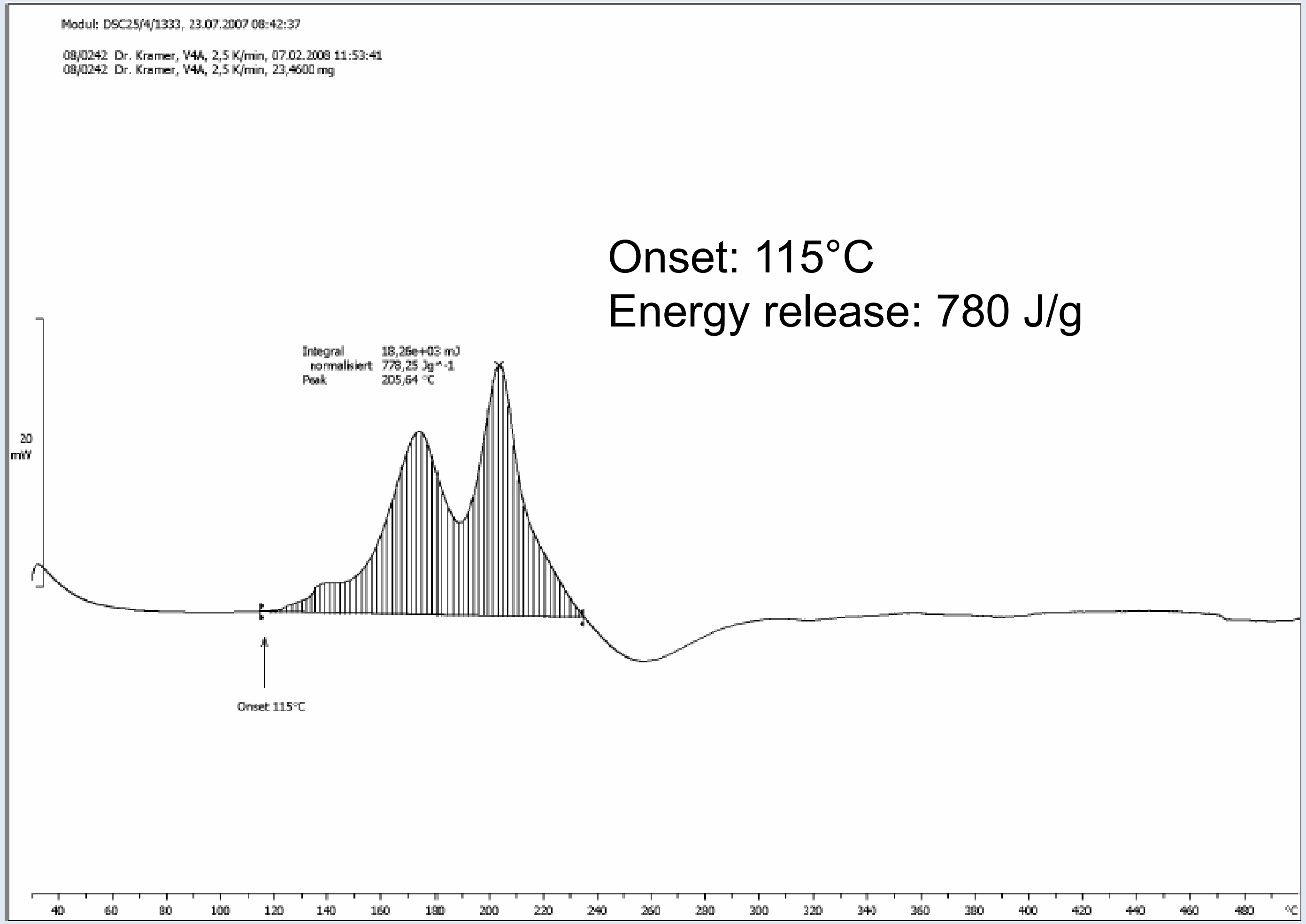
Sensitivity of the measurement methods vs. heat losses of different storage containers



- DSC: Sensitivity 5 - 10 W/kg at the "Onset"
- DWS/C80: Sensitivity 0.1 – 0.5 W/kg
- Critical heat flow is often not directly accessible
  - Extrapolations needed
  - **Extrapolations need to be validated**
    - Thermal Activity Monitor measurement (TAM)
- TAM: Sensitivity 0.001 W/kg

Initial Screening: DSC



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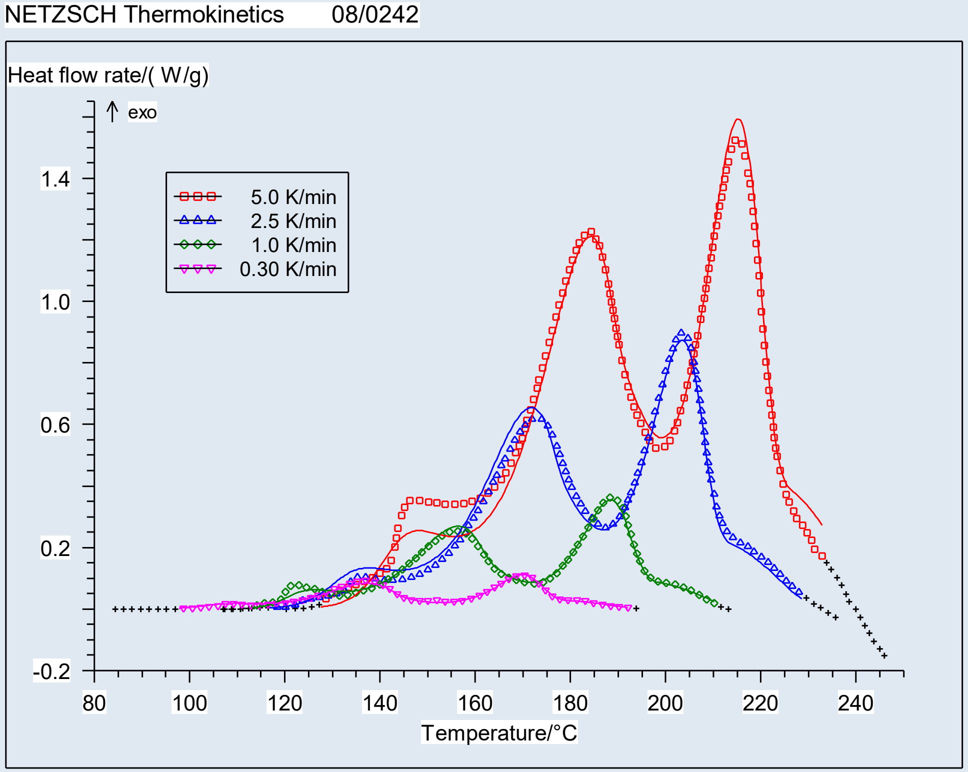
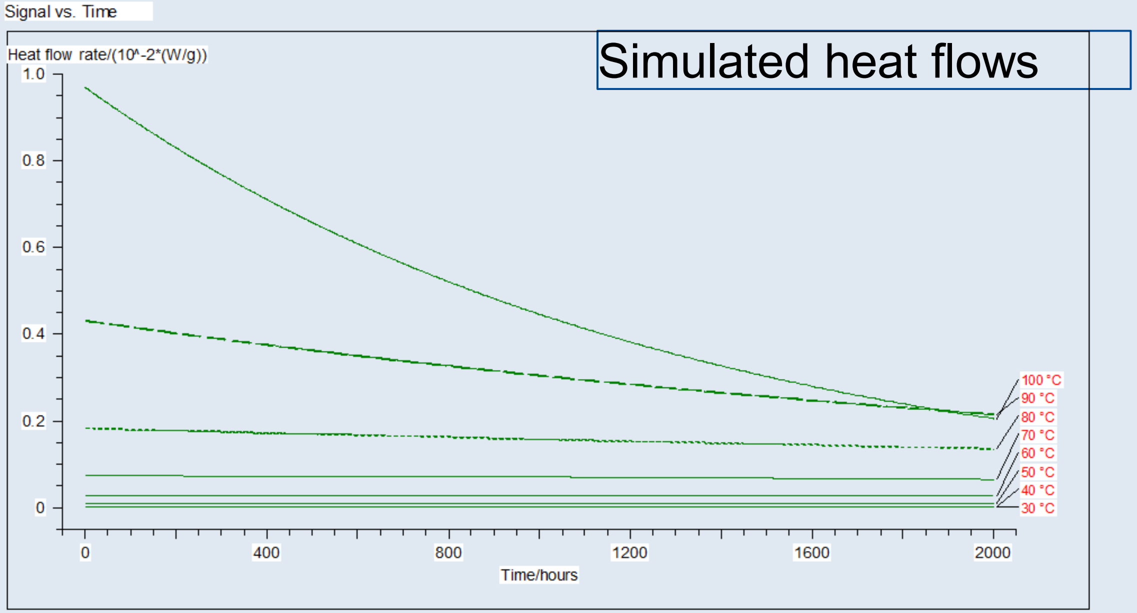
Extrapolation of Heat Flux
Kinetic Modelling of DSC Measurements (option 1)

- Scans must be deconvoluted
- One model must describe all measurements
- Strongly different heating rates recommended

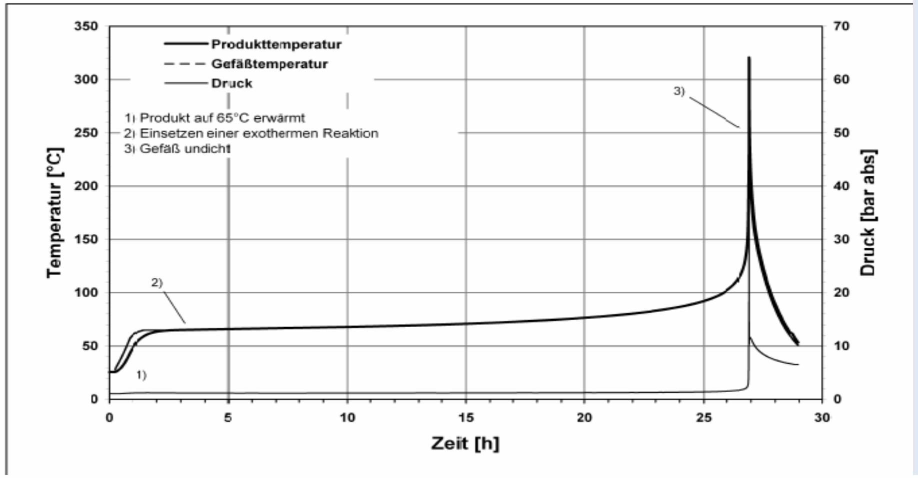


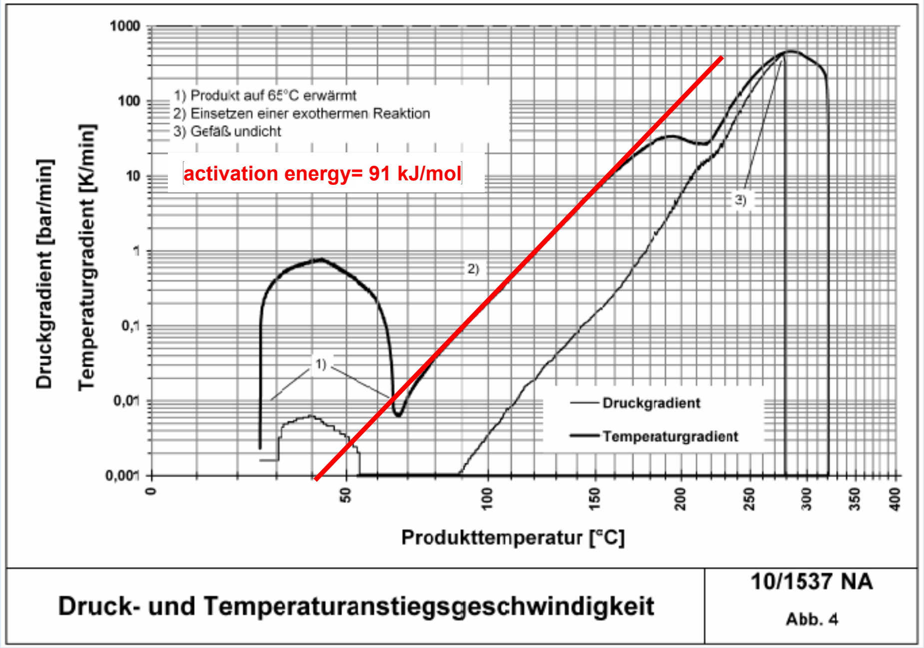
Points are measured values/solid line corresponds to the kinetic model



Extrapolation of the heat flux

Extrapolation of adiabatic measurements (Option 2)





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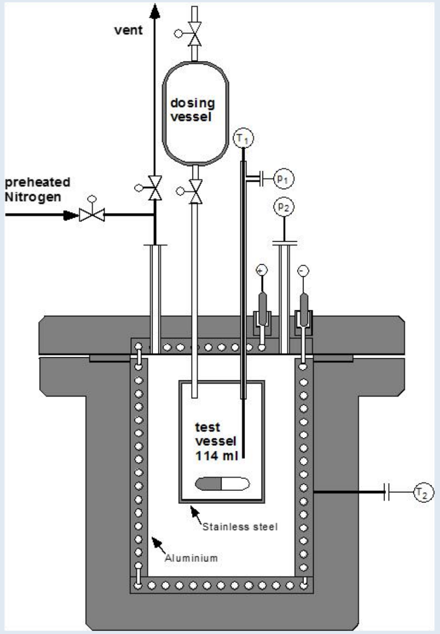

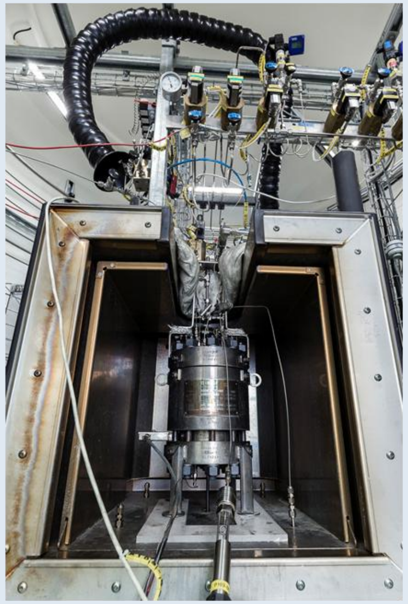

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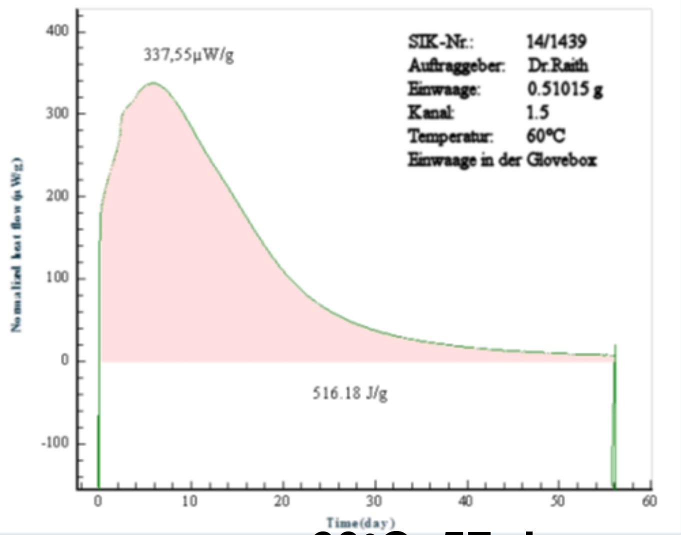
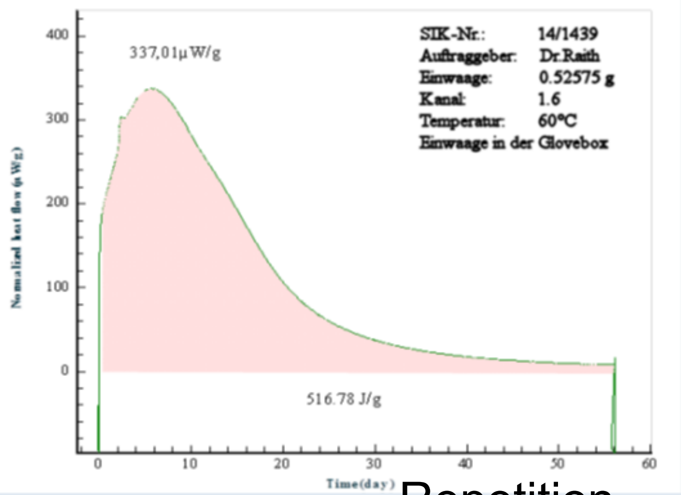
Model validation at low temperatures
Application of isothermal microcalorimetry



60°C, 57 days

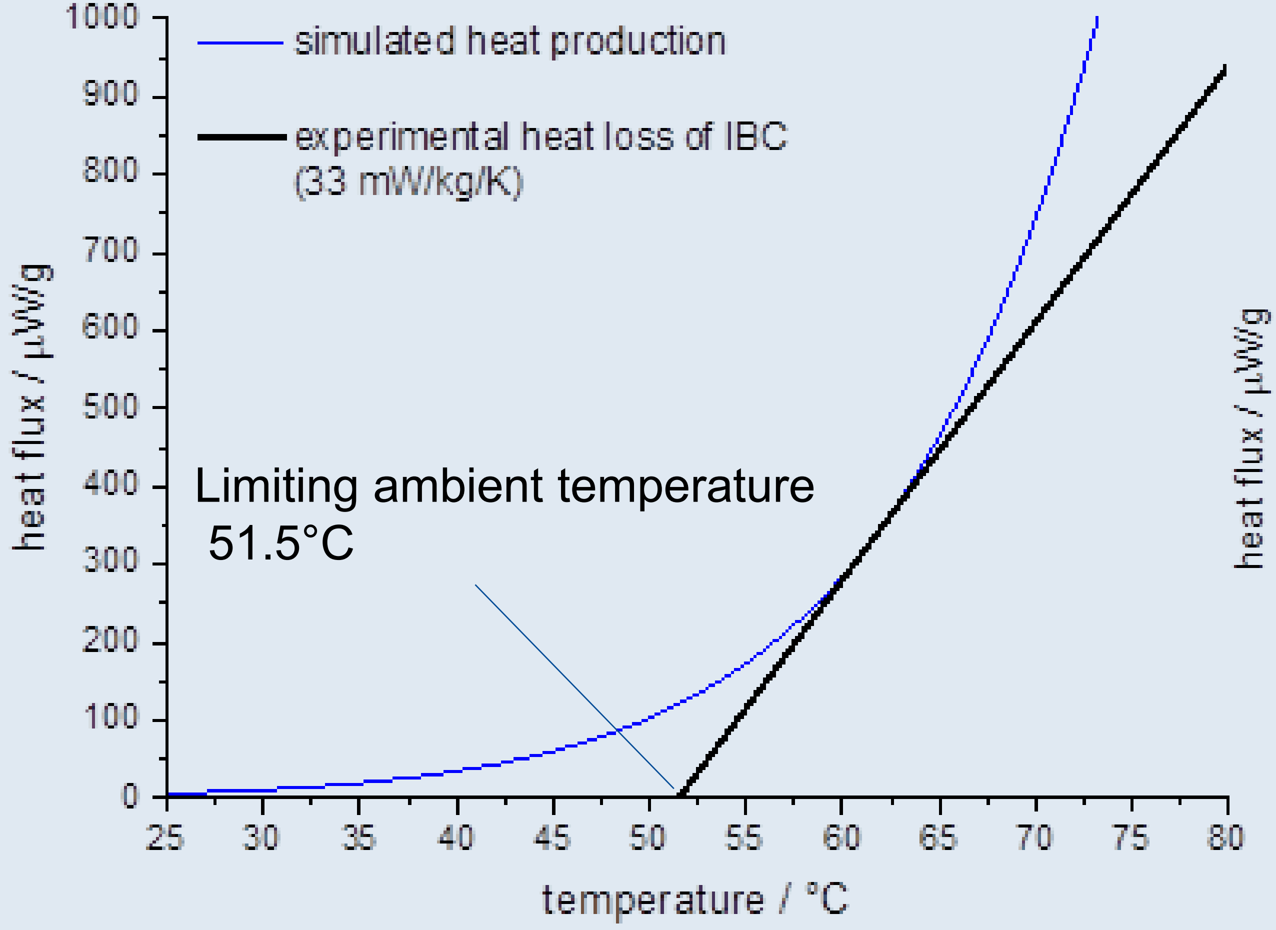


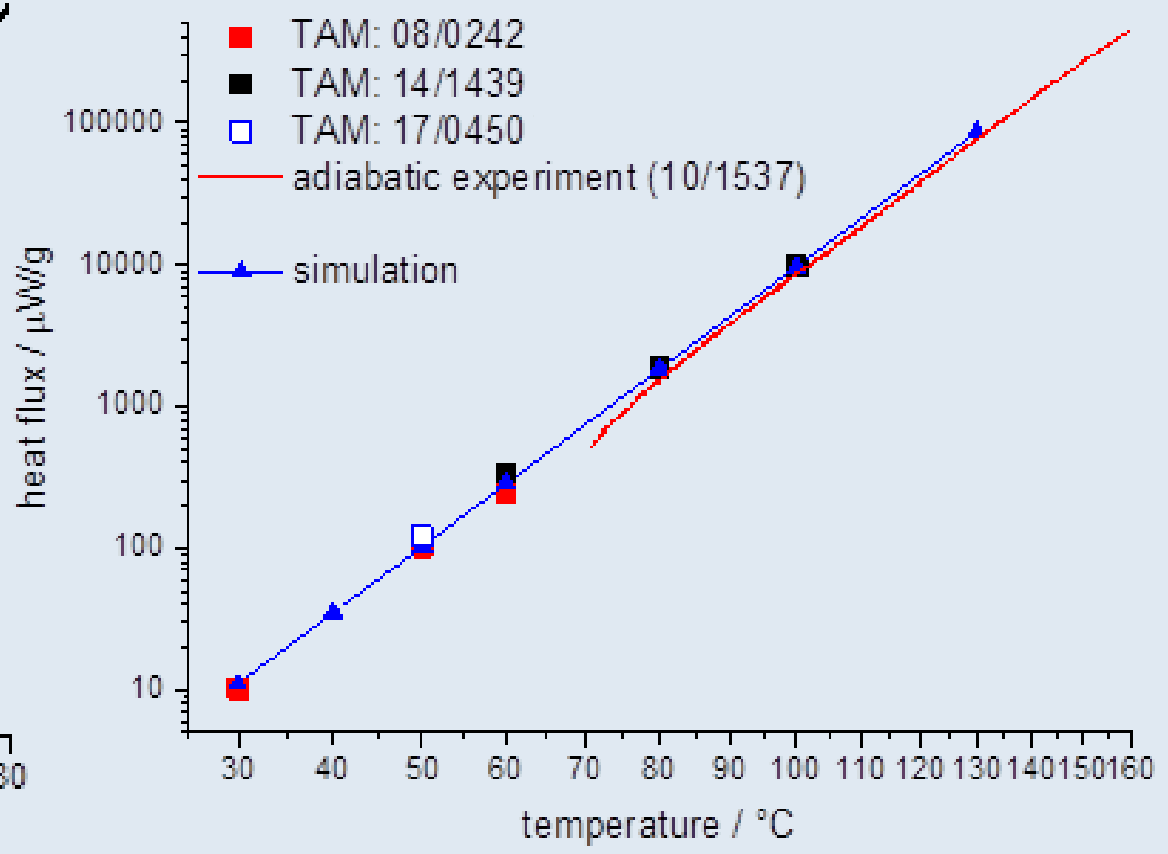
Repetition

Microcalorimetry

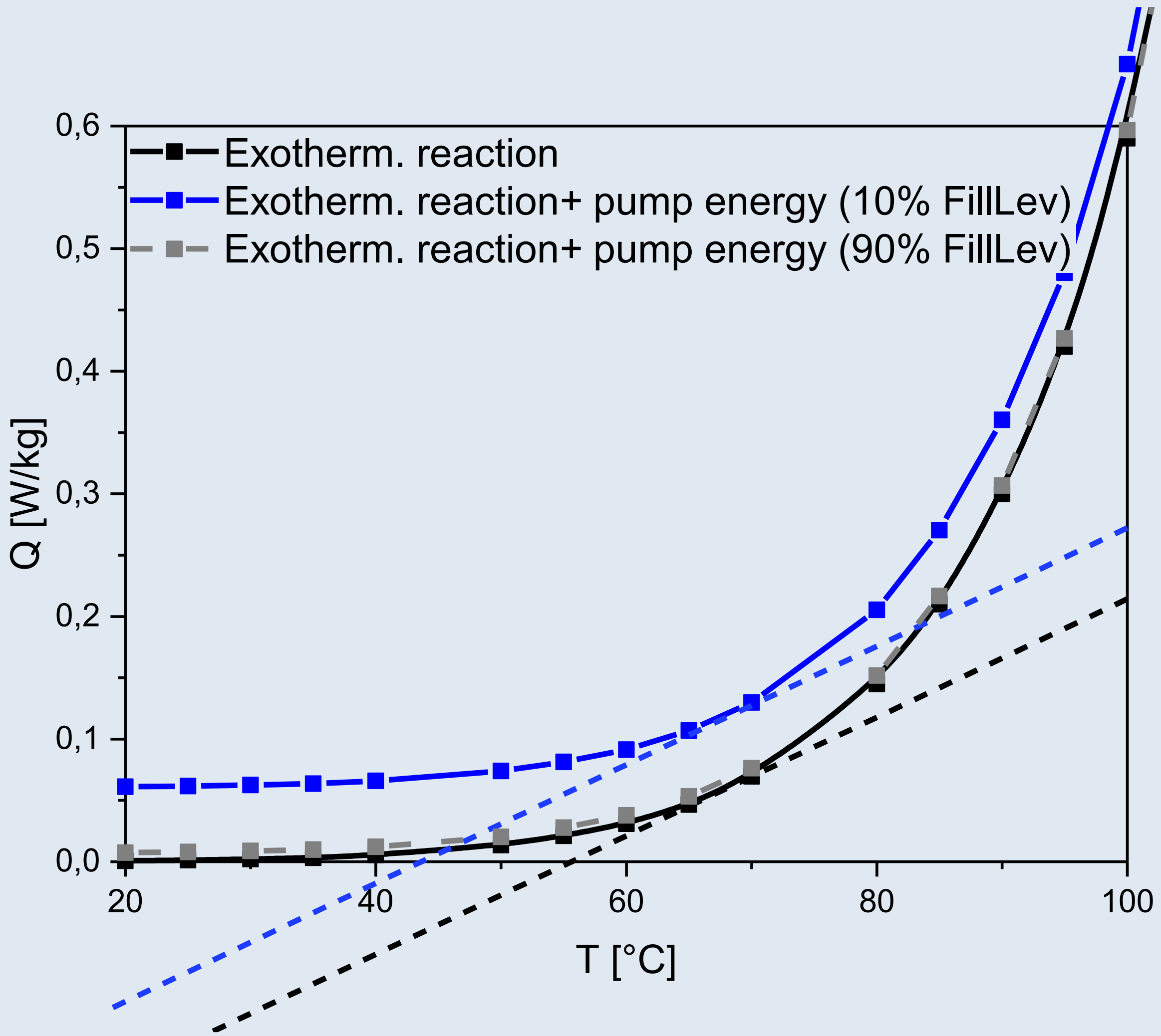
- Very high sensitivities in the range of 0.001 to 0.01 $W\ kg^{-1}W\ kg^{-1}$
- Low temperatures
- Catalytic effect of additives on decomposition reactions can be tested

Evaluation of Heat Flux Curve vs. Heat Loss Curve





Influence of other energy sources
(pumps, heat tracing in storage tanks)



- Input of other energies must be taken into account in addition to the heat production rate from the reaction.
- Energy input can depend on the filling degree (example mixing pump storage tank)!

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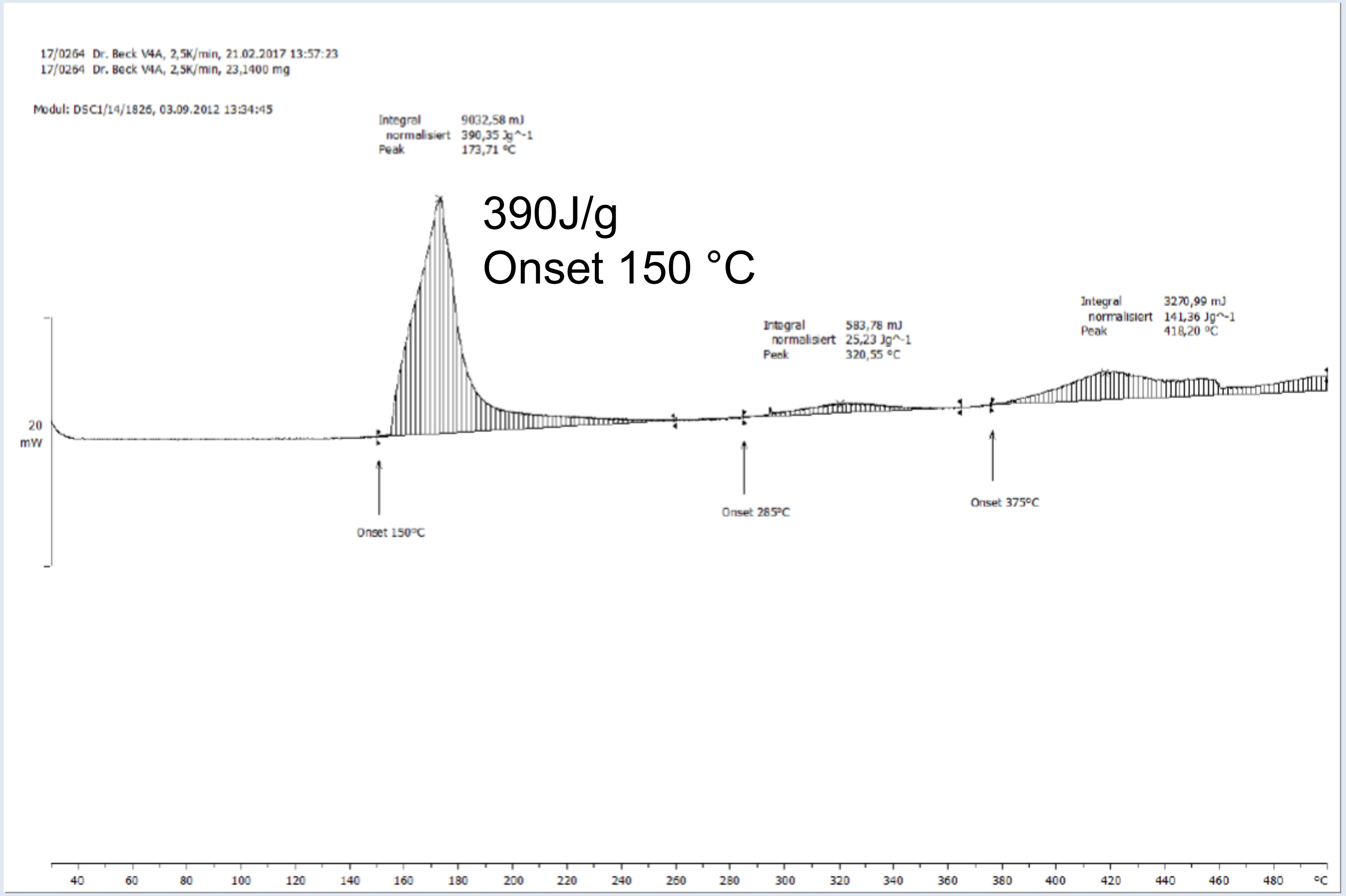
Stability of Inhibited Substances (monomers)

Special Features

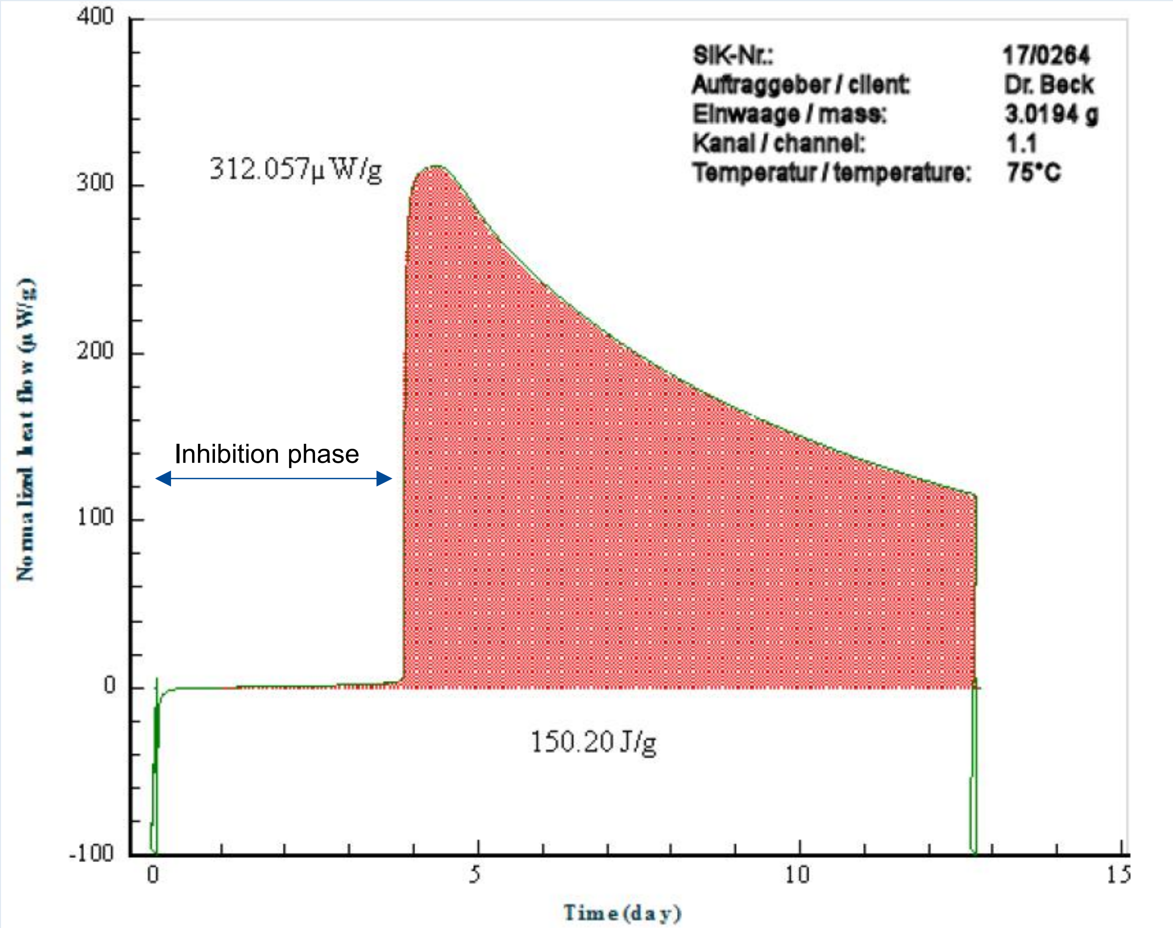
- Induction phase before the start of heat-production
- Onset (DSC) is highly dependent on sample history (temperature & time)
- Heating rate in dynamic DSC strongly influences the onset
- No 0th order approach allowed for initial heat production
- No simple onset rules applicable without further testing

➡ **PIT-Konzept (Polymerisation Induction Time)**

Inhibited Monomer Solution
Screening DSC (dynamic, 2.5 K/min)



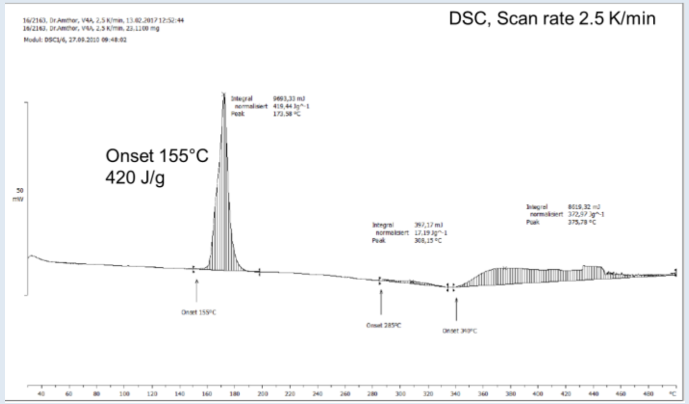
Inhibited monomer solution
isothermal measurement in TAM @75°C

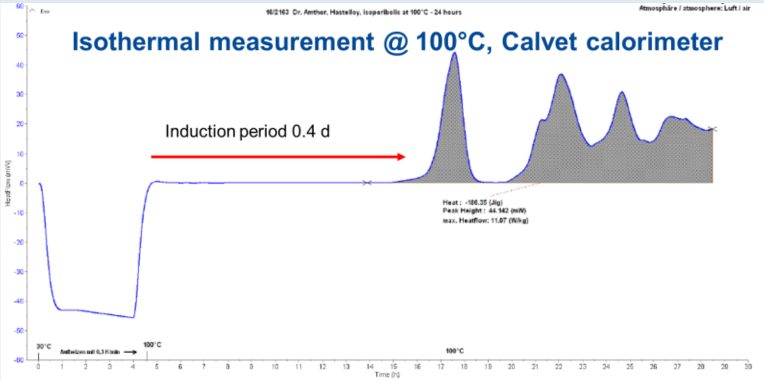


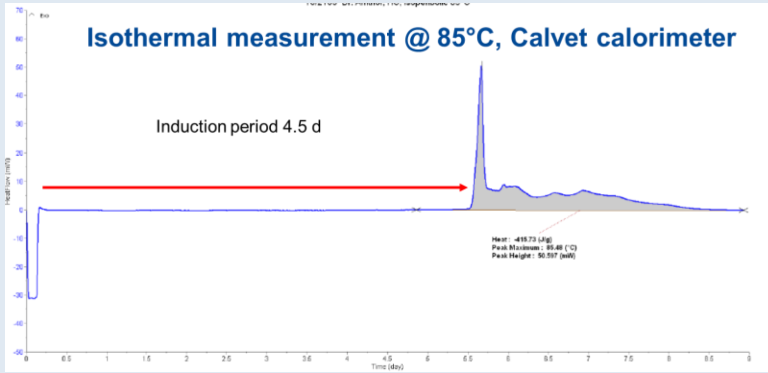
- Induction phase depends on the stabilizer depletion rate
- Polymerization induction time increases with decreasing temperature
- Max. heat flux after stabilizer depletion is sufficient for a thermal explosion in the package

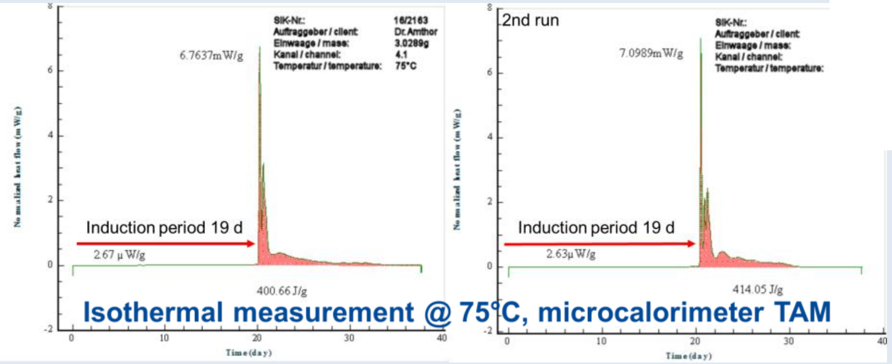
  Cf. Q_{crit}: 100mW/kg for 50kg)

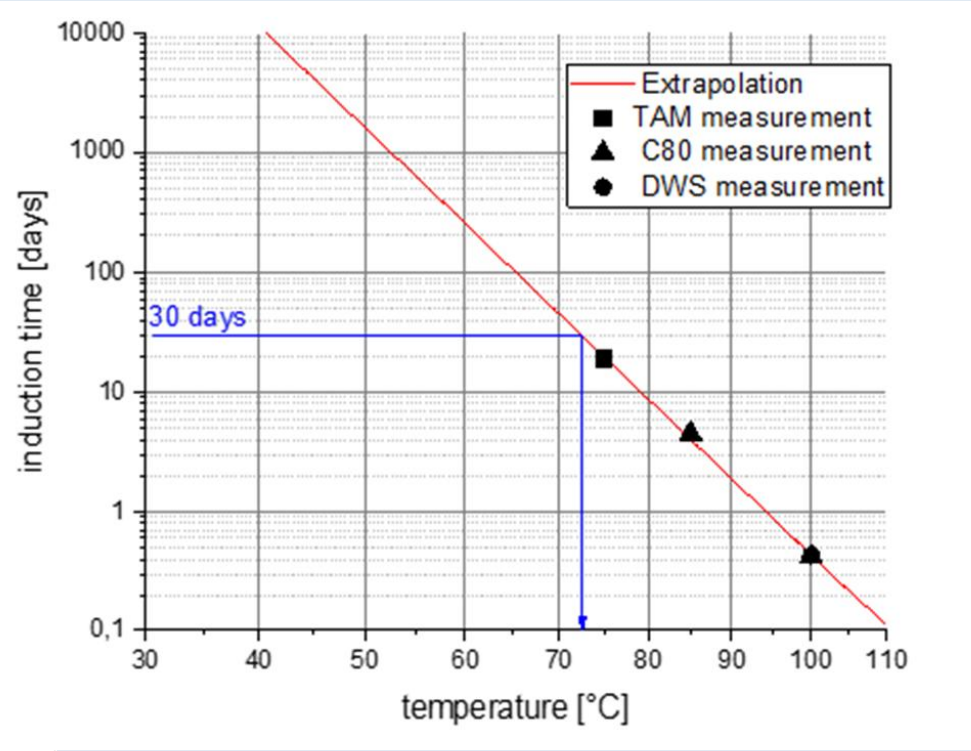
Assessment of a stabilized monomer solution- Extrapolation of PIT









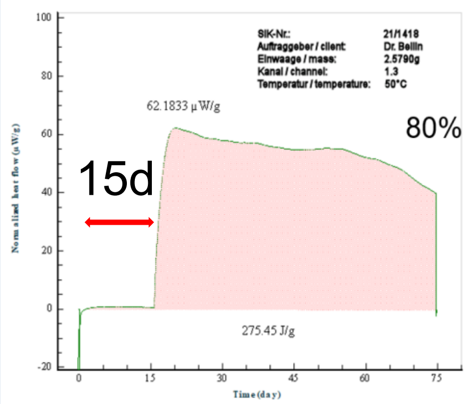


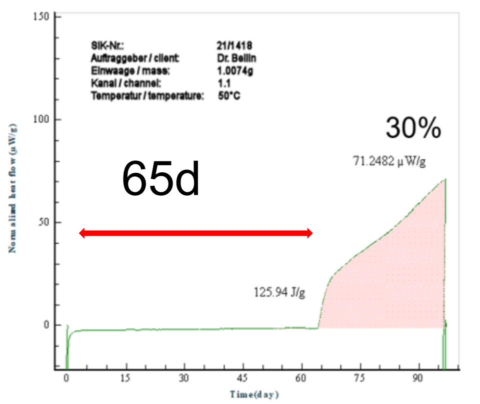
Meaningful extrapolation possible!

Important influencing factors in the evaluation of stabilized systems

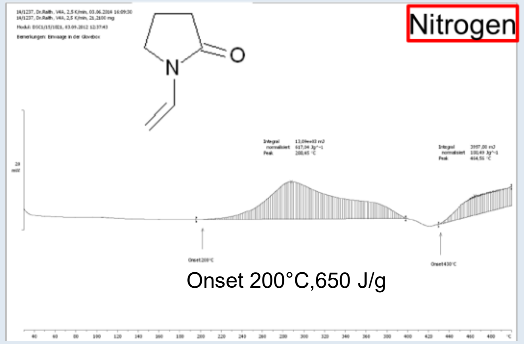
- **Amount of stabilizer**
  - Stabilizer is slowly consumed, degradation leads to polymerization
  - Duration of storage/transport
- **Type of stabilizer**
  - Is a specific gas atmosphere needed for effective stabilization? (E.g. MEHQ vs. PTZ for acrylates)
- **Influence of the gas atmosphere**
  - Oxygen can also trigger polymerization (e.g. vinyl monomers)
  - Fill level
  - Mixing
  - Condensation of non-stabilized monomer
- **Material**
  - Metals can affect the onset
- **Impurities** (example: peroxidation, acids, bases)
- **Non stabilized side reaction**
- **Heat loss of the container/tank under consideration**

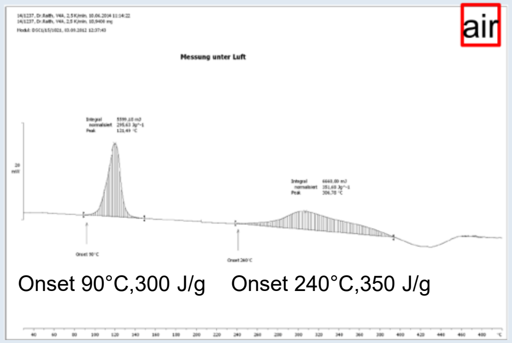
Examples - Influencing factors



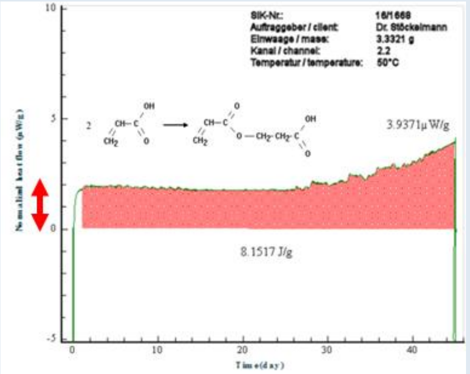


Fill level- closed cell – change of inhibition time
Stabilized Styrene, air, closed test cell, different fill levels





Gas atmosphere: nitrogen vs oxygen in DSC Screening-
Oxygen induces exothermic reaction



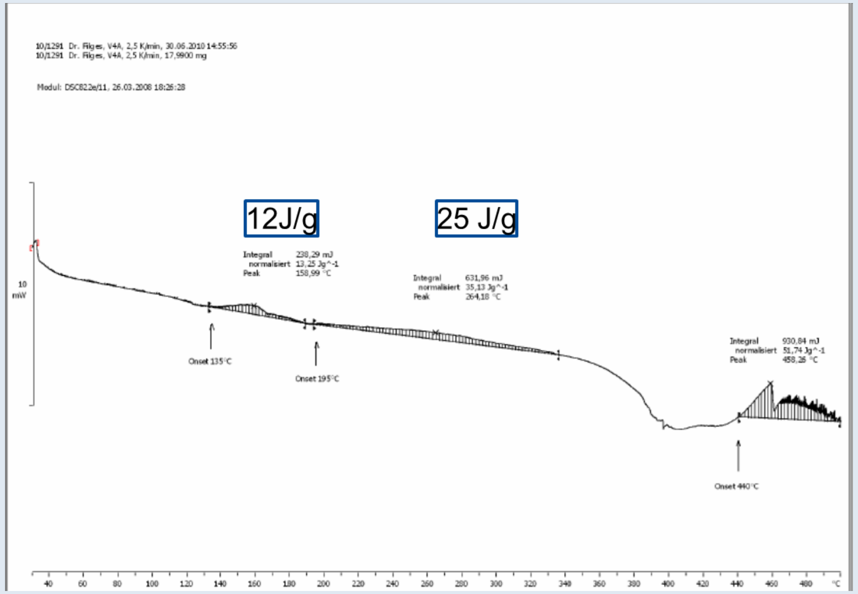
Heat release despite stabilization **by side reaction**!
May be relevant in large or well-insulated containers

Self-heating

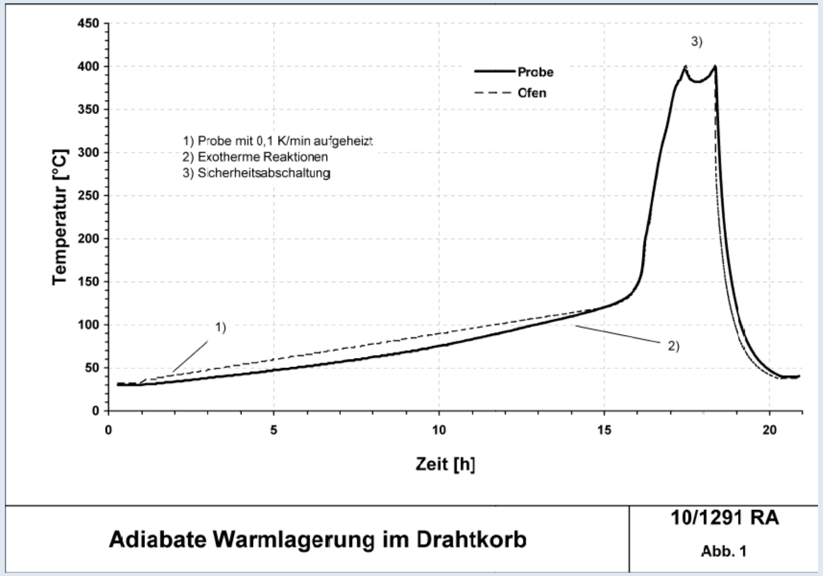
Thermal Stability of Solids, Powders

- Main thermal resistance lies in the powder itself
- Powders have large surface area
  - Additional heat production due to oxidation in addition to decomposition
  - Biological processes can provide heat
  - Adsorption of moisture can create additional temperature increase

Plastics Powder DSC Closed Crucible

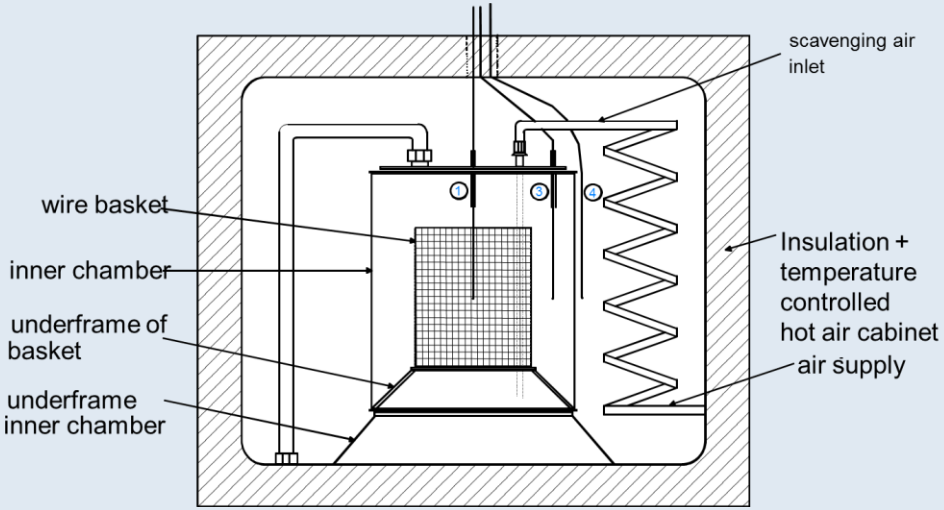


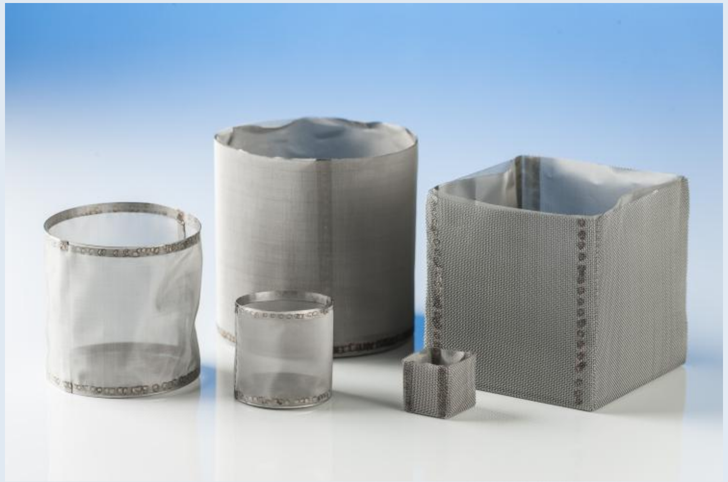
Self-heating test under air



Self-Heating tests for dusts and porous materials
(oxidative processes/self-heating)

Self-heating tests in wire baskets

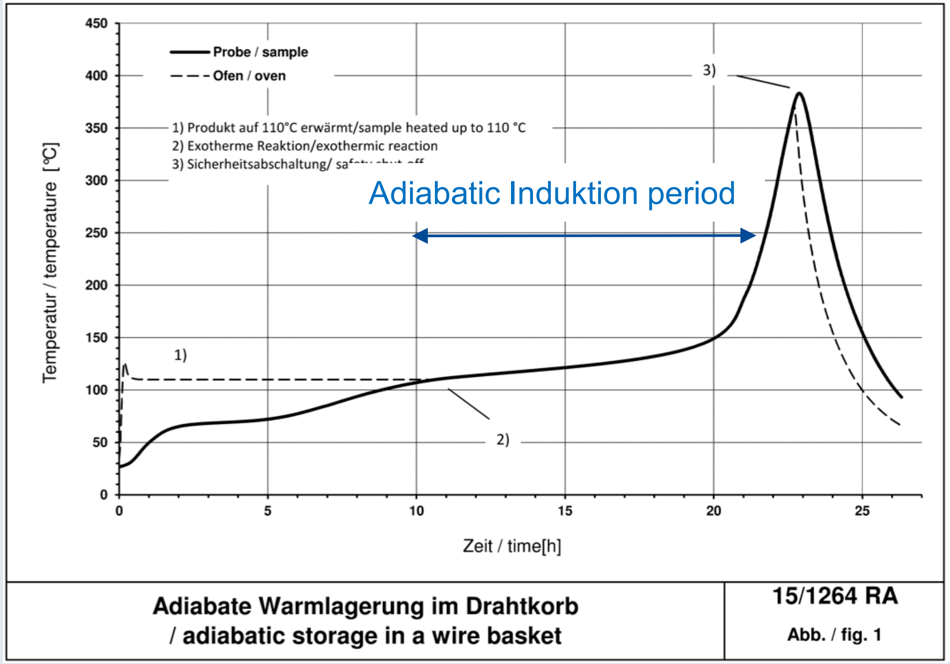




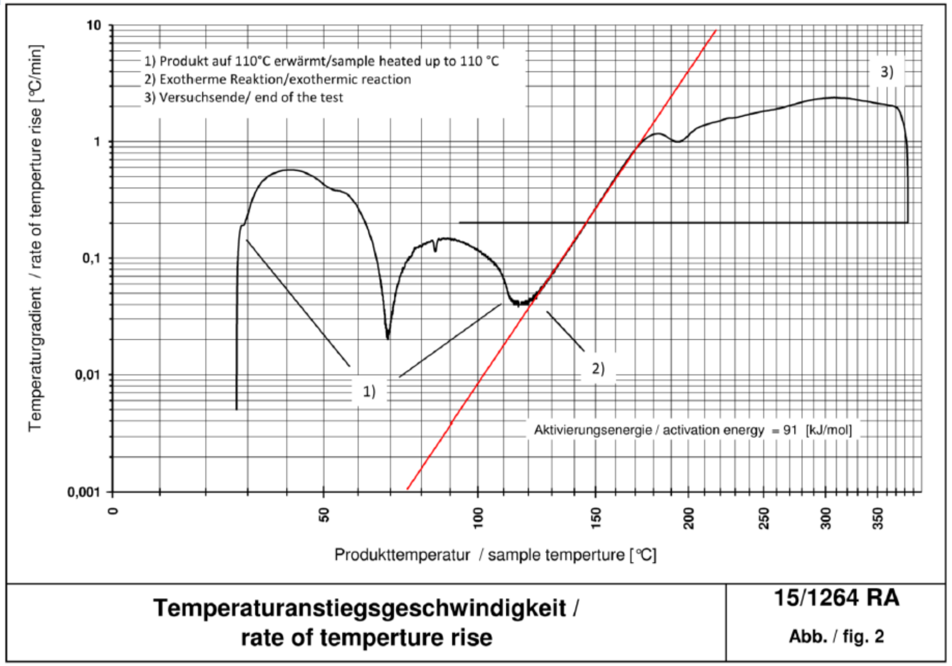
- Isoperibolic or adiabatic mode
- Temperature range up to 400°C
- 100ml -1000 ml

Example
(oxidative self-heating)

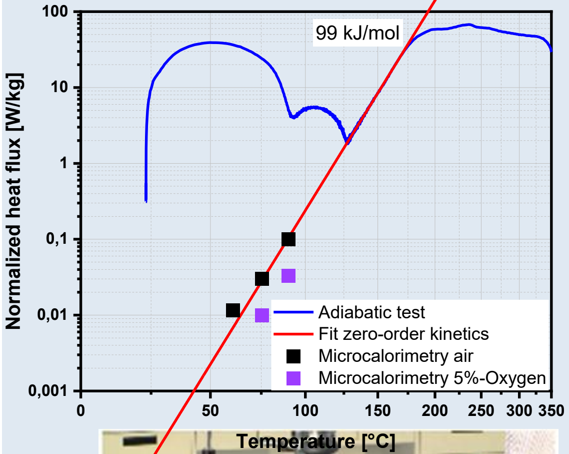
Adiabatic self-heating test

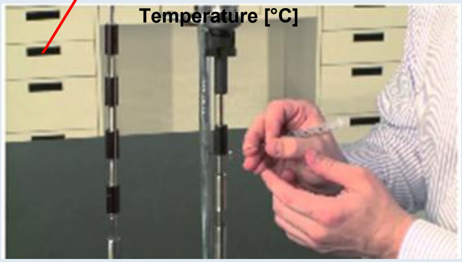


Kinetic evaluation



Check of model





TAM-perfusion cell

Estimation of apparent activation energy

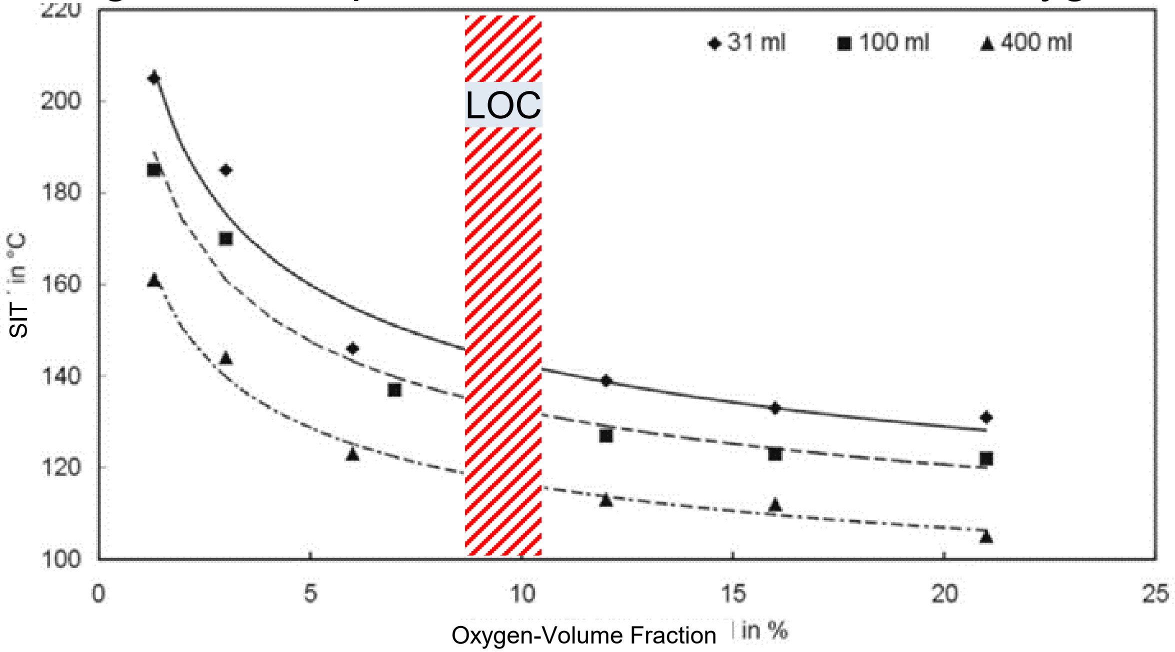
➡ Estimation of volume dependancy of SIT

$$\ln(k) = -\frac{E_A}{R} \cdot \frac{1}{T} + \text{const.}$$

y m x const.

Assessment of Self-heating

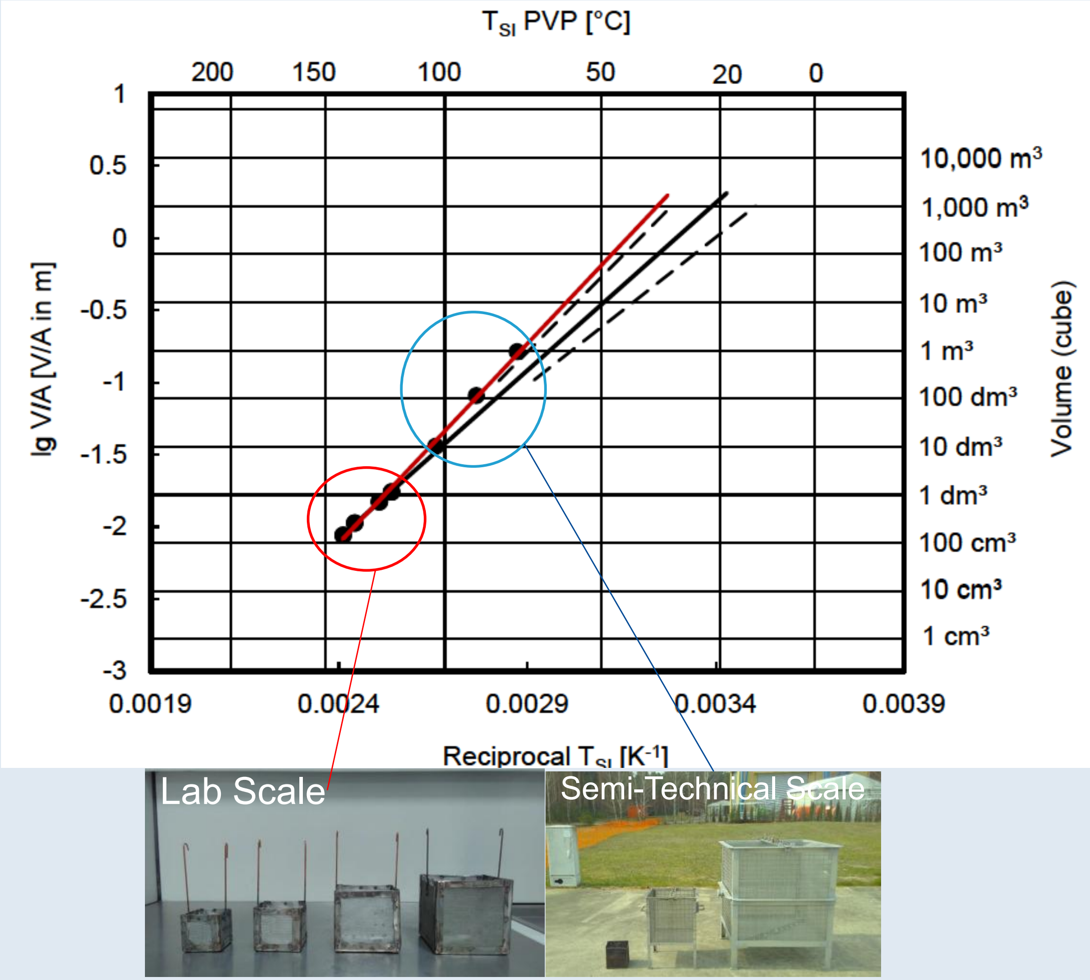
Self-Ignition-Temperature vs. Volume Fraction Oxygen



- Closed DSC is not sufficient for the assessment of self-heating
- Additional tests with air access required (wire basket tests)
- Self-heating is also possible in an oxygen-reduced atmosphere, even below LOC for dust explosion!

Source: BAM/BASF Research Report

Validation of Extrapolation Methods

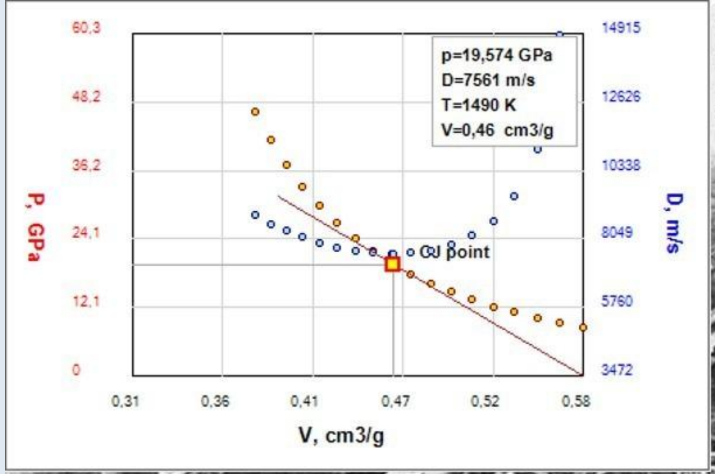


T_{SI} (1 m³) extrapolated from laboratory tests:

64.8 ± 6.5 °C (58.3 … 71.3 °C)

T_{SI} (1 m³) determined in semi-scale test:

75.1 °C

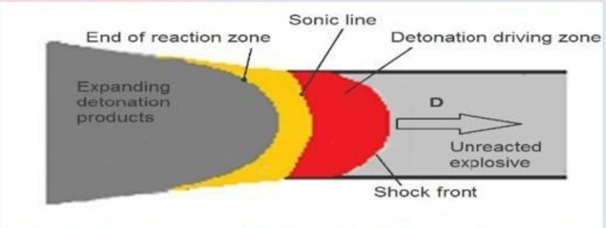



```
Detonation parameters (at the C-J point) :
------------------------------------------

      Heat of detonation                  = -1973,985   kJ/kg
      Detonation temperature              = 1490,314    K
      Detonation pressure                 = 19,57367  GPa
      Detonation velocity                 = 7560,572    m/s
      Particle velocity                   = 1491,443    m/s
      Sound velocity                      = 6069,129    m/s
      Density of  products                = 2,162405    g/cm3
      Volume of  products                 = 0,4624481   cm3/g
      Exponent 'Gamma'                    = 4,069279
      Moles of gaseous products           = 3,293894    mol/mol explosive
      Moles of condensed products         = 0,2061041   mol/mol explosive
      Volume of gas at STP                = 887,3507   dm3/kg
      Mean molecular mass of gas. prod. = 21,42324  g/mol
      Mean molecular mass of cond.prod. = 98,079  g/mol
      Mean molecular mass of all prod.  = 25,93727  g/mol
      Entropy of products                 = 5,658  kJ/kg K
      Internal energy of products         = 3086,198    kJ/kg,  i.e.  5,357133  kJ/cm3
```

Explosive Properties

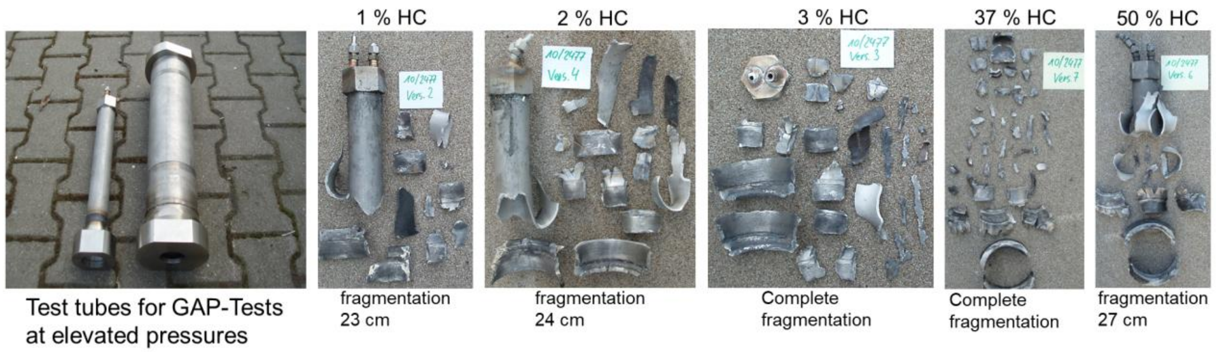
VUE AÉRIENNE DE L'USINE DE LA « BADISCHE ANILIN UND SODA FABRIK », A OPPAU, APRÈS LA FORMIDABLE EXPLOSION DU 21
Au premier plan, le cratère formé par la mystérieuse déflagration et à demi rempli d'eau par les canalisations rompues et par les infiltrations souterraines; au delà, les bâtiments rasés ou déf
Photographie prise d'un avion spécialement envoyé sur les lieux, pour L'Illustration, par la Compagnie Aérienne Française — Tous droits réservés.



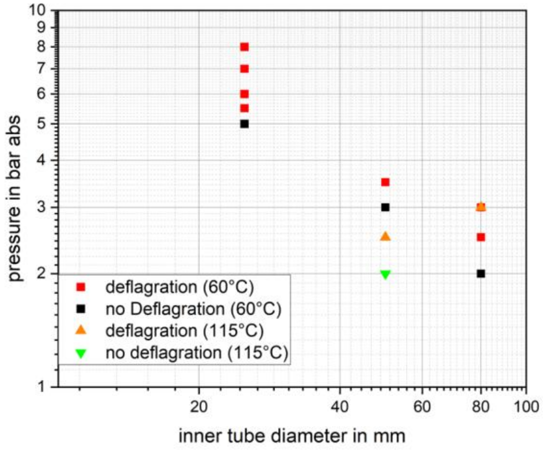
Exclusion of Explosive Properties for Insensitive Energetic Materials

- Evaluation of mass explosion hazard is carried out analogous to UN gap test in 2" and 4" steel tubes.
- Evaluation is carried out in the cavitated state, without gap
- Testing of sensitizers
- Deflagration properties: test also at elevated pressures
- Design of deflagration traps to protect large volumes (Ignition by feed pumps, runaway in the reactor, transition from gas phase deflagration)

Sensitisation of a liquified Oxidizer with Hydrocarbon



Deflagration as function of pressure and diameter



$v = a \cdot p^n + b$, n= 0,5 to 1

$d_{quench} \propto p^m$, m≈-1

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Onset rules for storage stability
Estimation via DSC-Onset

Maximum permissible heat flux:

$$\dot{Q}_{crit\_SADT} = \frac{R \cdot T^2}{E} L \cdot \frac{1}{e}$$

Calculation of corresponding onset:

$$T_{onset\_DSC} = \frac{1}{\frac{R}{E} \cdot \ln\left(\frac{\dot{Q}_{crit\_SADT}}{\dot{Q}_{DSC\_onset}}\right) + \frac{1}{T_{SADT}}}$$

DSC Onset Sensitivity: 5 – 20 W/kg, (20 W/kg for estimation)
Activation energy: 50 – 200 kJ/mol

$$\frac{\tau_{relax}}{\tau_{chem}} = const. = 1/e$$

$$L = \frac{\ln 2}{t_{1/2}} \cdot c_p = \frac{c_p}{\tau_{relax}}$$

$$\tau_{chem} = \frac{c_p \cdot R \cdot T^2}{E \cdot \dot{Q}_T}$$

$$\dot{Q}_{crit} = \frac{R \cdot T^2}{E} L \cdot \text{const.}$$

Examples:

BASF-Onset –Rules for non viscous liquids:

- **Onset > 175° C => SADT> 75° C up to 50 kg (non insulated)**
- **Onset > 175° C => SADT> 50° C for IBC (L=30 mW/kg K)**
- **Onset > 200° C => SADT/SAPT > 45° C for 20 m^3-Container (insulated) (L=1.7 mW/kg K)**

Note: Only valid, if no onset shift due to autocatalysis or loss of inhibition during storage.
Further DSC-scan of thermally aged material always required!

Screening Procedures for Self-Reactive Substances, Differential Scanning Calorimetry-Onset and Heat-Flux Criteria
Dr. Markus Gödde, Jörg Clemens, Dr. Marcus Malow
Chemical Engineering & Technology, Volume 48, Issue3, March 2025

Correlation of T. Yoshida - Identification of Explosive Properties via DSC

Prediction of fire and explosion hazards for reactive chemicals (I):
Estimation of the explosive properties of self-reactive chemicals from SC-DSC data, T. Yoshida, 1997

- Correlation for shock sensitivity (Drop-hammer):
  $$SS = \log(Q_{dsc}) - 0.72 \times \log(T_{dsc}-25) - 0.98$$
- Correlation for explosion propagation (Detonation)
  $$EP = \log(Q_{dsc}) - 0.38 \times \log(T_{dsc}-25) - 1.67$$

with Q_{dsc} in cal/g ; T_{dsc} in °C

T in °C	limit SS in J/g	limit EP in J/g
50	405	664
100	894	1009
150	1291	1225
200	1645	1392
250	1971	1531
300	2278	1652
350	2569	1761
400	2848	1859
450	3116	1950
500	3376	2034

- Check of Yoshida Correlation with BASF data: Yoshida plots are applicable for “normal” organic substances
- Positive results below Yoshida’s curve for shock sensitivity can be obtained for heavy metal salts or inhomogeneous mixtures, thermites (DSC-onset >500°C)
- Explosion propagation EP-curve (detonation propagation) not violated by data for test series 2

Conclusions

- Consideration of the heat balance required, attention to other energy inputs
- For chemically stabilized materials, the PIT concept based on isothermal measurements is preferred
- High sensitivity of test methods required
- Extrapolations must be validated
- Interaction of the substances with container materials, the gas atmosphere (stabilization, peroxidation,..)
- Oxidative self-heating of solids ≠ decomposition
- For energetic substances mass explosion hazards should be excluded
- DSC-based screening is possible

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We create chemistry

2004-2022
Head of "Exothermic Reactions & Classification Tests“ and Senior Principal Scientist Safety Assessment , BASF Safety Engineering,

2003-2004
BASF Process Safety Consultant

1999-2003
Research Engineer, BASF Safety Engineering,
Assessment of ignition sources, explosion phenomena of gases, vapours and dusts

1994-1999
Physikalisch-Technische Bundesanstalt, Braunschweig, Department of Thermodynamics and Explosion Protection, Physical Ignition Processes, Safety Characteristics

Markus Gödde, BASF Process Safety- Group Research
Phone: +49 621 60-78673, Mobile: +49 174 3495957, Email: markus.goedde@basf.com
Postal Address: BASF SE, RG/PE - B1, Carl-Bosch-Strasse 38, 67056 Ludwigshafen am Rhein, Germany