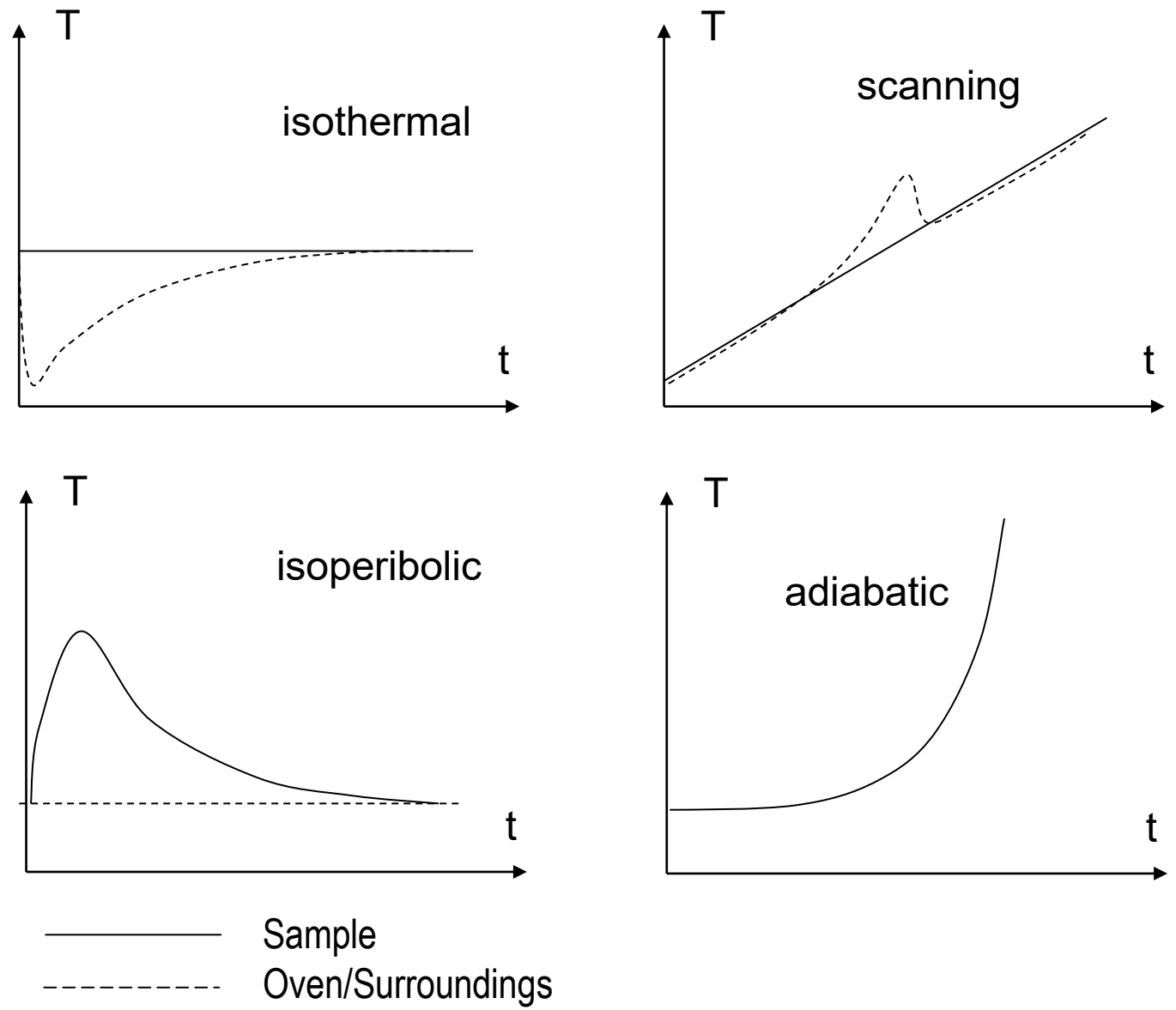
Calorimetry and Thermal Analyses
Applications in Process Safety

Module 3

ENG 431: Safety of chemical Processes

Annik Nanchen

Temperature programme (mode of operation)



Adiabacity Factor

Φ-Factor

- Thermal Inertia of the System/Apparatus
- Part of the reaction heat is used to heat up the calorimetric cell

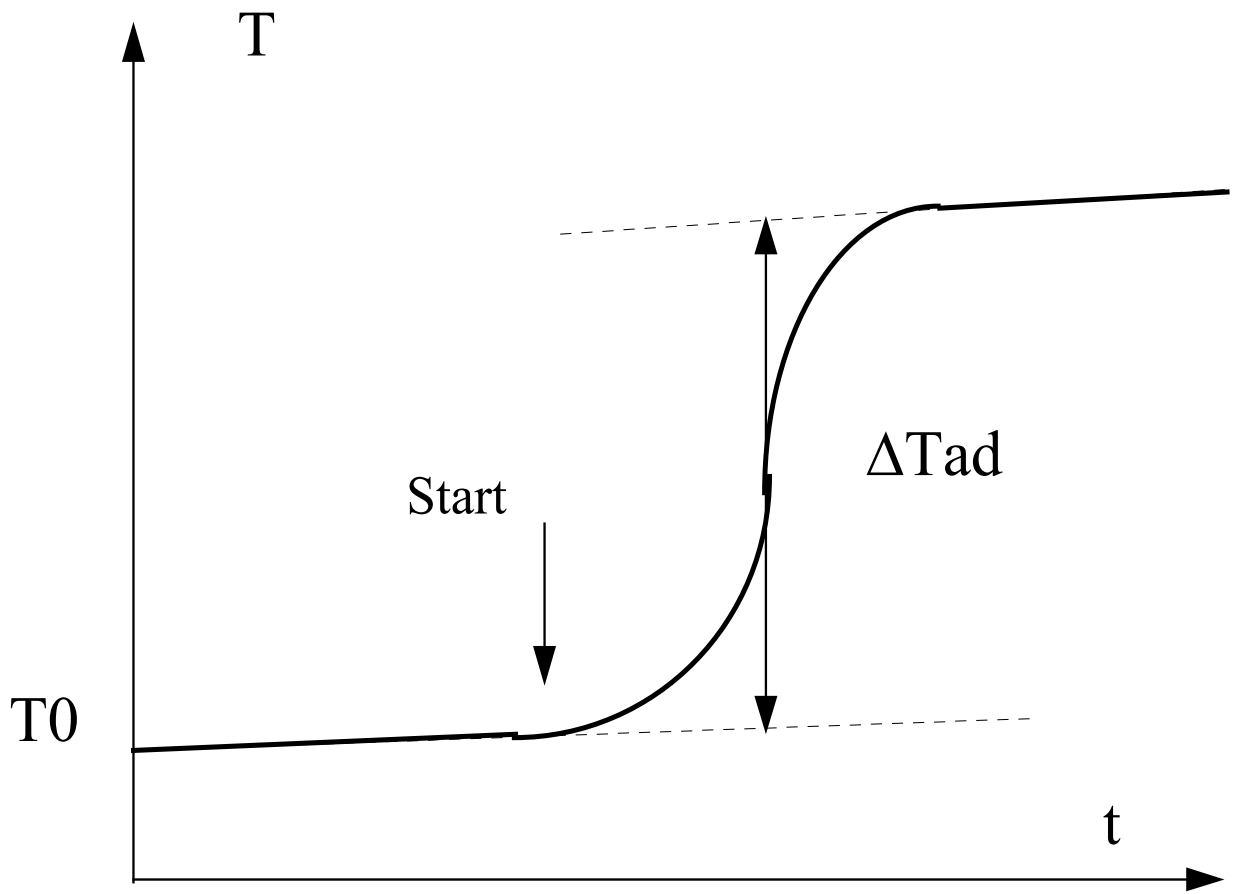
$$\Phi = \frac{M_r \cdot c'_{p,r} + M_{cell} \cdot c'_{p,cell}}{M_r \cdot c'_{p,r}} = 1 + \frac{M_{cell} \cdot c'_{p,cell}}{M_r \cdot c'_{p,r}}$$

- A perfectly adiabatic system has a Φ factor of 1
- M_{cell} large → Φ factor increases

Correction for Φ > 1

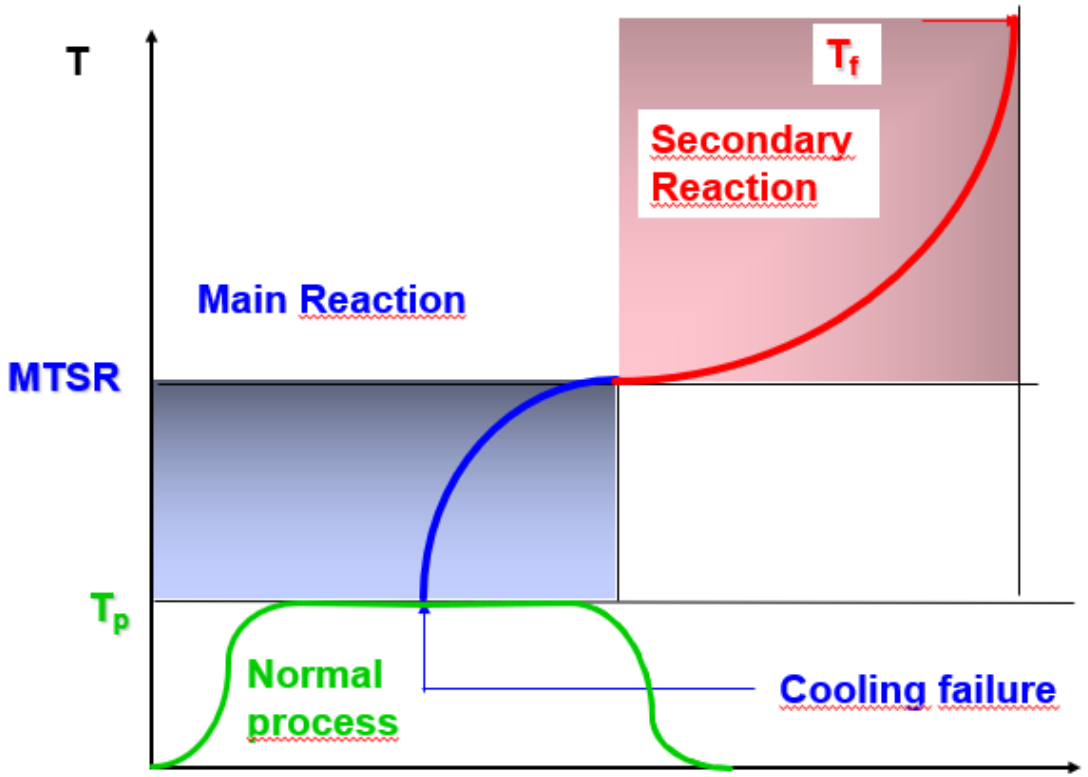
$$\Delta T_{ad} = \Phi \cdot \Delta T_{mes}$$

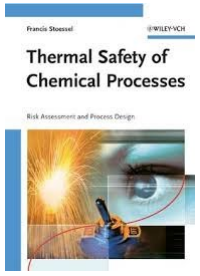
$$T_f = T_0 + \Phi \cdot \Delta T_{mes}$$

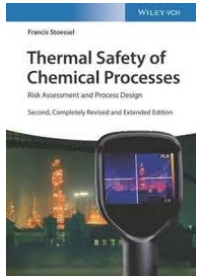


What calorimetric measurements are used to assess the cooling failure scenario?

- Main reaction
  - Mainly Reaction Calorimetry
  - Screening: micro-calorimetry
- Secondary reaction
  - Micro-calorimetry
  - Adiabatic measurements
  - High sensitivity calorimetry
- Both
  - Adiabatic measurements
  - Micro-calorimetry





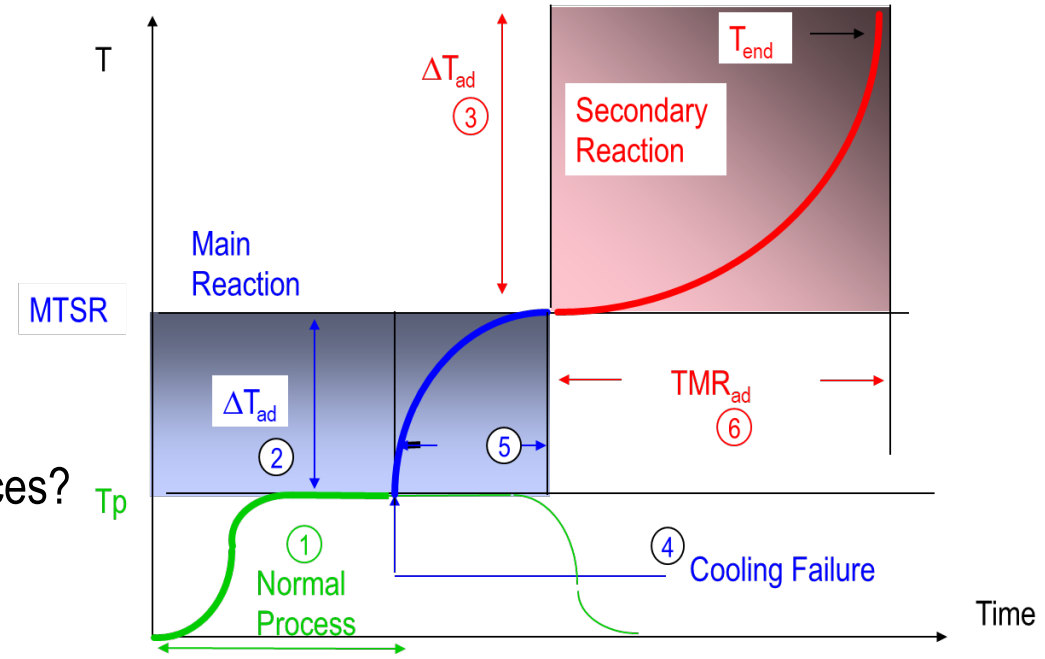


Chapter 4

Synthesis Reaction - Data

- Heat release rate under normal process conditions
  - Question 1: is there enough cooling capacity for isothermal conditions?
- Reaction Energy
  - Thermal Potential/Consequences
  - Question 2: how high is the MTSR (maximum temperature of the synthesis reaction)?
- Accumulation
  - Thermal Potential/Consequences
  - Question 2: how high is the MTSR (maximum temperature of the synthesis reaction)?
  - Question 4: when does the cooling failure have the worst consequences?

- Reaction calorimetry to get heat release rate, reaction energy and accumulation
  - RC1, CPA
- Screening methods will only provide the reaction energy
  - DSC, C80



Reaction Calorimetry

- Reproduce the reaction as done/foreseen at industrial scale

Reaction Calorimetry

Principles

- Heat Balance
  - Balance on the heat carrier in the jacket

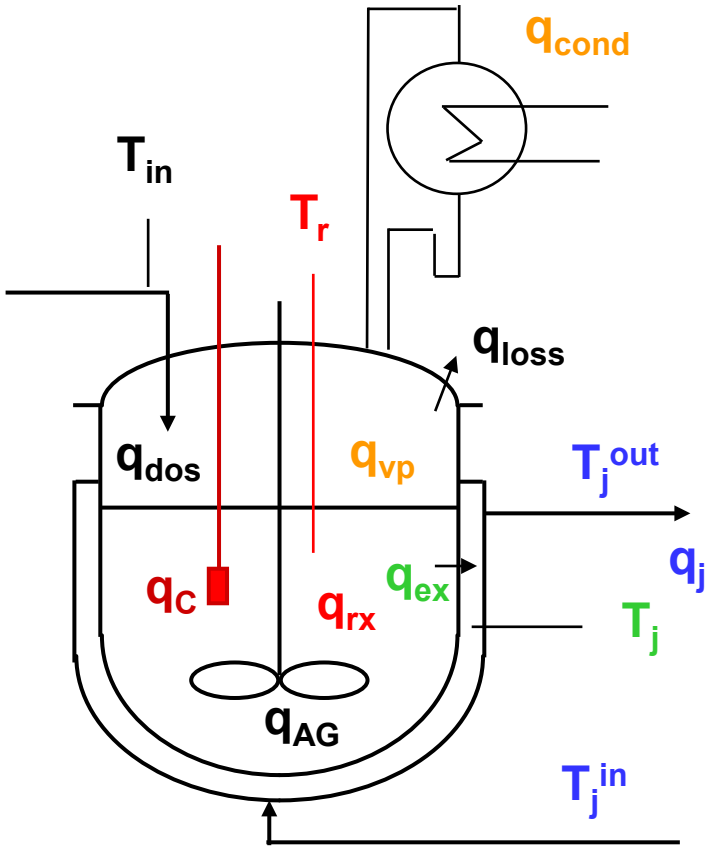
$$q_j = \dot{m} \cdot Cp' \cdot \left(T_{j,out} - T_{j,in} \right)$$

- Heat flow
  - Measuring the heat flow exchanged with the jacket

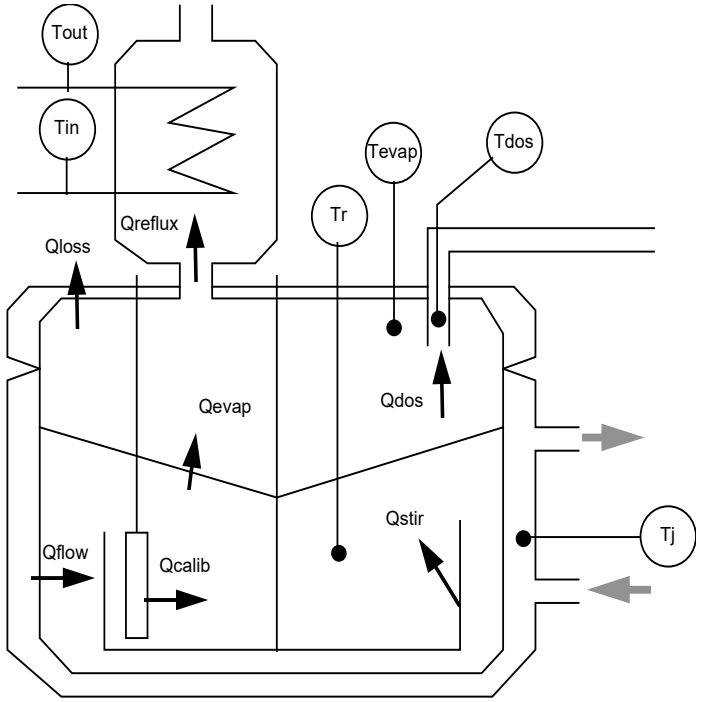
$$q_{EX} = U \cdot A \cdot \left(T_j - T_R \right)$$

- Compensation
  - Measuring the power of an electrical heater maintaining the temperature at set point with surplus cooling

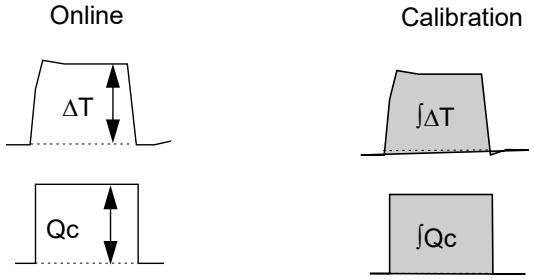
q_{RX} linked to q_c



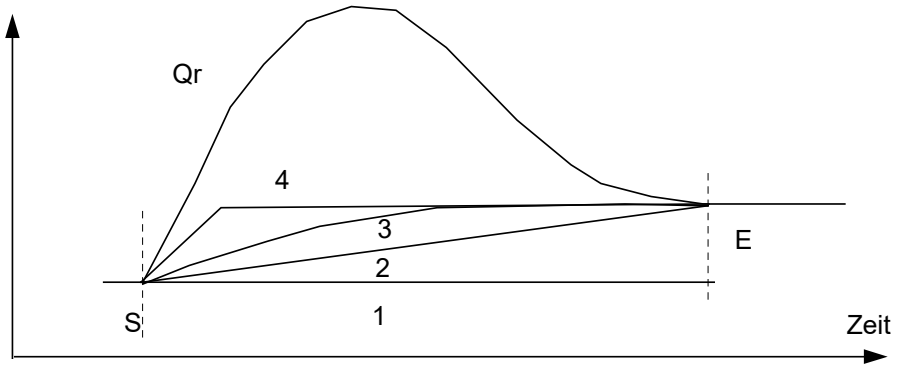
Reaction Calorimetry



Calibration



Baseline



Heat flow calorimetry

$$q_{AC} = q_{RX} + q_{EX} + q_{dos} + q_{VP} + q_{AG} + q_{Loss}$$

=0

Unknown

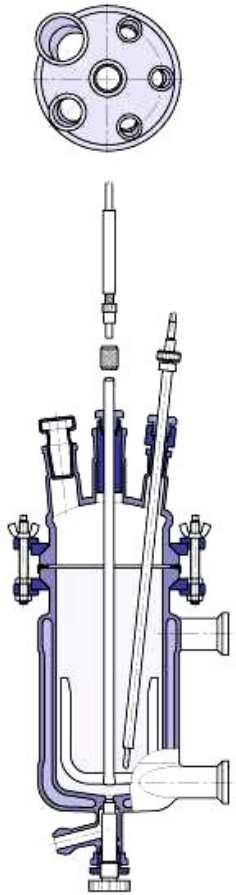
Measure

Calculated

Baseline

Reaction Calorimetry

- Preparative scale (100 ml to 2 L)
- Stirred tank reactor
- Controlled feed of reactant
- Distillation
- Mimics industrial processes
- Physical similarity
- Scale up data

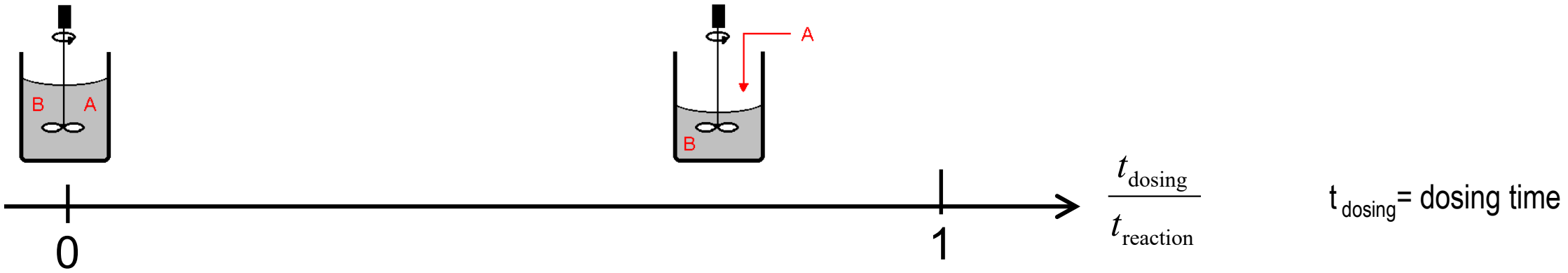


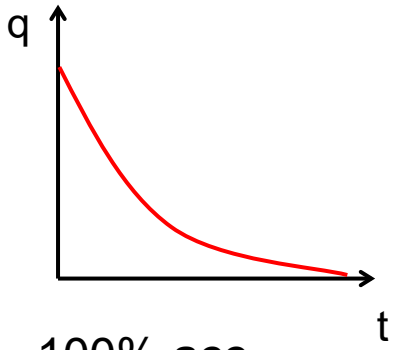
RC1 Reaction Calorimeter

RC1-Calorimeter, Mettler-Toledo:

- T: -20 – 200°C
- P: 0 – 50 bar
- V: 200 – 800 ml

Dosing of Reagents – Batch - Semi-Batch:

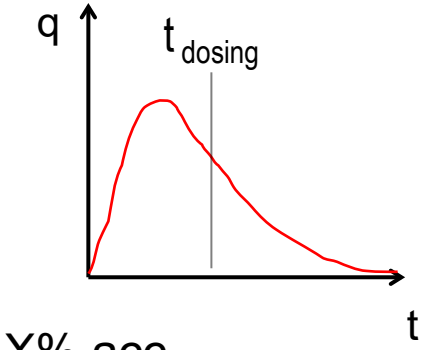




100% acc.

$\Delta T_{acc} = \Delta T_{ad}$

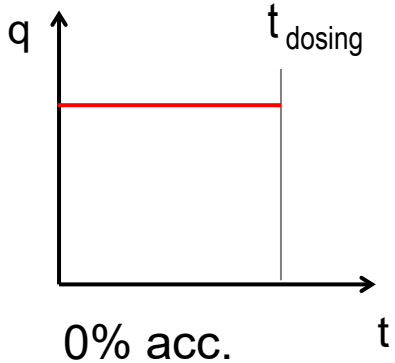
Batch



X% acc.

$\Delta T_{acc}(t) = \Delta T_{ad} \cdot X_{acc}(t)$

Semi-Batch



0% acc.

$\Delta T_{acc} = 0$

Semi-Batch
controlled by dosing

- ΔT_{acc} is the temperature increase that has to be considered when calculating the MTSR

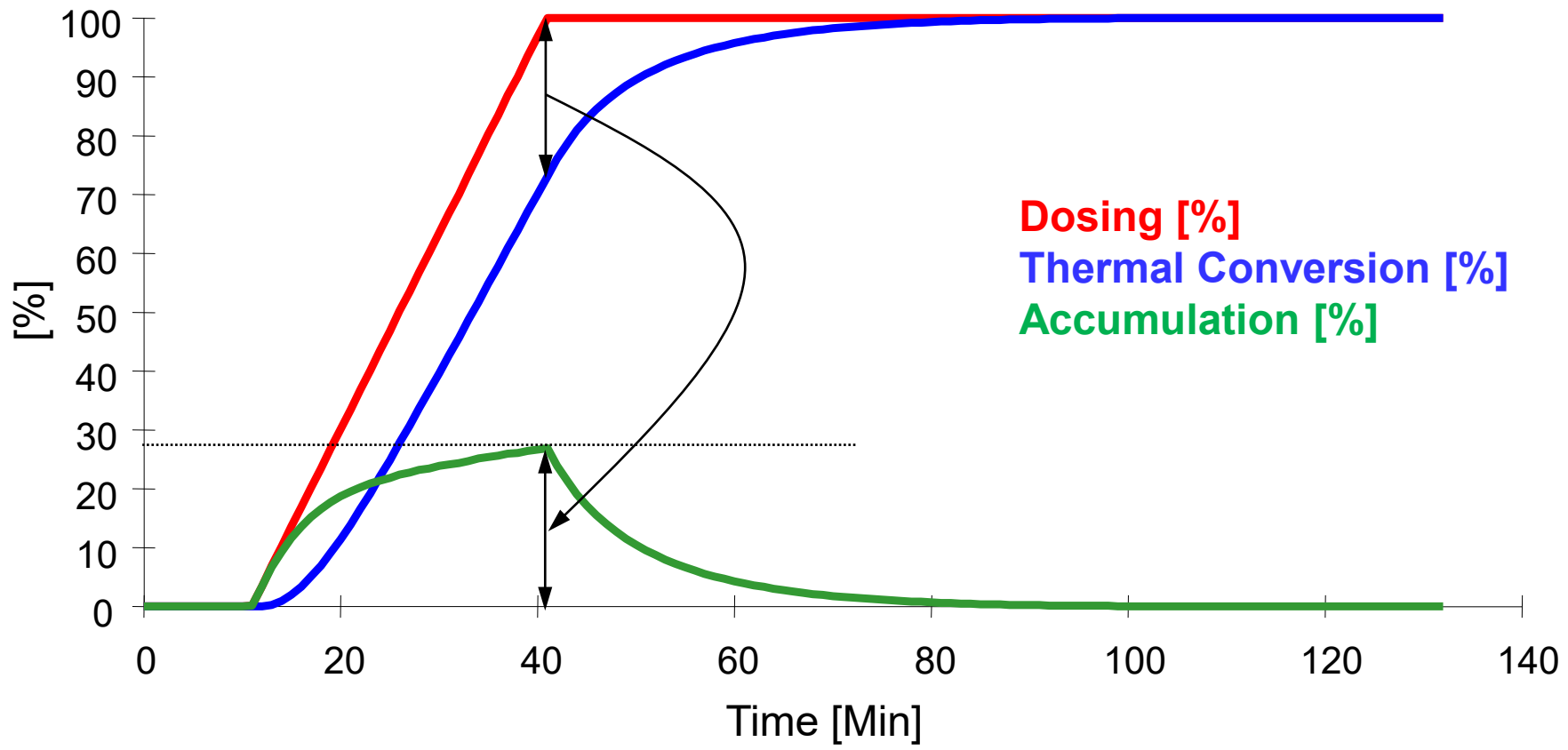
Reaction Calorimetry

Given by the measurement (known)

Derived from measured data

Parameter of interest

Accumulation [%] = Dosing [%] – thermal Conversion [%]



Chemisens CPA 202

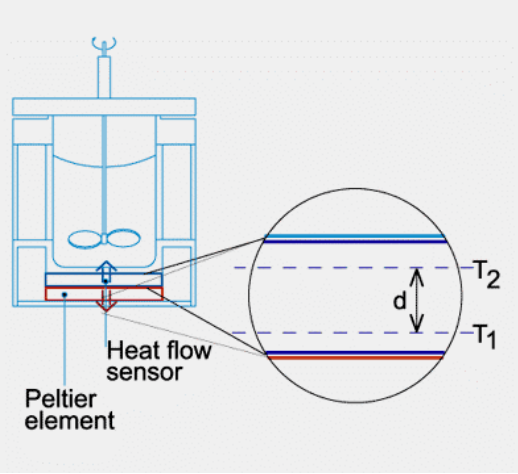
- **Heat Flow Calorimeter**
  - Uses a Peltier array for heating and cooling rather than jacketed vessel
  - Uses a heat flow sensor which measures power directly

Advantages

- Calibrations not required on individual tests
- Small volume 30-180 ml

Disadvantages

- Solids charging difficult
- Difficult to see inside vessel
- No bottom run



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- Main reaction
  - Mainly Reaction Calorimetry
  - Screening: micro-calorimetry
- Secondary reaction
  - Micro-calorimetry
  - Adiabatic measurements
  - High sensitivity calorimetry
- Both
  - Adiabatic measurements
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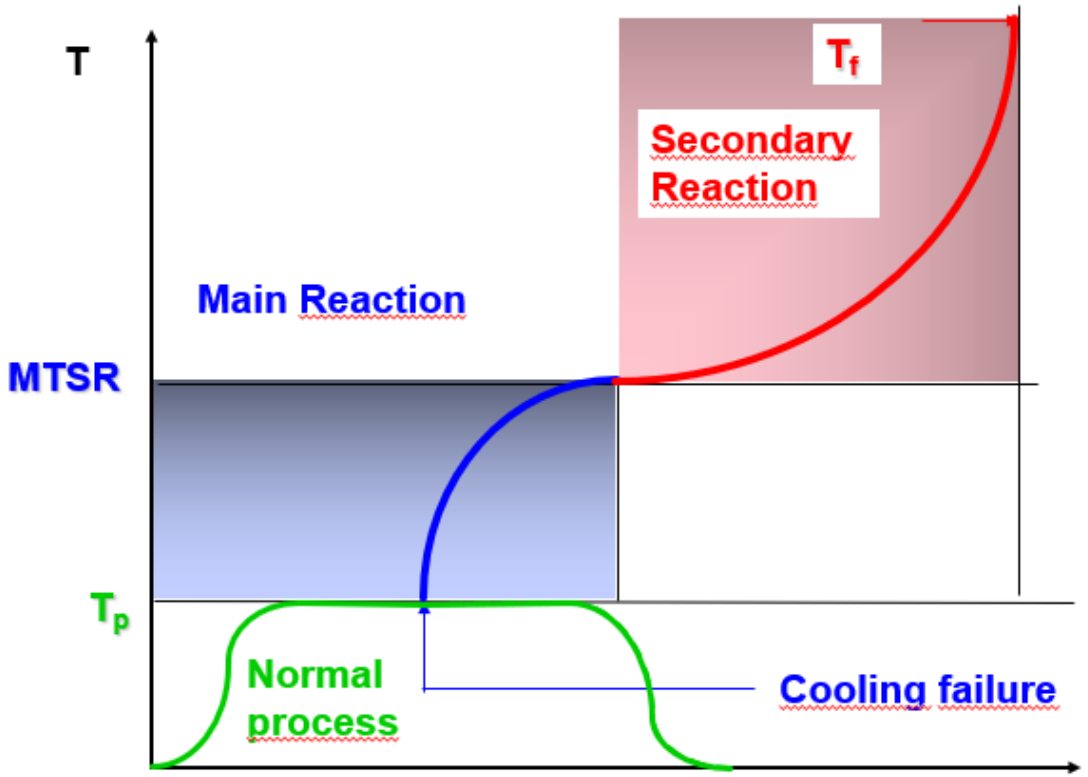
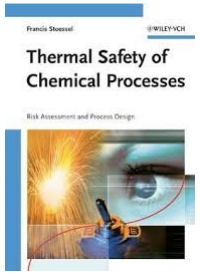
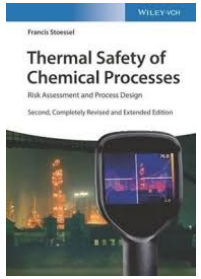




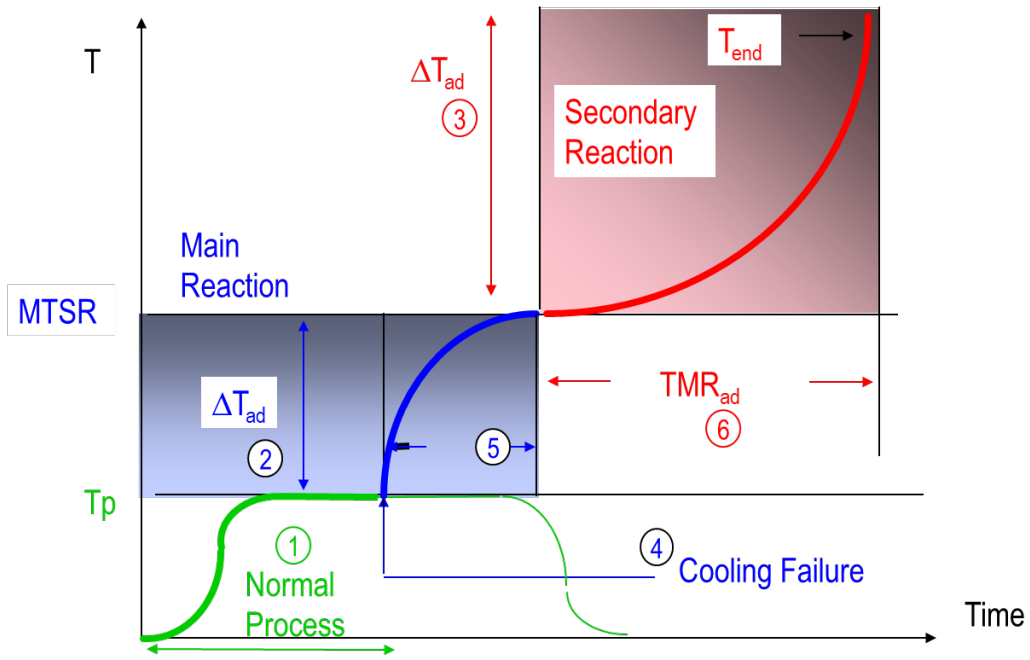


Chapter 4

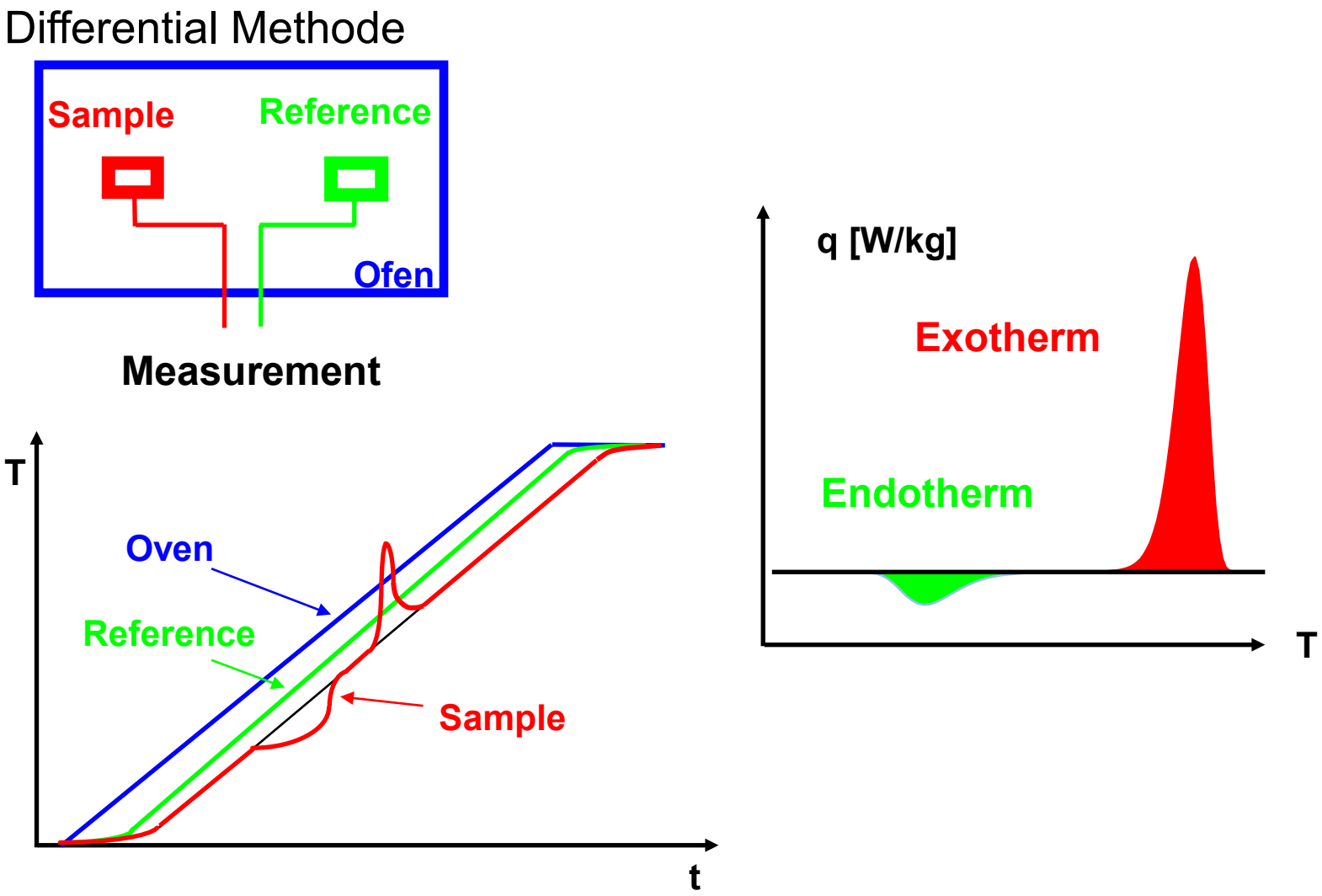
Secondary reaction- Data

- Reaction/Decomposition Energy
  - Thermal Potential/Consequences
  - question 3 cooling failure scenario: how high is the final temperature?
- TMRad (or tmr_{ad})
  - Probability of triggering the decomposition
  - question 6 cooling failure scenario: how long does it take from the MTSR to the final T?

- Micro-calorimetry will provide the reaction/decomposition energy and will be used to determine q' as a function of T (to calculate TMRad)
  - DSC, C80
- Adiabatic measurements :TMRad at one T and decomposition/reaction energy
  - ARC, Dewar



Differential Scanning Calorimetry (DSC)



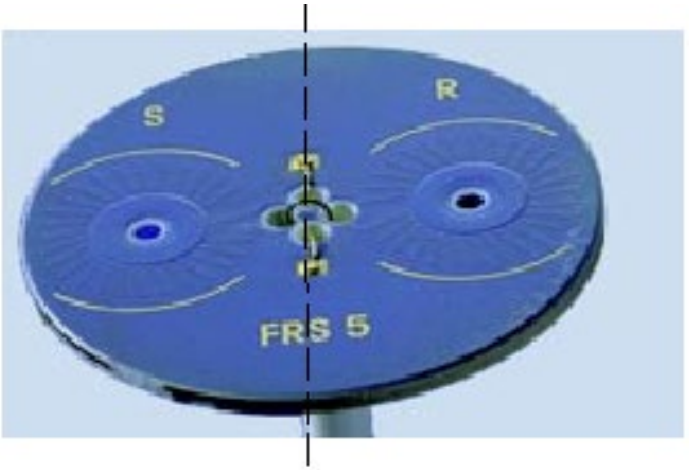
DSC

- « Micro scale »
  - Amount mg
  - Safe, even with highly exothermic samples
  - Mostly used to study decompositions (stability)
- Quantitative Measurement
  - Energy and power
  - Large T-range
- Short Cycle times → used for screening
  - Process deviations / route selection
  - Catalytic effects
  - Solvent effects
- Mode:
  - Isothermal
  - Scan (typically 4°C/min from 30 to 400°C)

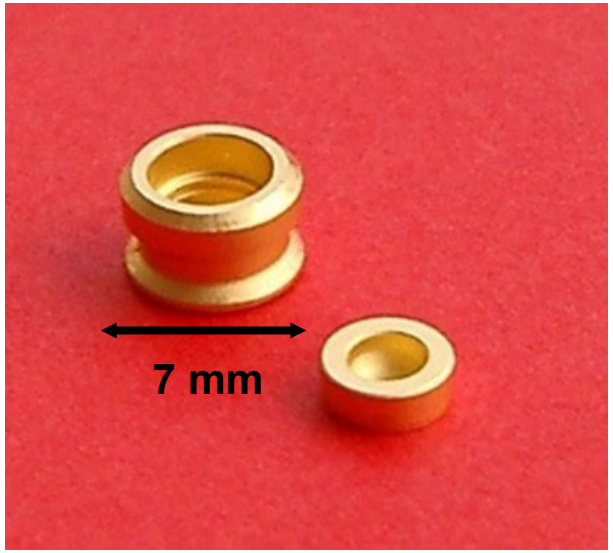
Practical Sensitivity: ~ 20W/kg

DSC for safety studies

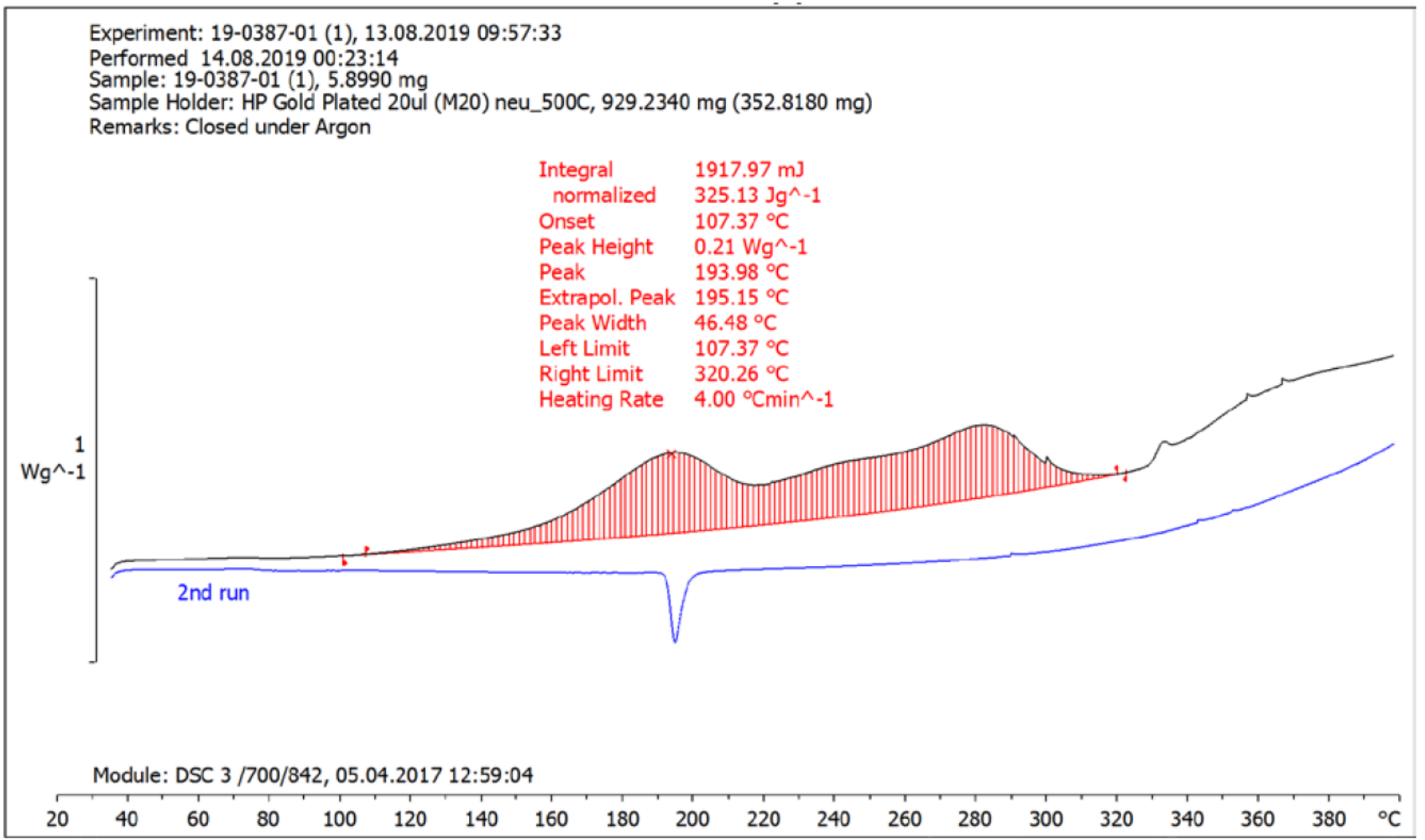
- Robust and sensitive sensor head
- Pressure resistant tight crucibles
  - No evaporation
  - No product loss
  - No catalytic effects



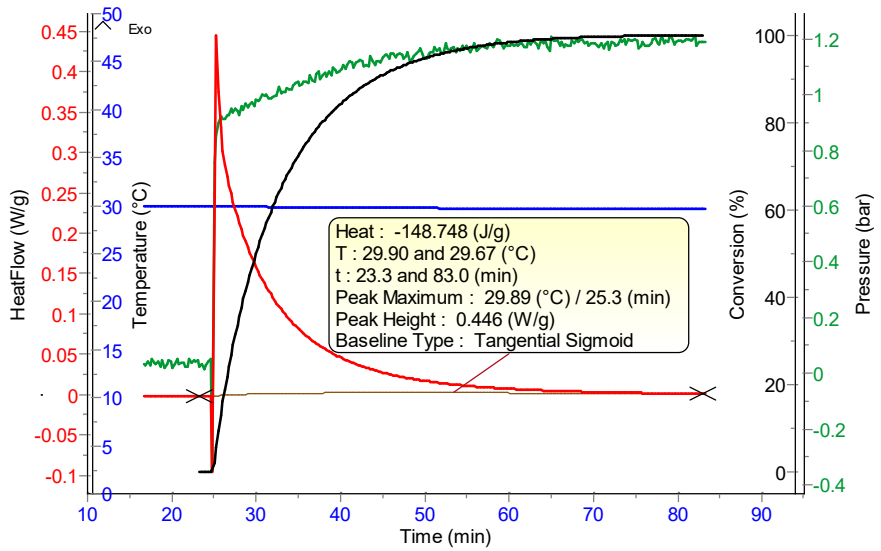
- Thermal finger print of a reactive system
- Determination of energy release by reaction(s)
- Working under controlled atmosphere is possible



DSC

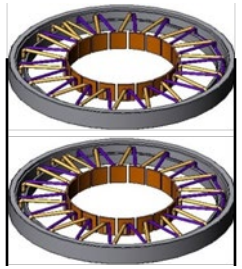

Experiment: 19-0387-01 (1), 13.08.2019 09:57:33
Performed 14.08.2019 00:23:14
Sample: 19-0387-01 (1), 5.8990 mg
Sample Holder: HP Gold Plated 20ul (M20) neu_500C, 929.2340 mg (352.8180 mg)
Remarks: Closed under Argon
Integral 1917.97 mJ
normalized 325.13 Jg^-1
Onset 107.37 °C
Peak Height 0.21 Wg^-1
Peak 193.98 °C
Extrapol. Peak 195.15 °C
Peak Width 46.48 °C
Left Limit 107.37 °C
Right Limit 320.26 °C
Heating Rate 4.00 °Cmin^-1
1
Wg^-1
2nd run
Module: DSC 3 /700/842, 05.04.2017 12:59:04
20 40 60 80 100 120 140 160 180 200 220 240 260 280 300 320 340 360 380 °C

Tian-Calvet Calorimeter (C80)



- T: -100 – 300°C (max. 1°C/min.)
- P: 0 – 200 bar
- V: 100 mg – 1 g
- Small scale reaction calorimetry
- Options: mixing, gas reactions, pressure measurement
- Mixing cell: combined measurement of synthesis and decomposition reaction (thermal stability)
- Practical Sensitivity (screening): ~ 2W/kg

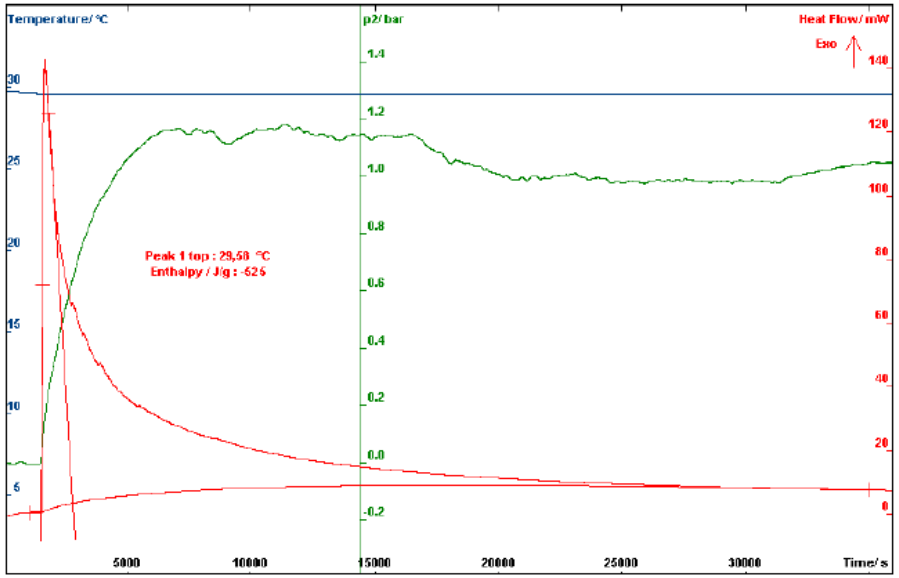
3D-Sensor
Calvet design

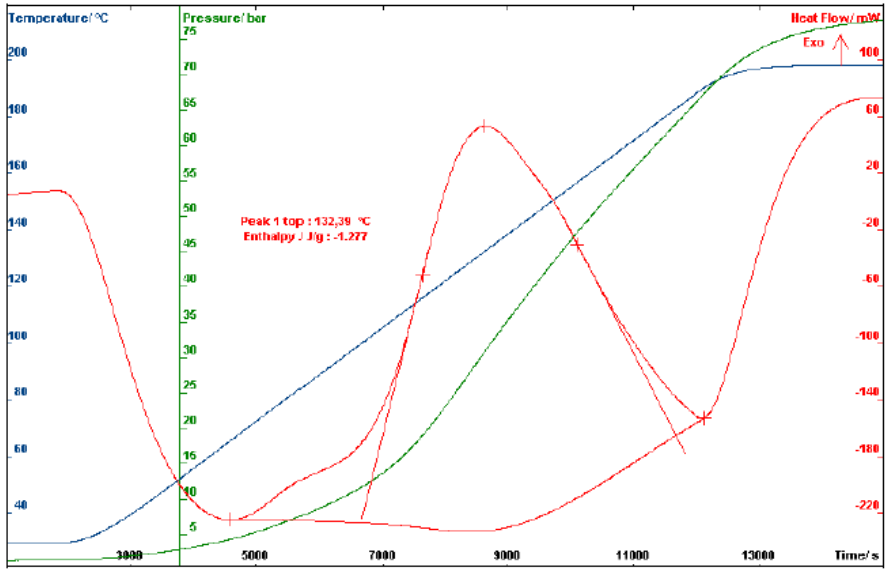


Mixing cell
(SWISSI)

Reaction in a Calvet calorimeter

- Setaram C80





Process under isothermal conditions

Thermal stability of final reaction mass

Micro-calorimetry to determine reaction energy

- Mix the reactant (cold mixture) and perform a dynamic measurement
  - Reaction energy
  - Decomposition energy

- Advantages
  - Small scale
  - Screening

- Disadvantages
  - No mixing
  - No information on heat release rate, accumulation
  - Does the reaction run to completion?

What calorimetric measurements are used to assess the cooling failure scenario?

- Main reaction
  - Mainly Reaction Calorimetry
  - Screening: micro-calorimetry
- Secondary reaction
  - Micro-calorimetry
  - Adiabatic measurements
  - High sensitivity calorimetry
- Both
  - Adiabatic measurements
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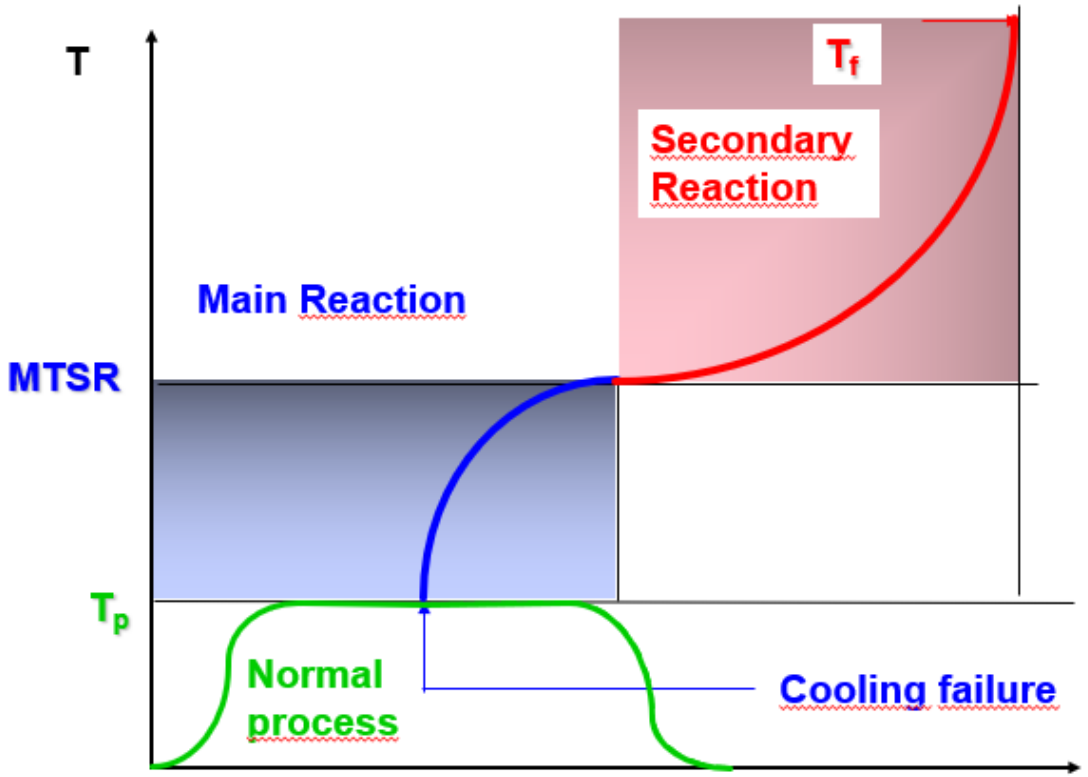
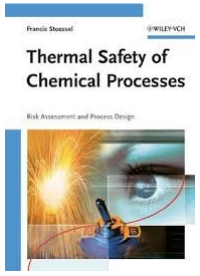
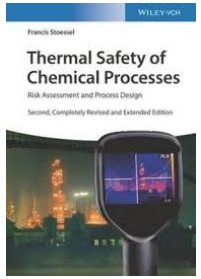
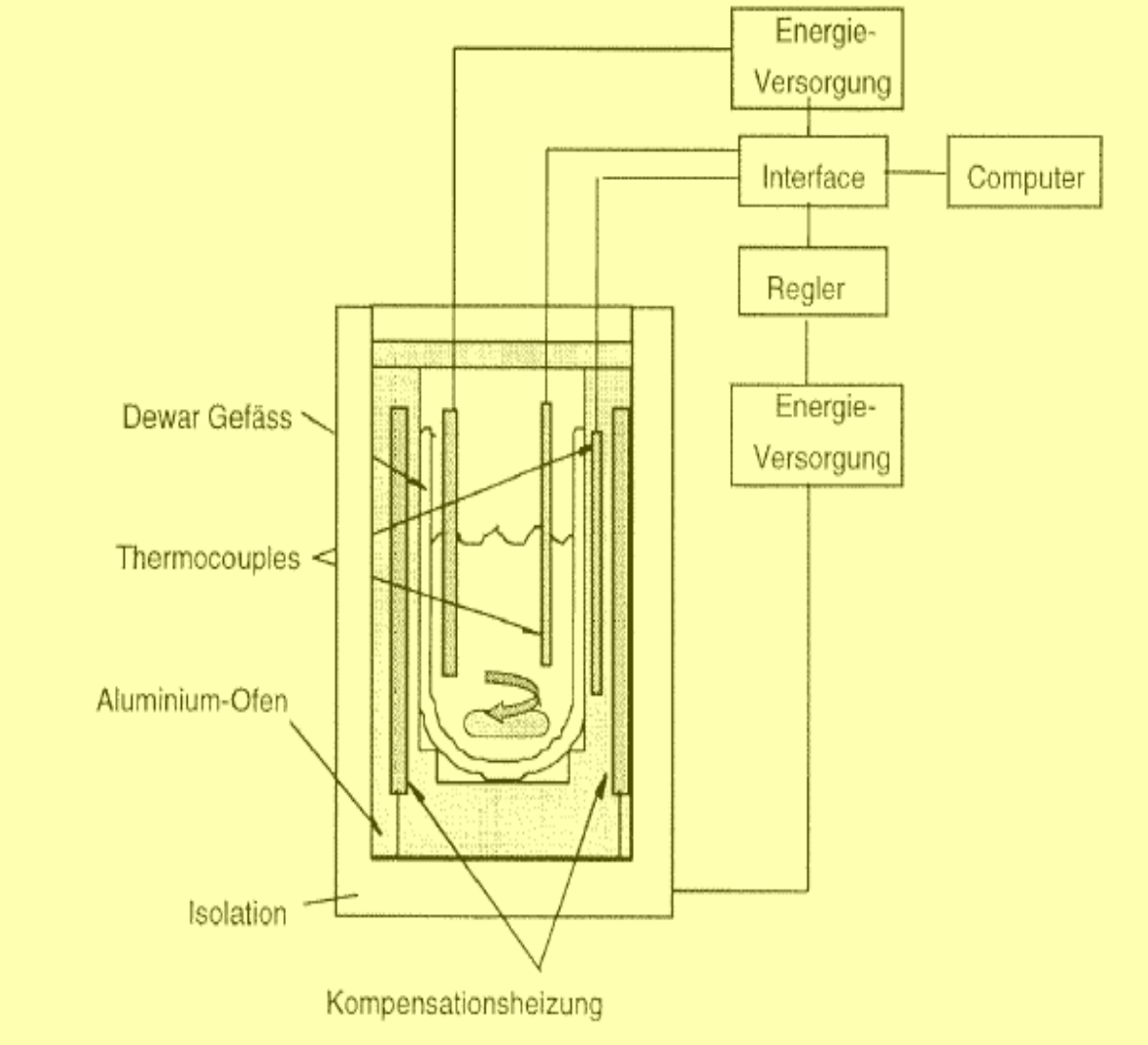






Chapter 4

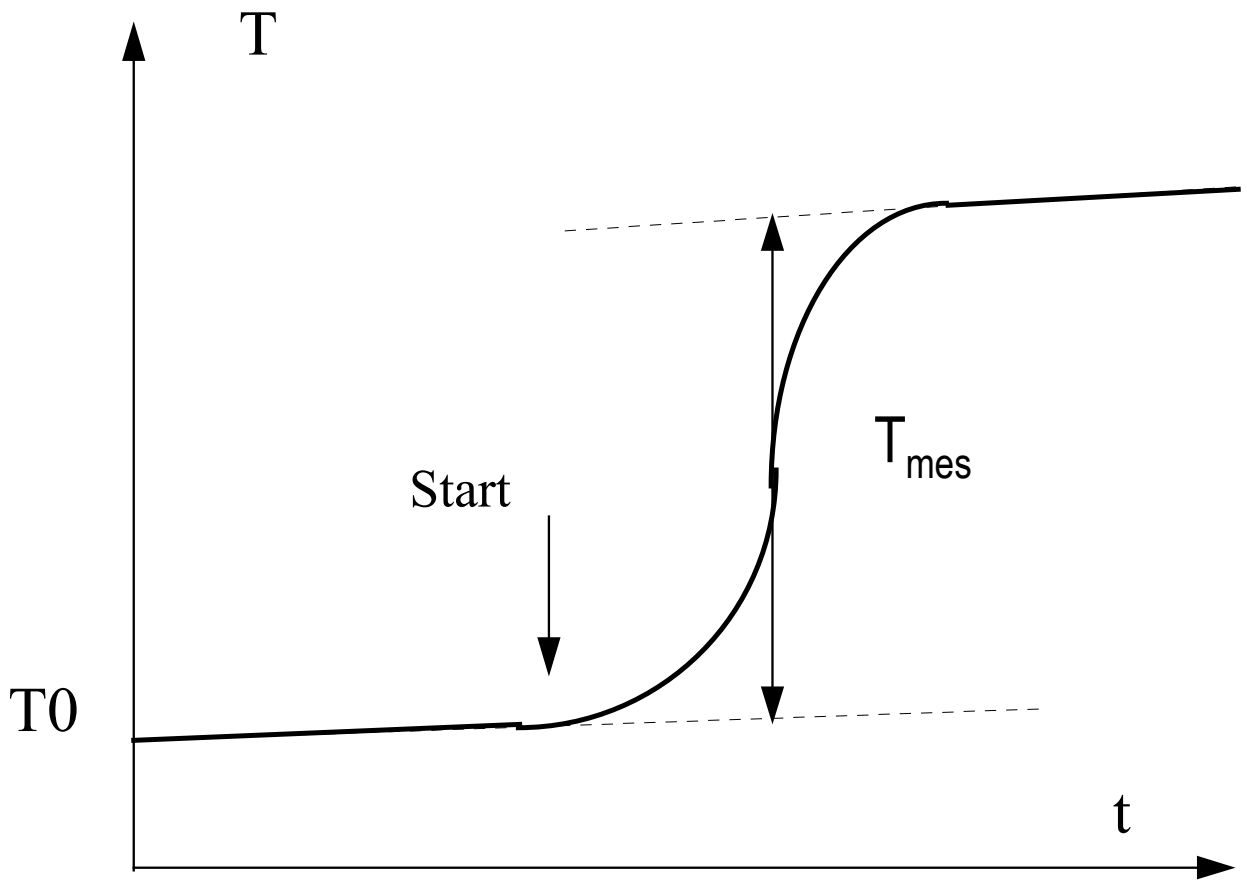
Dewar



- 300-800 ml
- Thermos flask with vacuum jacket to minimize heat losses
- Different materials (e.g. glass, stainless steel)
- With closure or open
- Stirrer, connections for addition of liquids, sampling, pressure and temperature sensors etc.
- Adiabatic tests performed in temperature controlled oven
- Hazards for the operator (destruction of oven/Dewar)

Dewar

- Measure a temperature increase
- Is this the adiabatic temperature increase?
  - Depends on the heat losses and on the energy required to heat the Dewar
    → adiabacity factor: Φ factor



Adiabacity Factor

Φ-Factor

- Thermal Inertia of the System/Apparatus
- Part of the reaction heat is used to heat up the calorimetric cell

$$\Phi = \frac{M_r \cdot c'_{p,r} + M_{cell} \cdot c'_{p,cell}}{M_r \cdot c'_{p,r}} = 1 + \frac{M_{cell} \cdot c'_{p,cell}}{M_r \cdot c'_{p,r}}$$

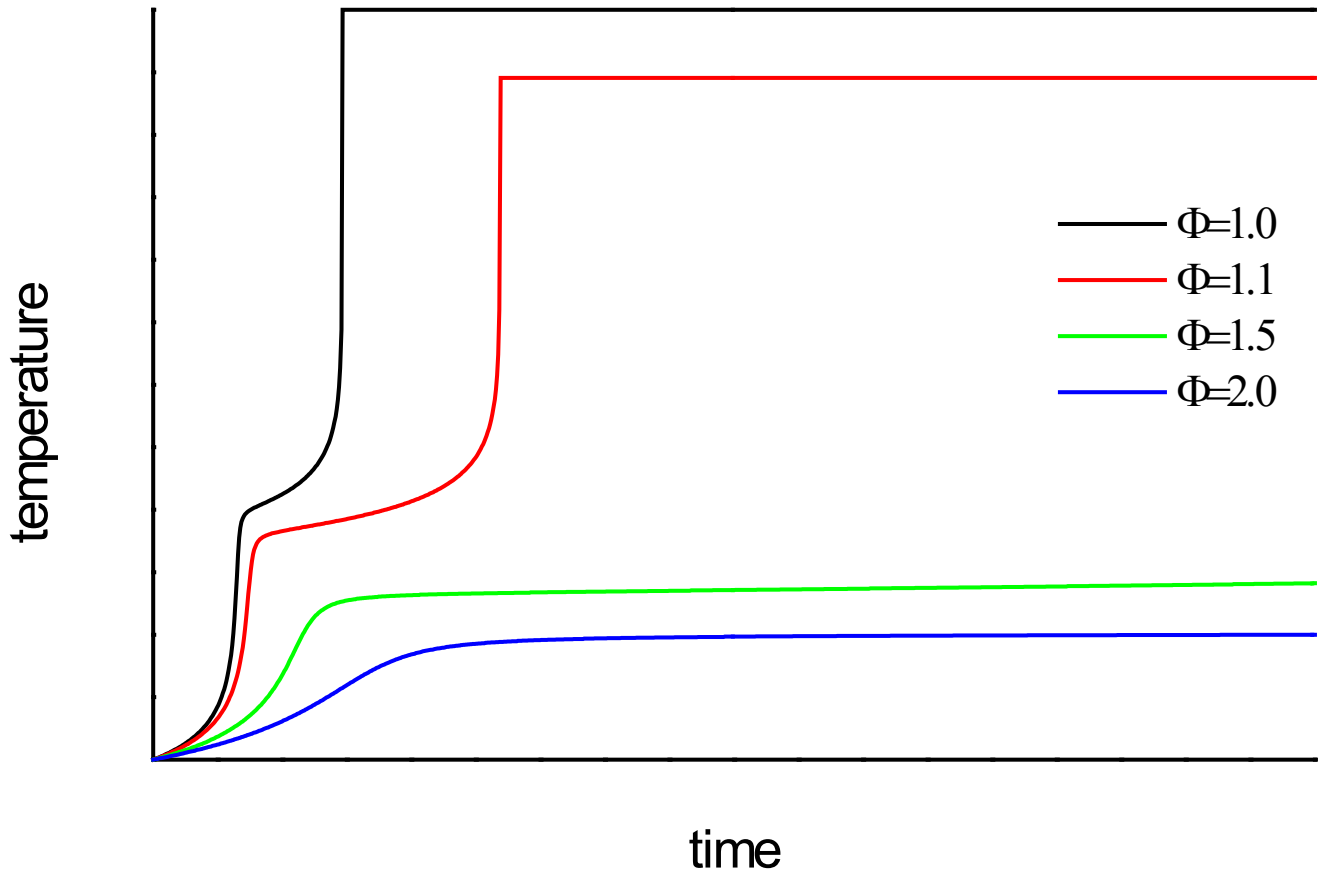
- A perfectly adiabatic system has a Φ factor of 1
- M_{cell} large → Φ factor increases

Correction for Φ > 1

$$\Delta T_{ad} = \Phi \cdot \Delta T_{mes}$$

$$T_f = T_0 + \Phi \cdot \Delta T_{mes}$$

Influence of the Φ-Factor



- Which is the plant situation?
- Which curve is the measured one?

Observations from the figure

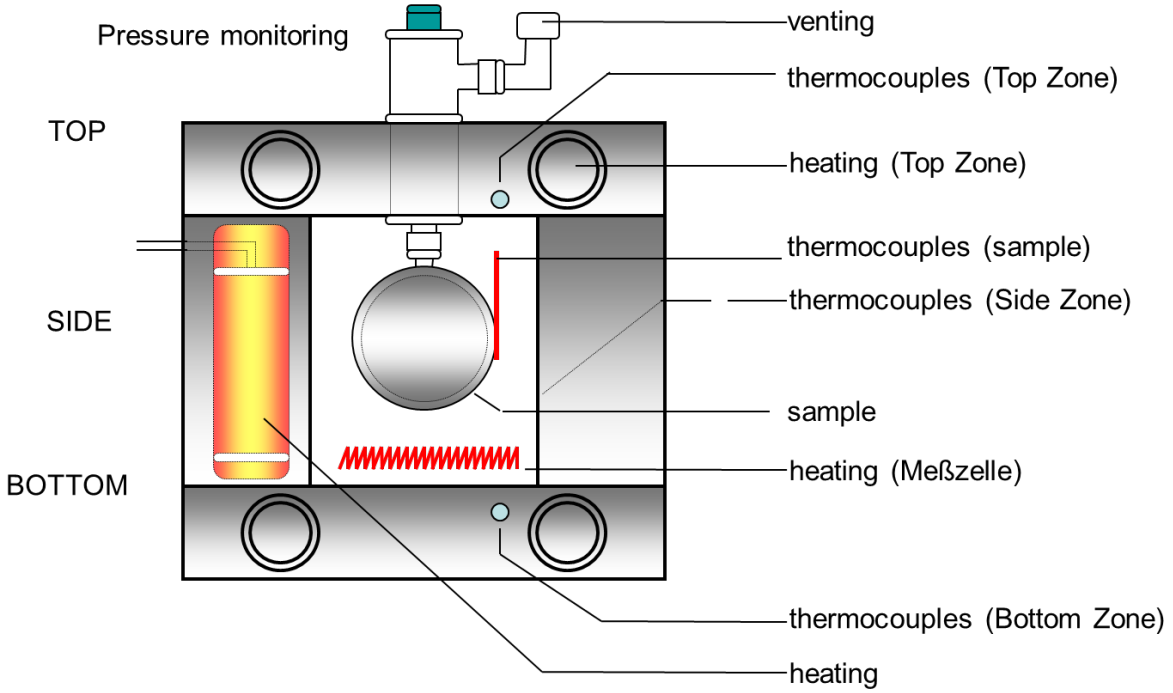
- The temperature rise is larger in the plant than in the test
- The time taken for the runaway reaction is shorter in the plant
- The rates of temperature and pressure rise are higher in the plant
- Runaway not measured at Φ 1.5 and 2.0

Conclusions

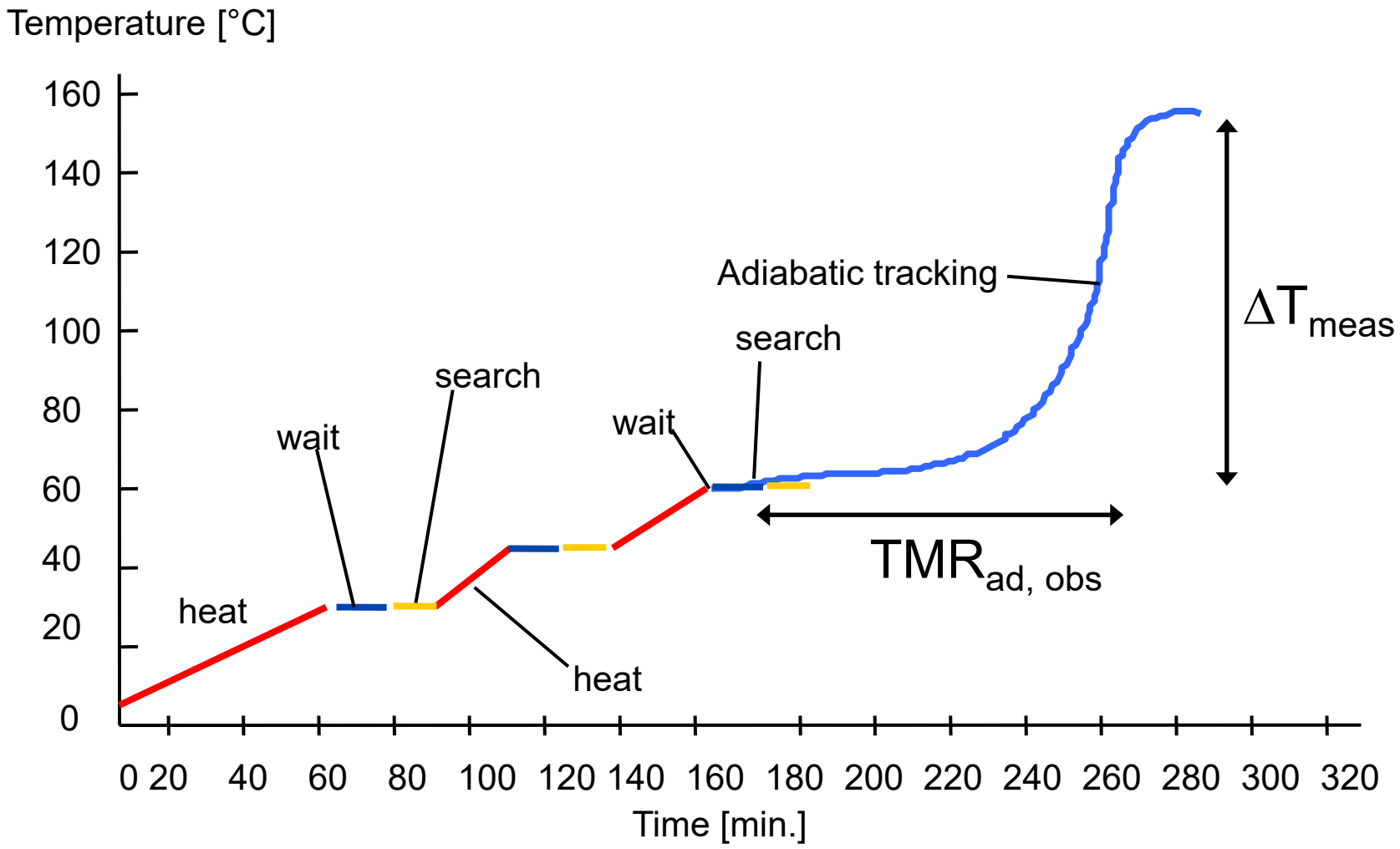
- Data must be corrected for Φ
- Need to measure at higher T

Accelerating Rate Calorimeter (ARC)

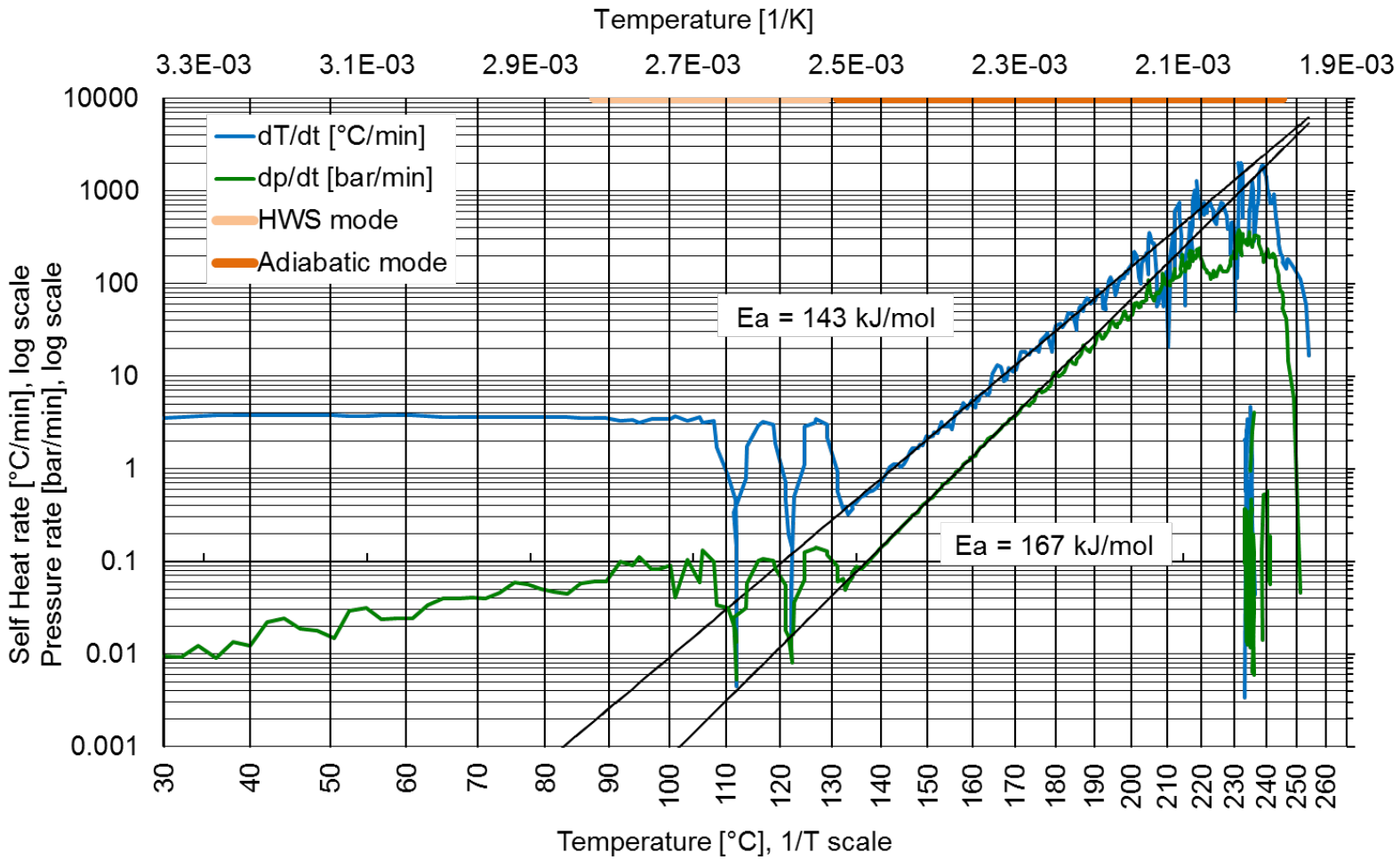
- T: 30 – 500°C
- P: 0 – 170 bar
- V: 4 – 50 ml
- Different test bomb material (HC, Ti)
- Different modes of operation (adiabatic tracking; heat-wait-search)



ARC: Heat - Wait - Search



Corrected adiabatic data

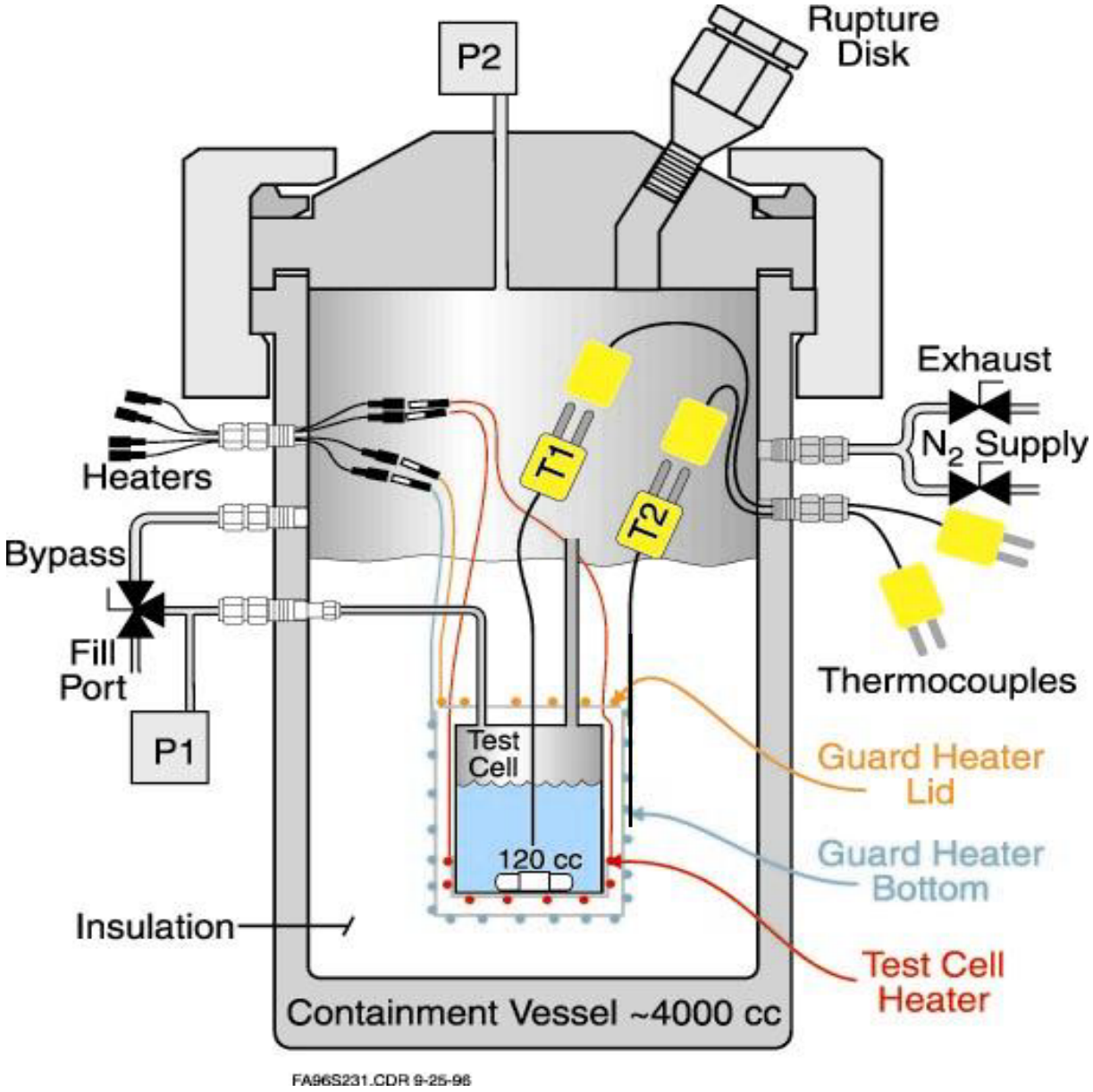


Temperature and pressure rate

Vent Sizing Package 2

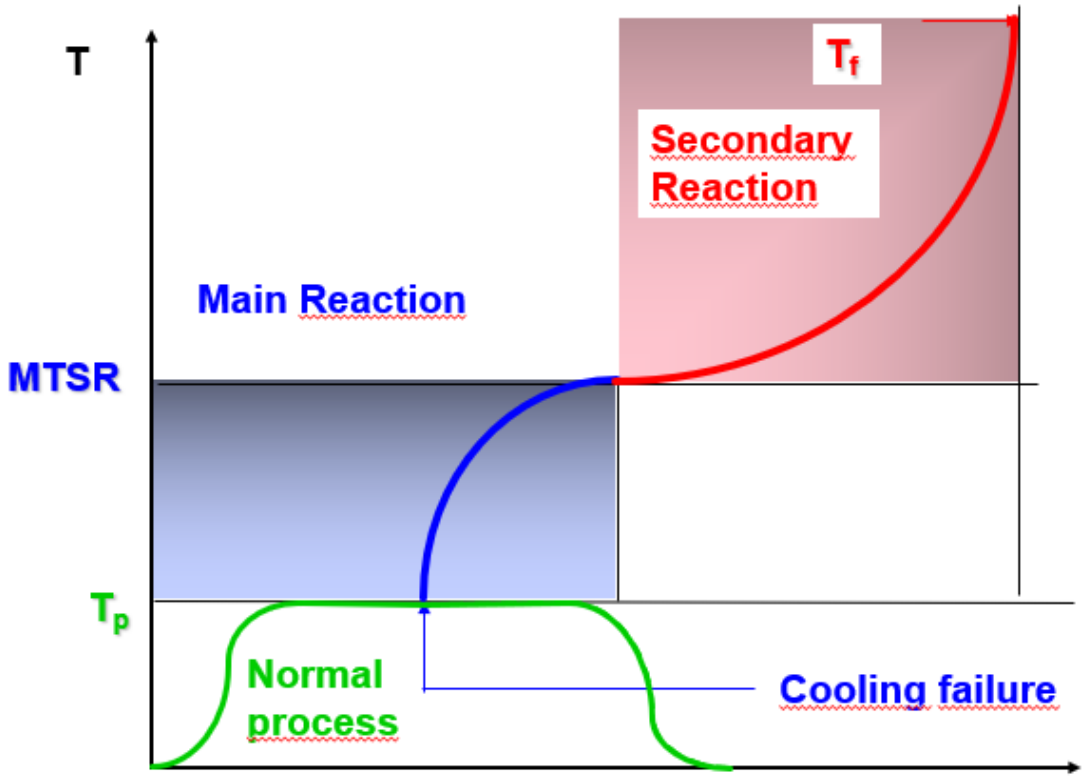
- T: 30 – 500°C (tracking up to 300°C/min.)
- P: 0 – 130 bar (tracking up to 650 bar/min)
- V: 50 – 100 ml
- Typical Phi-factor: 1.1
- Gas and Liquid Dosing, Sampling, Stirring
- Different modes of operation (e.g. Closed or Open System, Relief Valve simulation, Depressurization/Blowdown tests, Quench reactions)

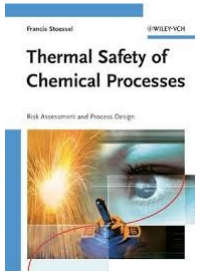
VSP2:

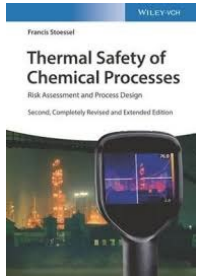

P2
Rupture Disk
Exhaust
N_2 Supply
Heaters
T1
T2
Bypass
Fill Port
P1
Thermocouples
Test Cell
120 cc
Guard Heater Lid
Guard Heater Bottom
Test Cell Heater
Insulation
Containment Vessel ~4000 cc
FA96S231.CDR 9-25-96

What calorimetric measurements are used to assess the cooling failure scenario?

- Main reaction
  - Mainly Reaction Calorimetry
  - Screening: micro-calorimetry
- Secondary reaction
  - Micro-calorimetry
  - Adiabatic measurements
  - High sensitivity calorimetry
- Both
  - Adiabatic measurements
  - Micro-calorimetry

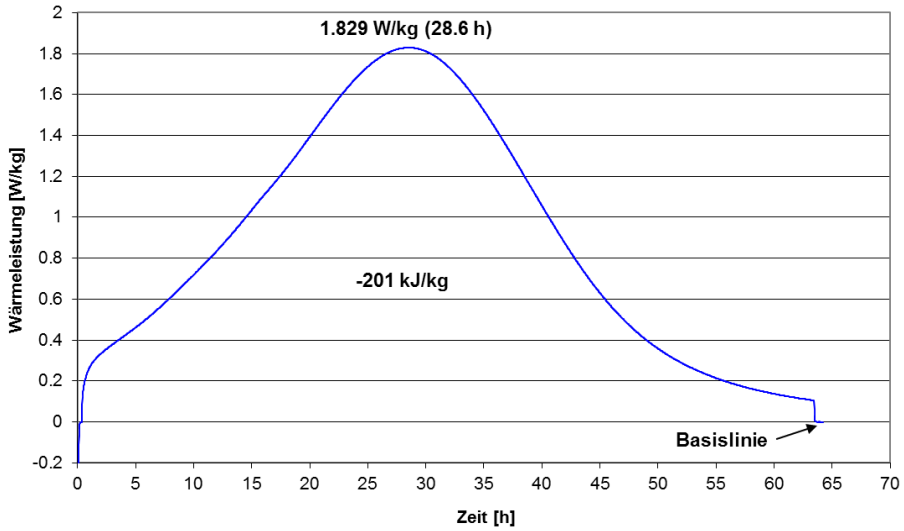






Chapter 4

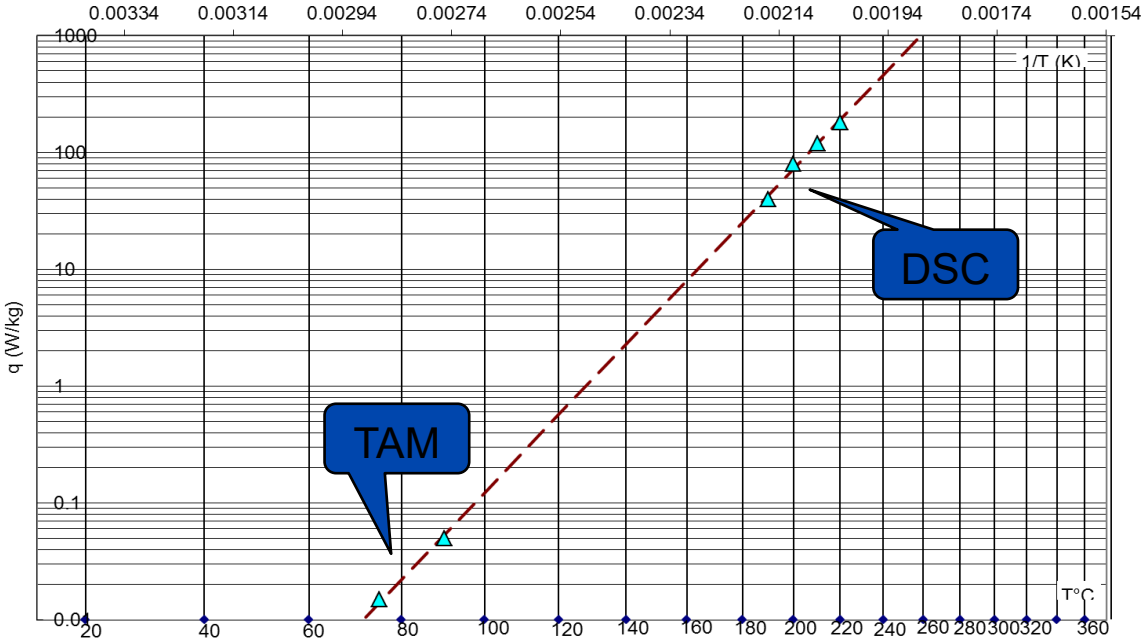
TAM Thermal Activity Monitor



- T: isotherm at 30 – 150°C
- V: 1-4 ml
- Very high sensitivity (0.01 W/kg)
- Measurement under defined gas atmosphere (e.g. N_2, air)

TAM Thermal Activity Monitor

- Stability assessment for storage or transportation
- Detection of very low heat generation rates



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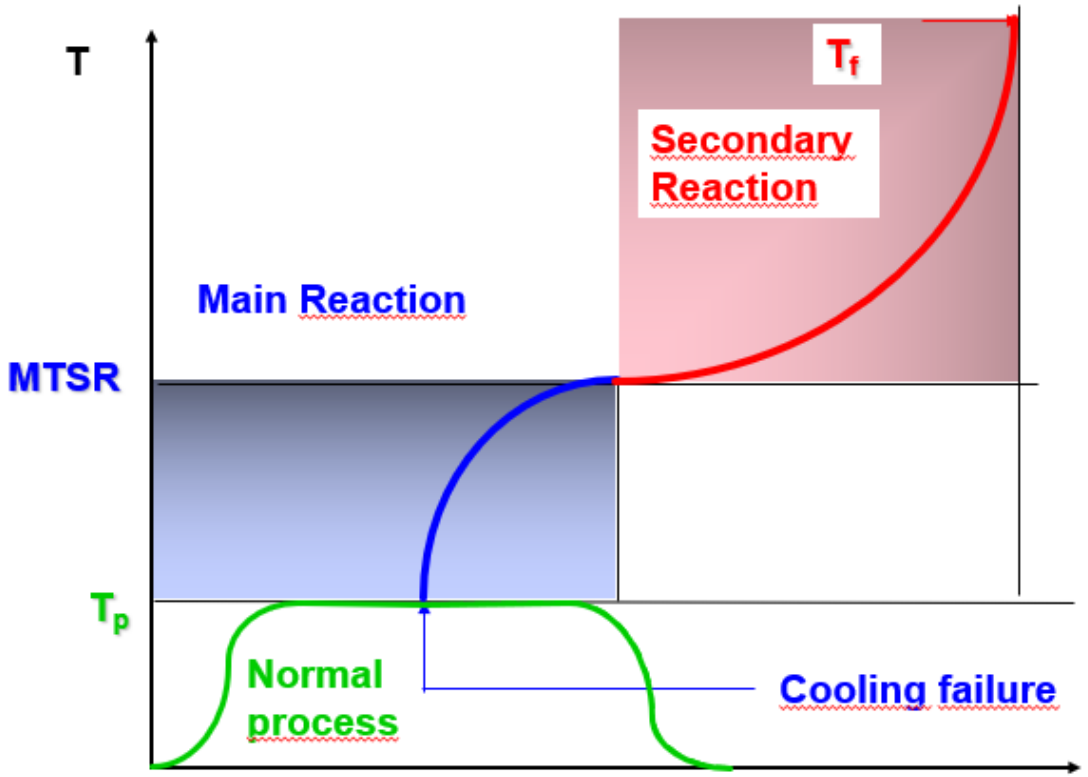
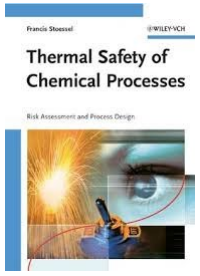
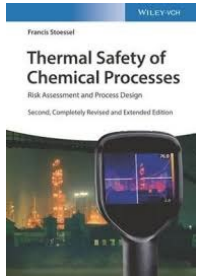






Chapter 4

Measuring both synthesis reaction and decomposition

- Micro-calorimetry: only energy information for the main reaction and no mixing
- Adiabatic measurements:
  - Careful with phi factor
  - Data for one starting temperature

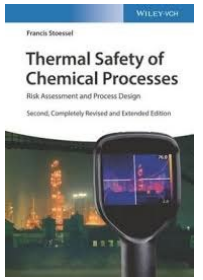
- Ideally: combination of measurements
  - Reaction calorimetry for main reaction
  - Micro-calorimetry for decomposition reaction
  - Adiabatic measurements to confirm or to look at specific situations

- High sensitive measurements (TAM) when assessing storage, transport (avoiding large extrapolation of data)

Comparison

Method	Measuring principles	Application field	Sample size	Temperature range	Sensitivity ($W\,kg^{-1}$)[a]
Differential scanning calorimetry (DSC)	Differential, ideal flux, or isoperibolic	Screening and secondary reactions	1–50 mg	−50 to 500 °C	2[b]–10
Calvet C80 (BT 2.15)	Differential, ideal flux	Main and secondary reactions	0.1–3 g	30–300 °C (−196 to 200 °C)	0.1–1[c]
Accelerating rate calorimeter (ARC)	Ideal accumulation	Secondary reactions	0.5–3 g	30–400 °C	0.5
Vent Sizing Package (VSP)	Ideal accumulation	Main and secondary reactions	50–100 g	30–350 °C	0.2
Sensitive detector of exothermal processes (SEDEX)	Isoperibolic, adiabatic	Secondary reactions, storage stability	2–100 g	0–400 °C	0.5[d]
RADEX	Isoperibolic	Screening, secondary reactions	1.5–3 g	20–400 °C	2
SIKAREX	Ideal accumulation, isoperibolic	Secondary reactions	5–50 g	20–400 °C	0.25
Reaction calorimeter	Ideal flux or heat balance	Main reactions	50–2000 g	−40 to 250 °C	1.0
Thermal activity monitor (TAM)	Differential, ideal flux	Secondary reactions, storage stability	0.5–3 g	30–150 °C	0.01
Dewar	Ideal accumulation	Main reactions and thermal stability	100–1000 g	30–250 °C	e)

a) Typical values.
b) Most recent instruments under optimal conditions.
c) Depending on the sample mass.
d) Depends on cell used.
e) Depends on volume and Dewar quality.



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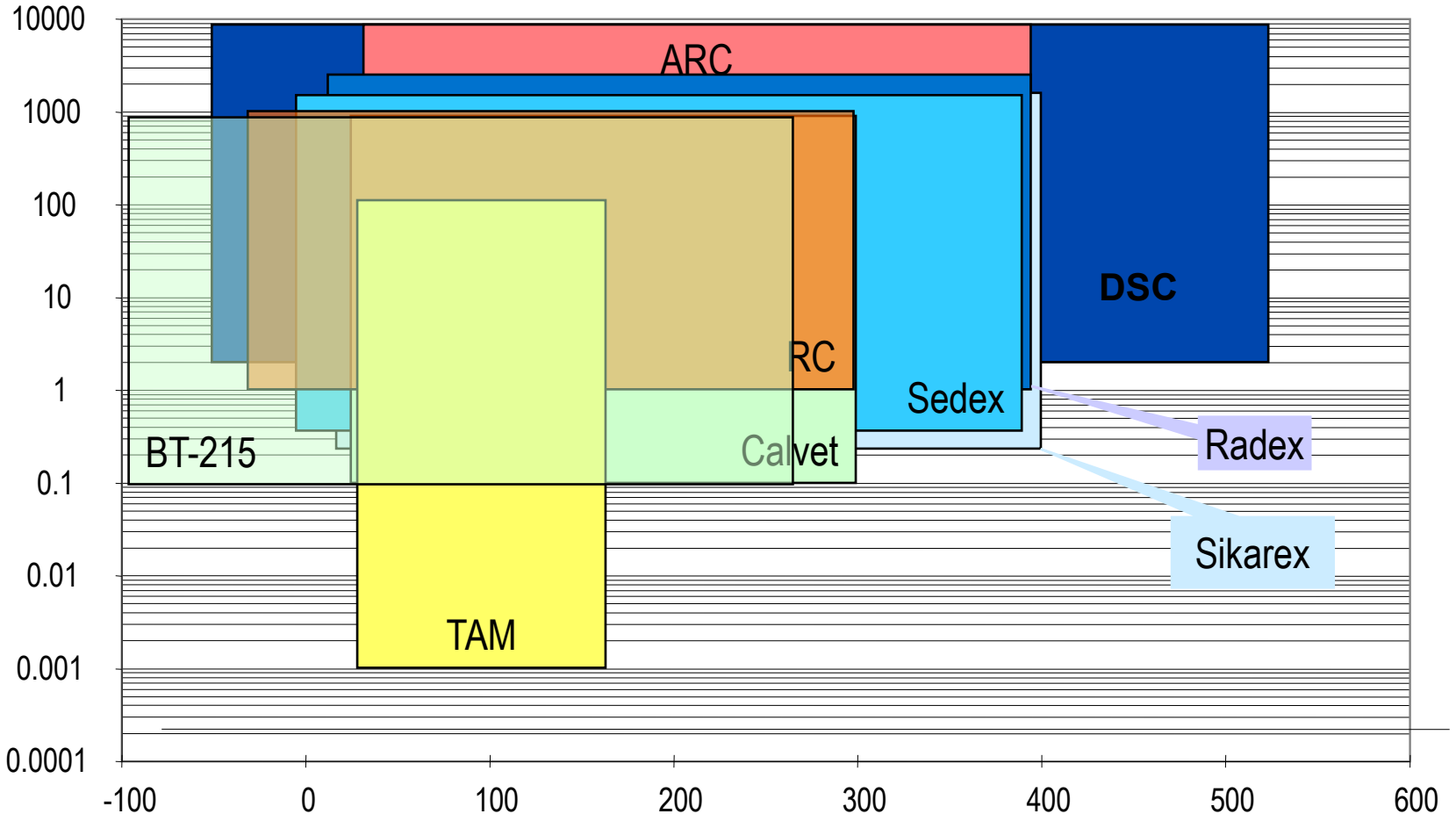
Application range



Summary

- Study of main reaction:
  - Reaction calorimeters (RC1, CPA)
  - Data obtained: Reaction energy Q'_{rxn}, heat release rate q'_{rxn}, accumulation X_{acc} → can calculate MTSR
  - Screening possible in DSC and C80
- Study of decomposition reactions
  - Screening: DSC, C80, ARC (adiabatic)
    - Data obtained DSC and C80 from scan experiment:
      - decomposition energy, information on gas production (C80).
      - TMRad is calculated (see lecture on thermal stability)
    - Data obtained for ARC
      - TMRad and ΔTad
      - Correction for non adiabacity (Φ factor)
  - Low heat release rate (e.g. Storage, Transport)
    - TAM; isothermal measurement
    - Data obtained: decomposition energy, heat release rate
    - TMRad calculated (see lecture on thermal stability), or heat balance calculated (see lecture on heat confinement)
  - Adiabatic: VSP, Dewar
    - Data obtained: TMRad and ΔTad
    - Correction for non adiabacity (Φ factor)