



# Thermal Stability

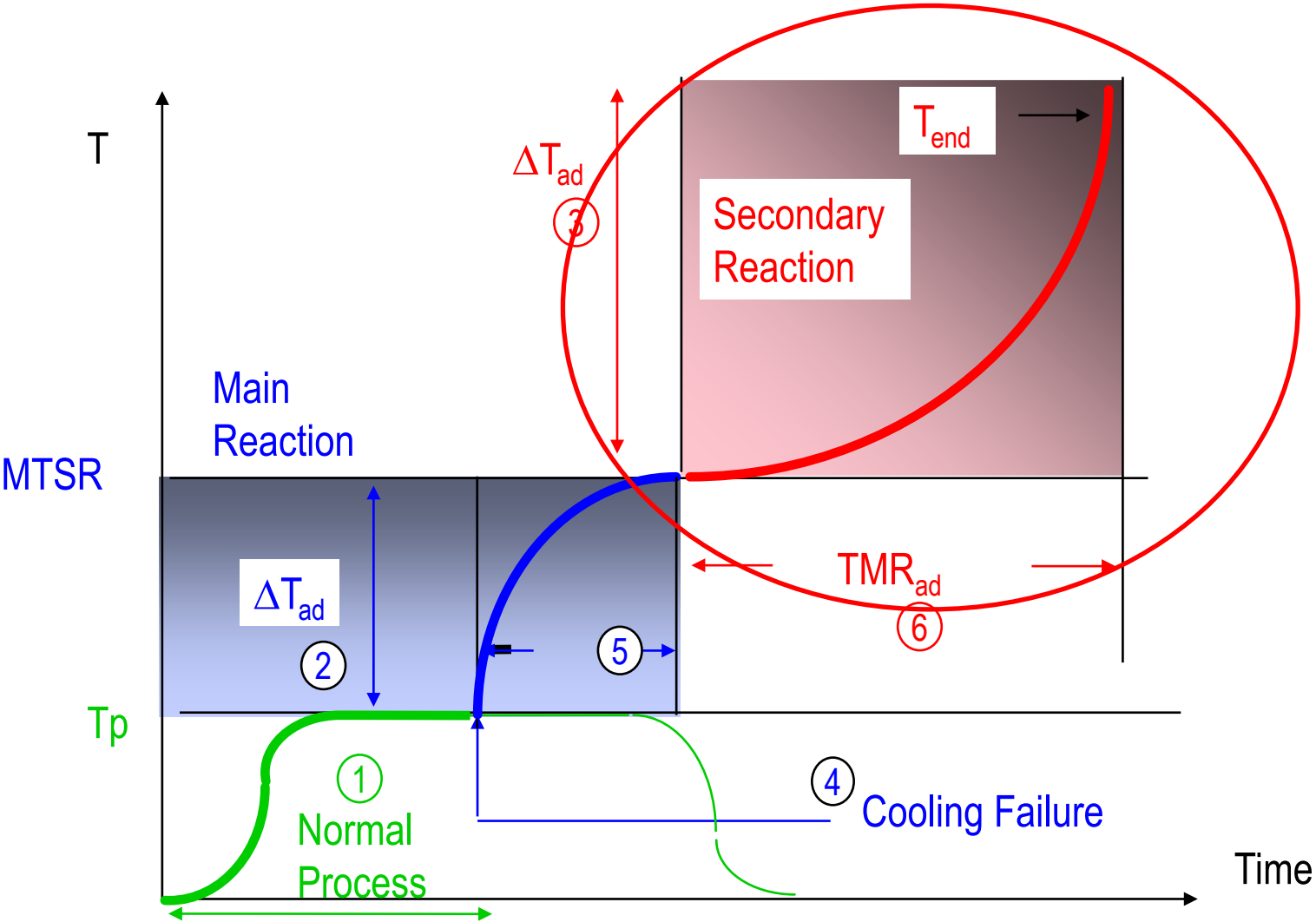
## The TMRad concept

Module 4

ENG 431: Safety Chemical Processes

Annik Nanchen

# Cooling Failure Scenario



# Decomposition Reactions

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- What are decomposition reactions?
- Characterisation of secondary reaction
  - Energy of decomposition
  - Onset and Safety Margin
  - Determination of  $TMR_{ad}$
- Examples
- Highly energetic molecules



Chapter 11



Chapter 10

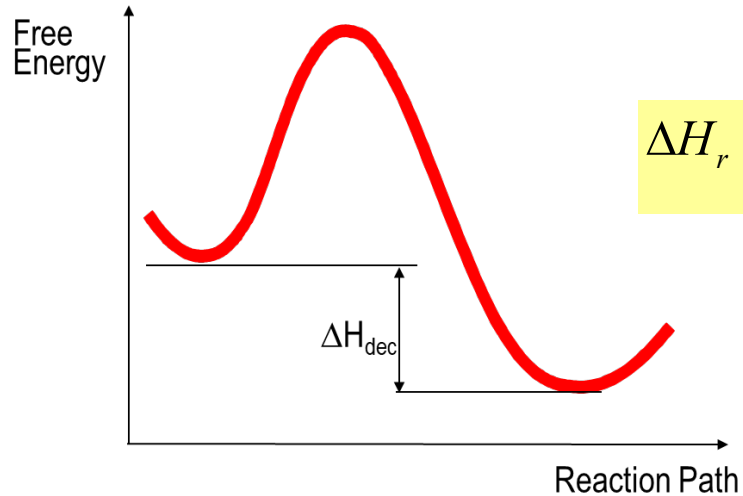
## Examples when the study of decomposition reaction is required

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# Decomposition Reactions

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- Stoichiometry often unknown: cannot estimate the decomposition energy



$$\Delta H_r = \sum_{\text{Products}} \Delta H_f - \sum_{\text{Reactants}} \Delta H_f$$

$\Delta H_r$ : reaction enthalpy      J/mol  
 $\Delta H_f$ : enthalpy of formation      J/mol  
 $\Delta H_{\text{dec}}$ : decomposition enthalpy      J/mol

- High energies
- Gaseous products
- Difficult to predict triggering conditions
  - Sensitive towards catalytic effects
  - Sensitive to impurities

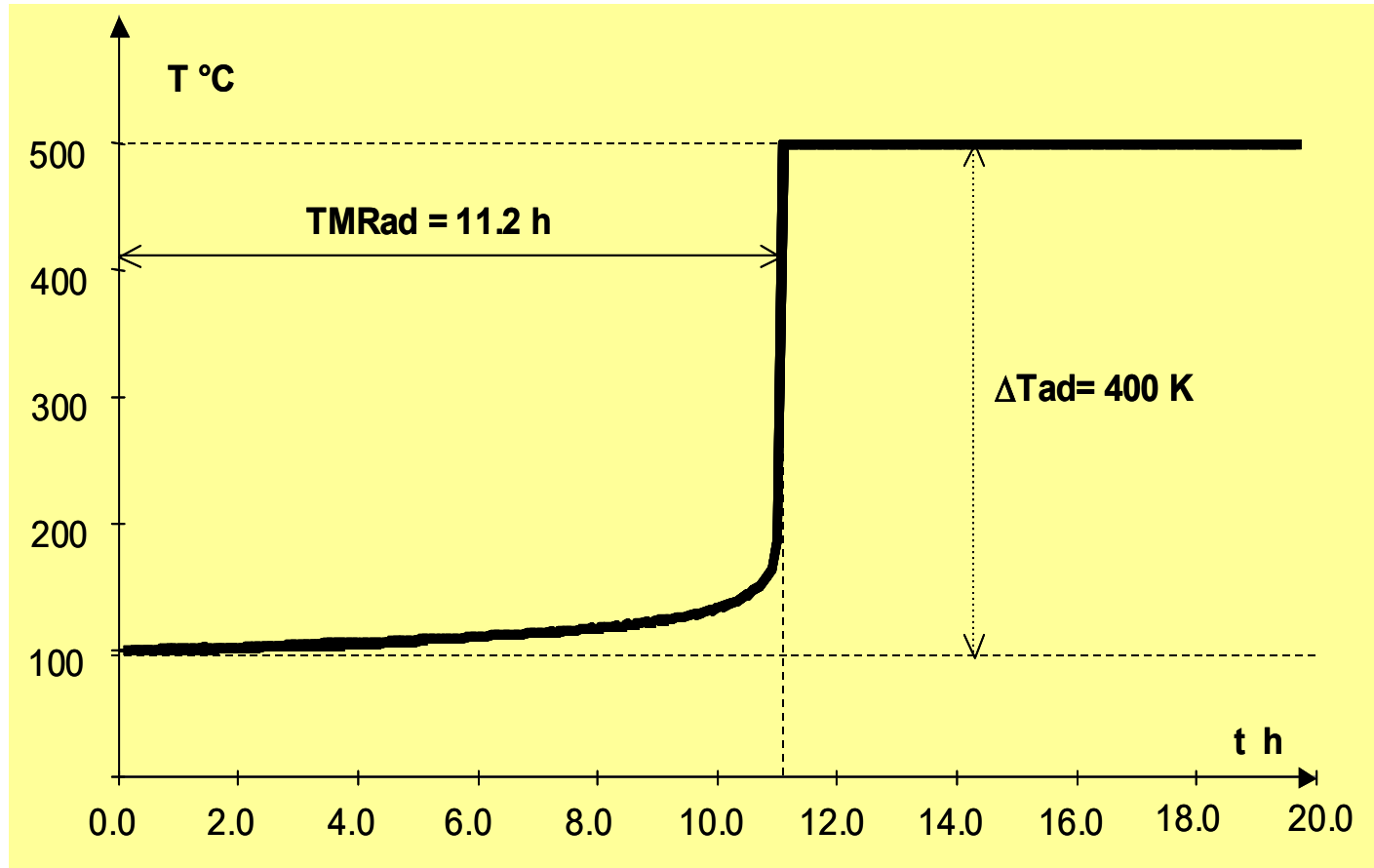
# Decomposition Reactions

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- What are decomposition reactions?
- Characterisation of secondary reaction
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- Examples

# Characterisation of Decomposition Reactions

- Characterisation: Risk: probability x severity



# Decomposition Energies

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- Can be estimated based on structure and functional groups

| Group       | $\Delta U$ (kJ/mole) |
|-------------|----------------------|
| Acetylene   | 120-170              |
| Epoxide     | 70-100               |
| Azo         | 100-180              |
| Diazonium   | 160-180              |
| Diazo       | 170-190              |
| Azide       | 200-240              |
| Triazene    | 250-270              |
| Aldoxime    | 190-230              |
| Ketoxime    | 140-170              |
| N-hydroxide | 180-240              |
| N-oxide     | 100-130              |
| Nitroso     | 150-290              |
| Isocyanate  | 50-70                |
| C-nitro     | 310-360              |

Compiled from literature sources (Hasegawa & Nuba, 1992; Grever, 1994, Whitmore & Baker 1999)

$$\Delta T_{ad} = \frac{Q'_R \quad [kJ/kg]}{c_p' \quad [kJ/(kg.K)]}$$

$\Delta T_{ad}$     adiabatic temperature rise (°C or K)  
 $Q'_R$       heat of reaction (kJ/kg)  
 $c_p'$       specific heat capacity (kJ/kg/K)

Typical values for  $c_p'$ :

|                                |             |
|--------------------------------|-------------|
| H <sub>2</sub> SO <sub>4</sub> | 1.3 kJ/kg/K |
| H <sub>2</sub> O               | 4.2 kJ/kg/K |
| Organic liquids                | 1.8 kJ/kg/K |
| Organic solids                 | 1.3 kJ/kg/K |

# Decomposition Reactions

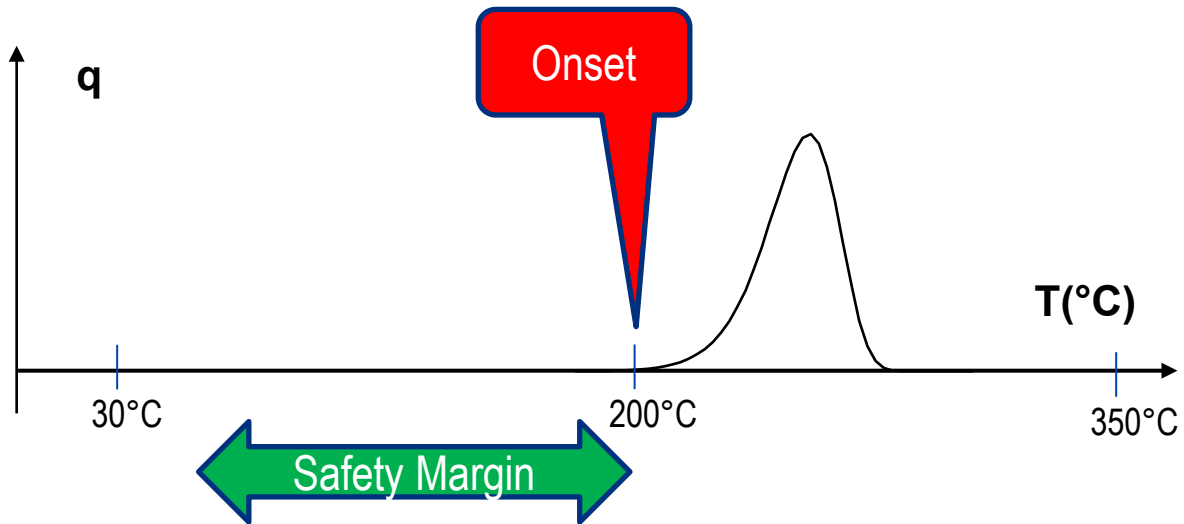
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- What are decomposition reactions?
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# Safety Margin

- What is a safe temperature?
  - Perform measurement and then?

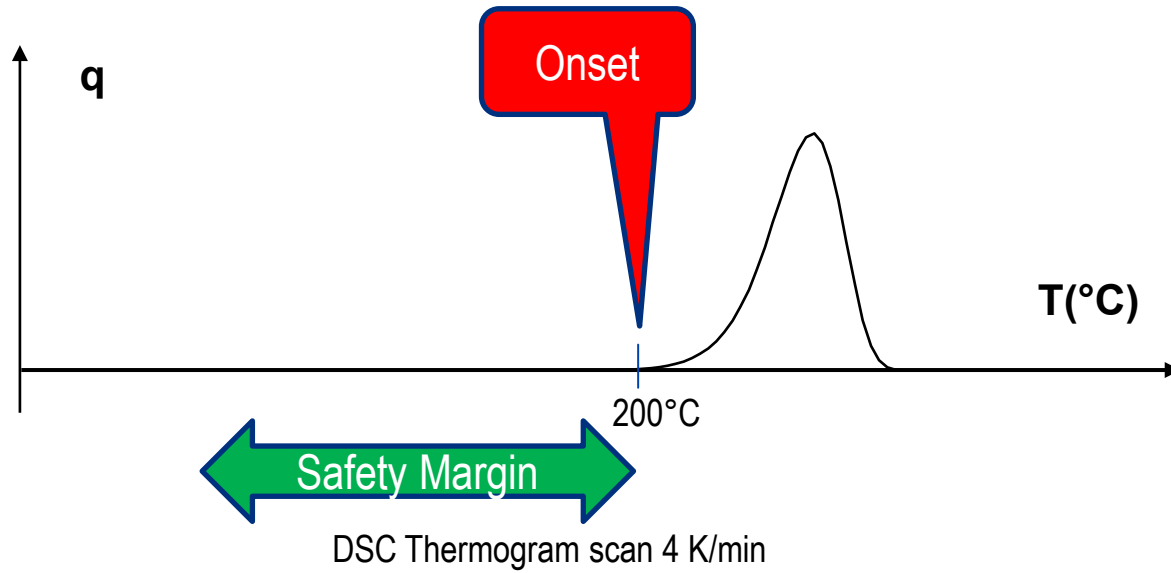
DSC Thermogram, measured in scan mode



DSC Thermogram scan 4 K/min



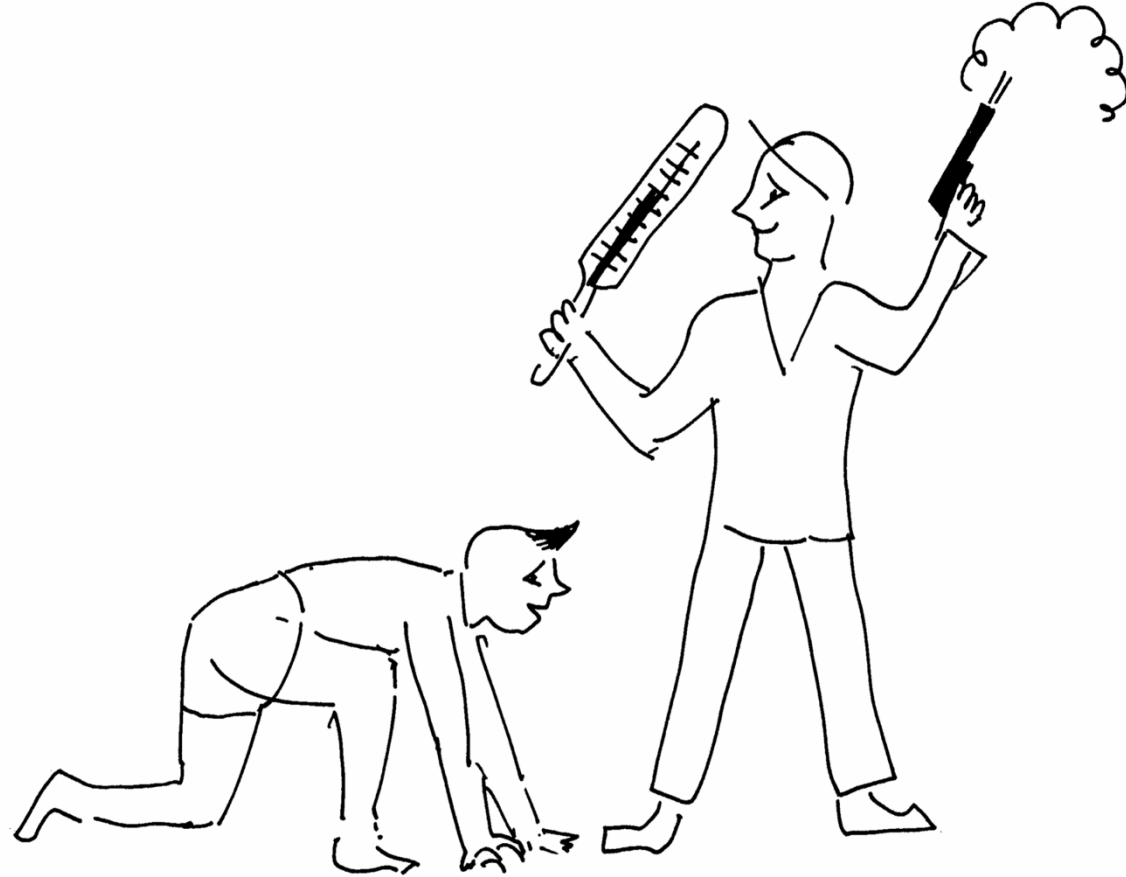
# What temperature is safe?



- A.  $< 250^{\circ}\text{C}$
- B.  $< 200^{\circ}\text{C}$
- C.  $< 150^{\circ}\text{C}$
- D.  $< 100^{\circ}\text{C}$
- E.  $< 50^{\circ}\text{C}$

Onset: The starting of a reaction

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## Onset: The starting of a reaction

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- When does the reaction start = Onset Temperature ?
- Arrhenius equation to describe reaction rate

$$r = k_0 \cdot \exp\left[\frac{-E_a}{RT}\right] \cdot f(X)$$

$r$ : reaction rate

$k_0$ : pre-exponential factor

$E_a$ : activation energy

$R$ : gas constant

$X$ : conversion

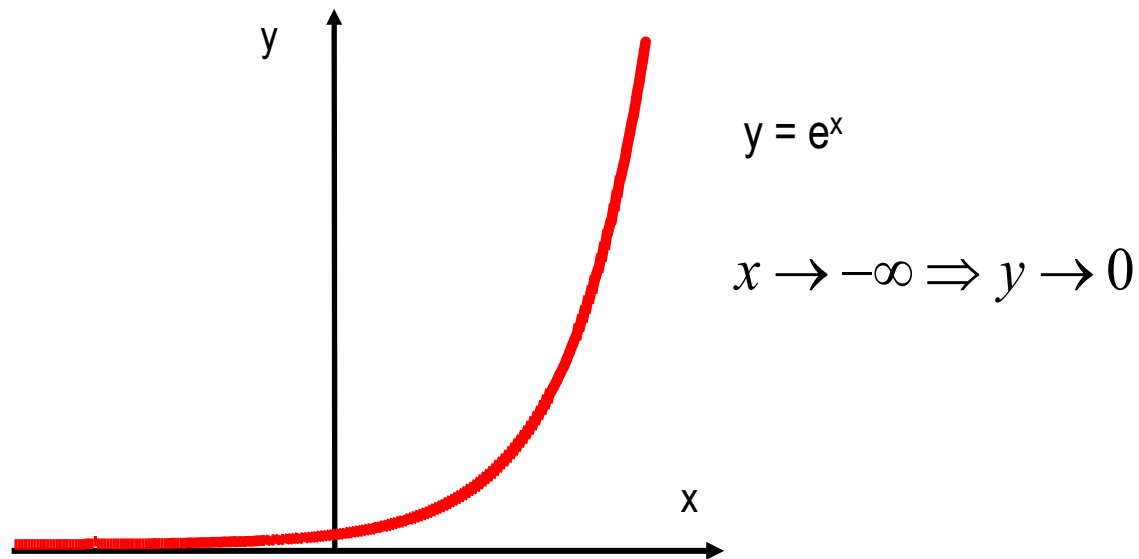
mol/(l·s)

units depend on reaction rate

J/mol

J/(mol·K)

-



$$T \rightarrow 0 \Rightarrow r \rightarrow 0$$

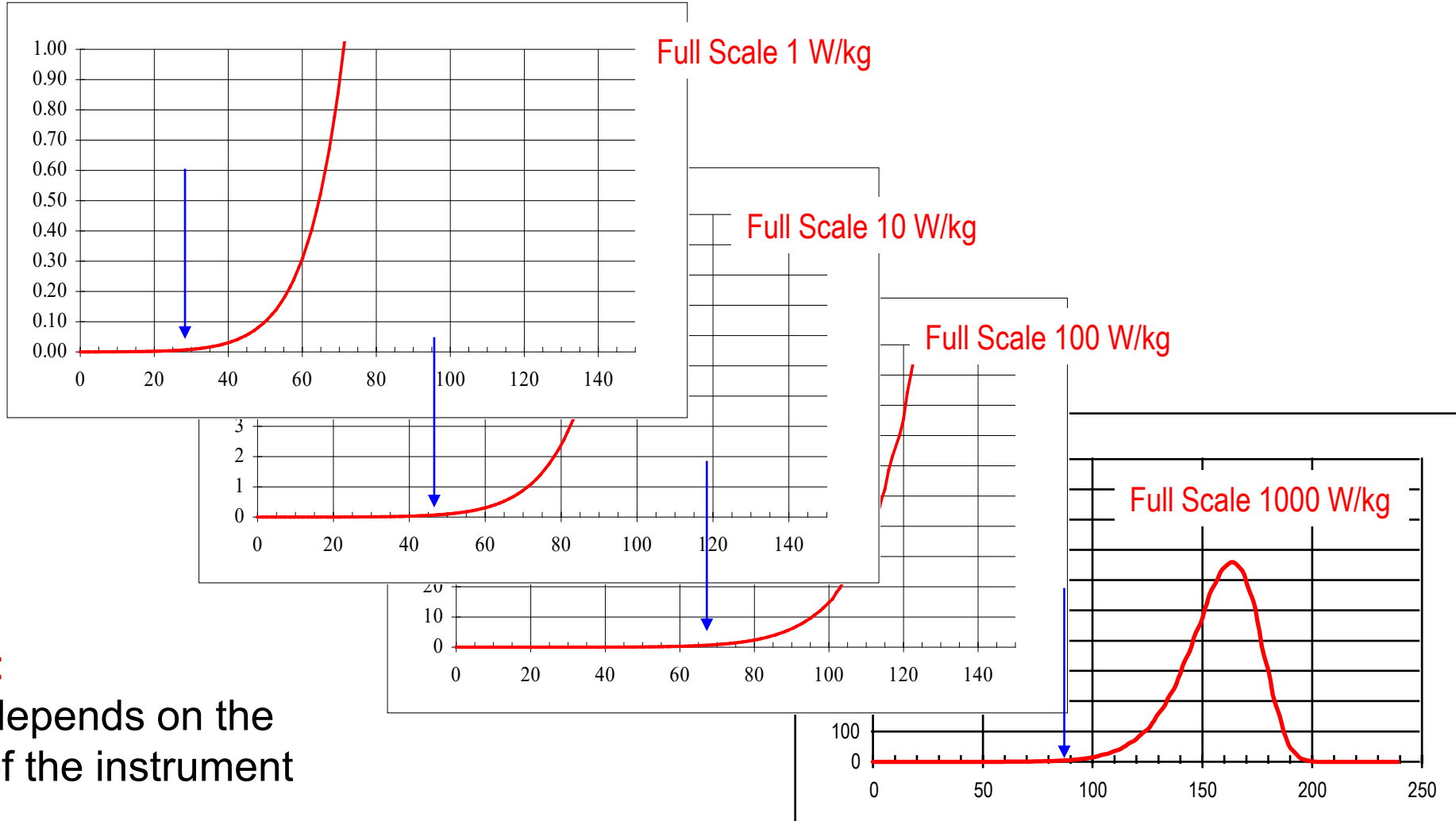
### Conclusion:

The reaction rate is zero at 0K. The reaction is always active. Whether the reaction rate is relevant depends on time and scale

There is no «onset temperature for the decomposition».

Onset temperature defined as the measured detection of a decomposition peak

# DSC: Sensitivity & Onset

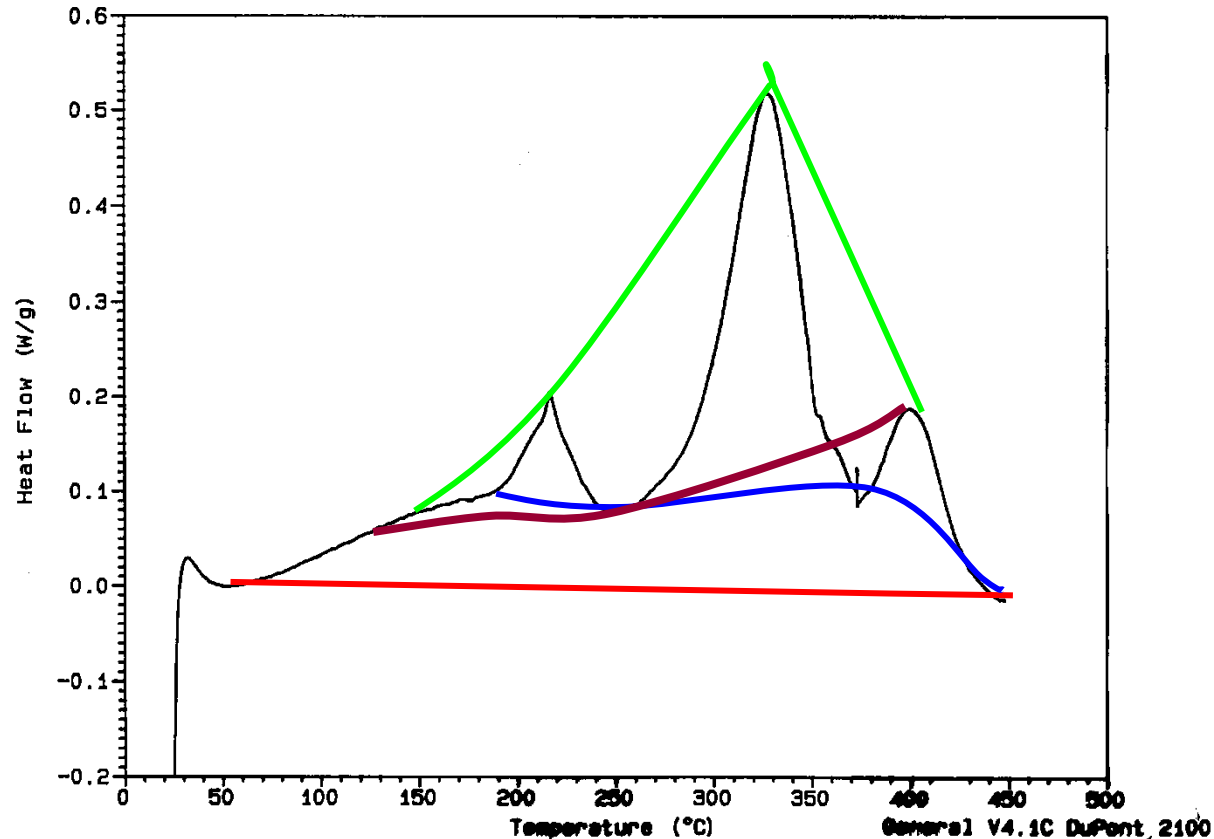


## Conclusion:

The onset depends on the sensitivity of the instrument

# DSC: Baseline

Sample: RM ZU PVC-STAB. (ST 3140) mRZS DSC File: A:RMPVCSTABI.322  
Size: 6.4720 mg Operator: V.Stocks  
Method: Standard-Run Run Date: 4-Aug-95 02:26  
Comment: BEI RT ALLE KOMPONENTEN MIT spez. Ruehrer gemischt



## Conclusion:

Setting a baseline requires experience and sometimes additional measurements.

The onset temperature depends strongly on the baseline.

Therefore, there is an uncertainty with respect to the onset temperature.

## Conclusion on “on-set”

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- There is no “on-set” temperature for a reaction
- The on-set temperature for a measurement depends on:
  - Sensitivity of the equipment → instrument and method dependent
  - Baseline
- Rules exist with safety margins (for example: 100°C below onset of DSC: safe situation). Those rules:
  - Are instrument and method dependent
  - Are not conservative: → there are exceptions to the rules
  - Depend on the situation/time to be assessed (storage of 100 m<sup>3</sup> is not the same than keeping a reaction mass in a reactor over a few hours)
  - Easy to have a first indication, but should not be used to exclude the risk of a decomposition

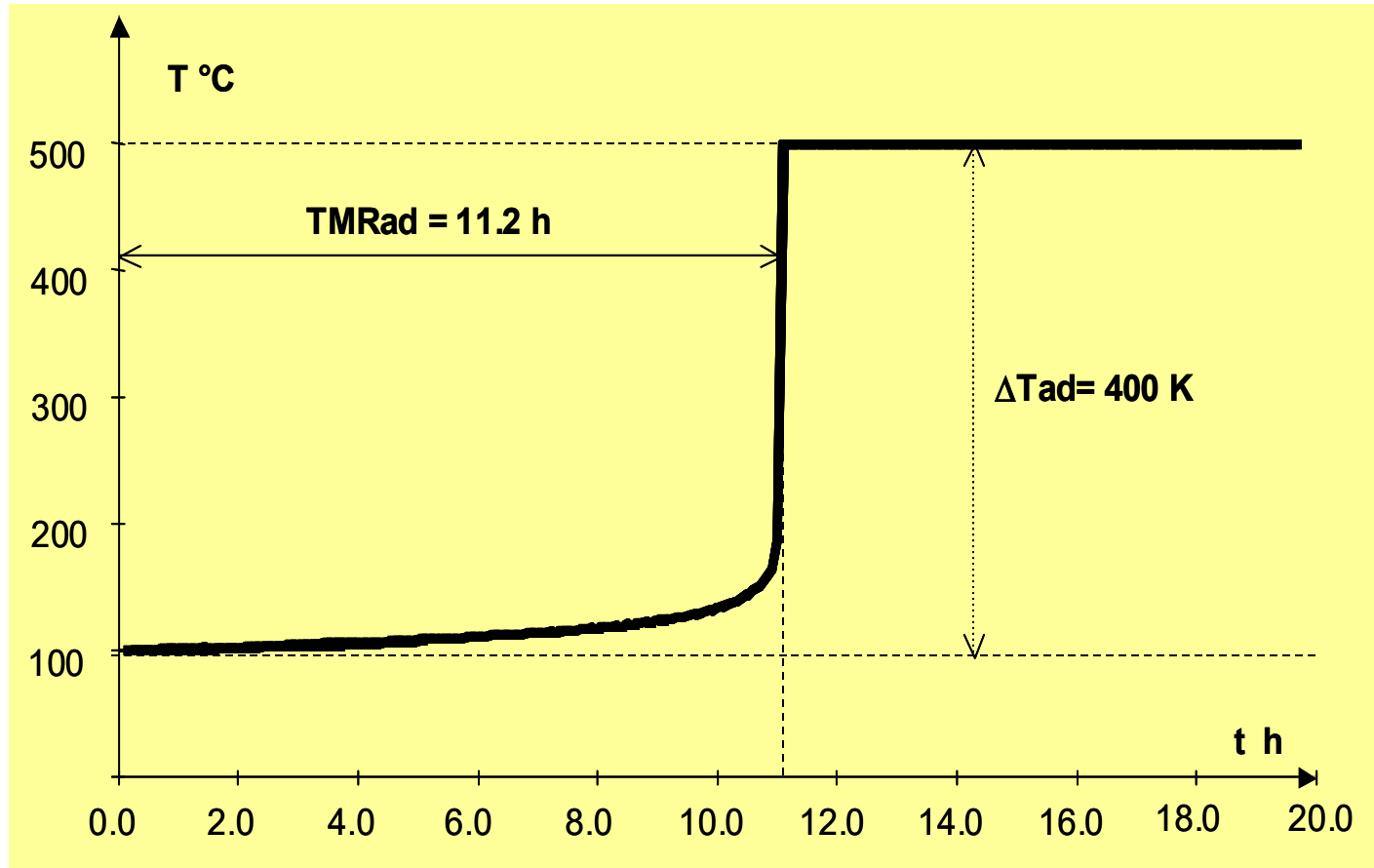
# Decomposition Reactions

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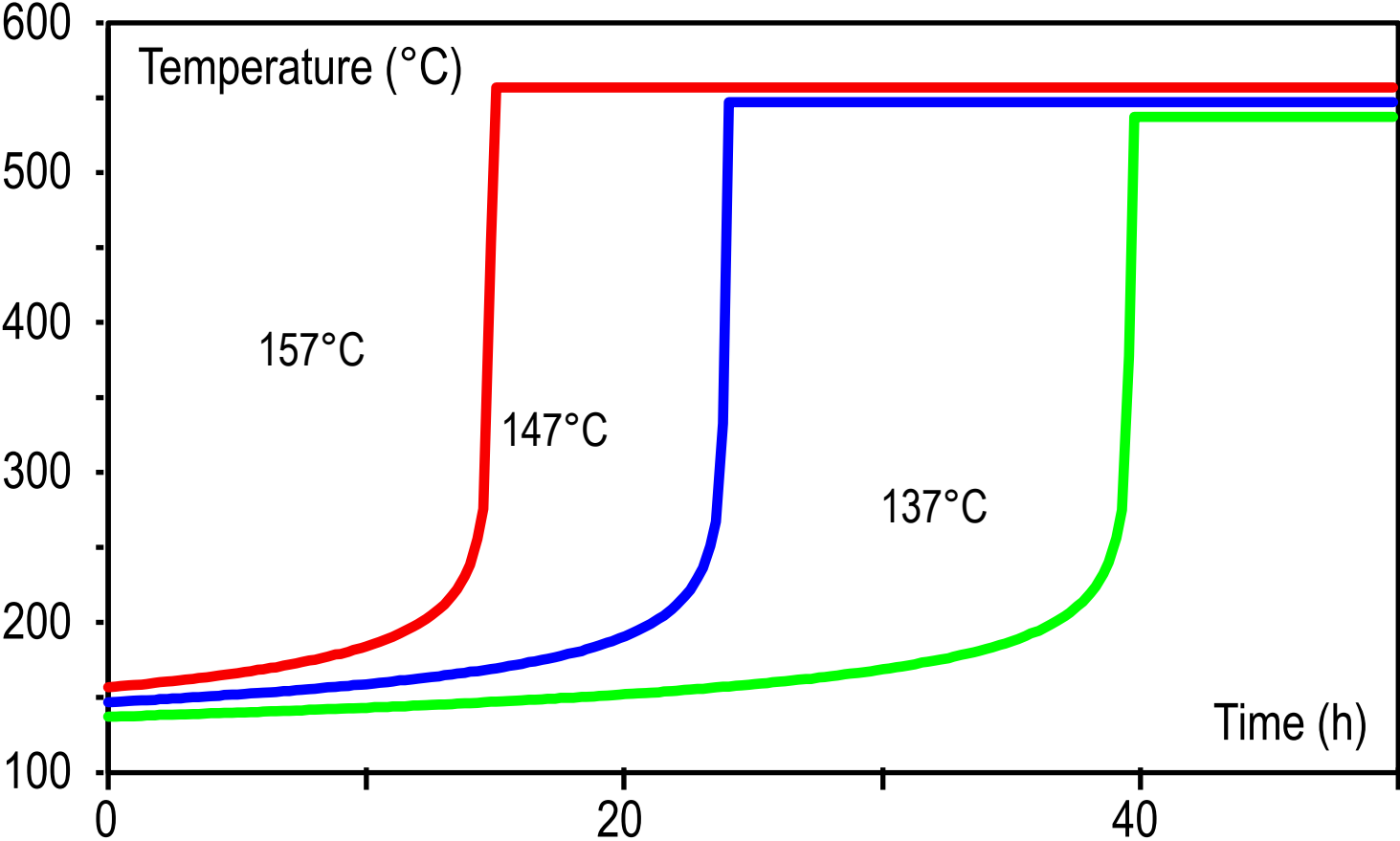
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    - Derivation of equation
    - Determination
- Examples
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# Characterisation of Decomposition Reactions

- TMRad: Time to Maximum Rate under Adiabatic Conditions



# Adiabatic Temperature Curves: Different Starting Temperatures



# TMR<sub>ad</sub>

$$\frac{dT}{dt} = \frac{q'}{c'_p} \text{ adiabatic conditions}$$

$$\frac{dT}{dt} = \frac{k_0 \cdot \exp\left(-\frac{E}{RT}\right) \cdot Q'_r}{c'_p} = \Delta T_{ad} \cdot k_0 \cdot \exp\left(-\frac{E}{RT}\right) \text{ Kinetic 0. Order}$$

$$q' = q'_0 \exp\left(-\frac{E}{R}\left(\frac{1}{T_0} - \frac{1}{T}\right)\right)$$

$$\frac{dT}{dt} = \frac{dT}{dt}\bigg|_{T_0} \cdot \exp\left(\frac{E}{R}\left(\frac{1}{T_0} - \frac{1}{T}\right)\right) \approx \frac{dT}{dt}\bigg|_{T_0} \cdot \exp\left(\frac{E}{R}\left(\frac{T - T_0}{T_0^2}\right)\right) \text{ conservativ approximation when } T > T_0$$

$$\Rightarrow t_T \cdot \frac{dT}{dt}\bigg|_{T_0} = \left[ -\frac{RT_0^2}{E} \cdot \exp\left(-\frac{E}{R}\left(\frac{T - T_0}{T_0^2}\right)\right) \right]_{T_0}^T = \frac{RT_0^2}{E} \cdot \left\{ 1 - \exp\left(-\frac{E}{R}\left(\frac{T - T_0}{T_0^2}\right)\right) \right\}$$

TMR reached when  $T = T_0 + \Delta T_{ad}$

$$TMR = \frac{RT_0^2}{E \cdot \frac{dT}{dt}\big|_{T_0}} \cdot \left\{ 1 - \exp\left(-\frac{E}{R}\left(\frac{\Delta T_{ad}}{T_0^2}\right)\right) \right\} \approx \frac{RT_0^2}{E \cdot \frac{dT}{dt}\big|_{T_0}} \text{ for relevant, i.e. interesting exothermies}$$

$$\text{with } \frac{dT}{dt}\bigg|_{T_0} = q'(T_0) / C_p$$

$$TMR(T_0) = \frac{RT_0^2 C_p}{E \cdot q'(T_0)} \quad q' \text{ in W/kg}$$

r: reaction rate

k<sub>0</sub>: pre-exponential factor

E<sub>A</sub>: activation energy

R: gas constant

T: Temperature

T<sub>0</sub>: Temperature of interest

t: time

Q': specific reaction energy

q': specific heat release rate

c'<sub>p</sub>: specific heat capacity

mol/(l·s)

units depend  
on reaction rate

J/mol

J/(mol·K)

K

K

s

J/kg

W/kg

kJ/(kg·K)

## Conclusion:

TMR<sub>ad</sub> based on heat balance

Hypothesis:

- 0 order reaction
- Adiabatic conditions

## Time to Maximum Rate under Adiabatic Conditions: $TMR_{ad}$

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Approximate estimation in seconds

$$TMR_{ad} = \frac{c_{p'} \cdot R \cdot T_0^2}{q'_{(T_0)} \cdot E}$$

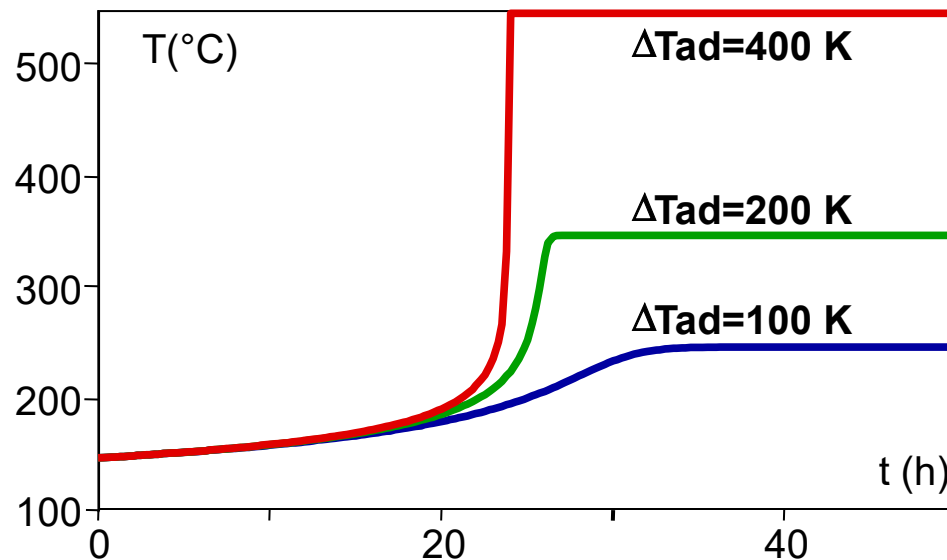
|              |                                            |
|--------------|--------------------------------------------|
| $c_p'$       | specific heat capacity [J / kg / K]        |
| $R$          | universal gas constant 8.314 J / ( mol. K) |
| $T$          | temperature (K)                            |
| $q'_{(T_0)}$ | Heat release rate at $T_0$ [W / kg]        |
| $E_a$        | Activation energy [J / mol]                |

# Decomposition reactions: 0 order approximation

$$r = k_0 \cdot \underbrace{\exp\left[-\frac{E}{RT}\right]}_{\text{Increases}} \cdot C_0 \cdot \underbrace{(1-X)}_{\text{Decreases}}$$

|                                         |           |
|-----------------------------------------|-----------|
| r: reaction rate                        | mol/(l·s) |
| k <sub>0</sub> : pre-exponential factor | 1/s       |
| E: activation energy                    | J/mol     |
| R: gas constant                         | J/(mol·K) |
| T: Temperature                          | K         |
| C <sub>0</sub> : initial concentration  | mol/l     |
| X: conversion                           | -         |

**Adiabatic conditions:** 1<sup>st</sup> order exothermic reactions with different reaction energies (same activation energy and initial concentration)



## Conclusion:

0 order approximation:

- Good estimation of TMR<sub>ad</sub> for high decomposition energies
- Conservative for lower decomposition energies

# Decomposition Reactions

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  - Determination of  $TMR_{ad}$ 
    - Derivation of equation
    - Determination
- Examples

# Determination: $TMR_{ad}$

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- Required data:

- $q'(T)$
- $E_a$

- Isothermal method

1

- Isoconversional method

2

- Simplified method (rule of thumb)

3

Approximate estimation in seconds

$$TMR_{ad} = \frac{c_{p'} \cdot R \cdot T_0^2}{q'_{(T_0)} \cdot E}$$

$c_{p'}$

specific heat capacity [J / kg / K]

$R$

universal gas constant 8.314 J / ( mol. K)

$T$

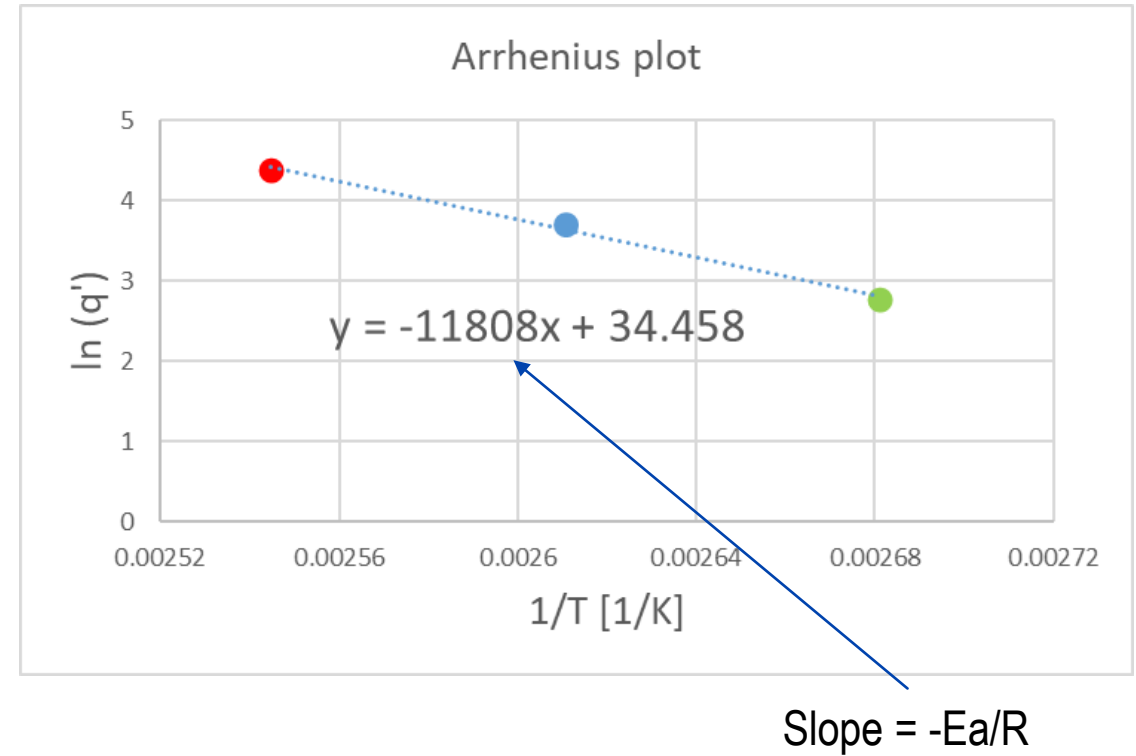
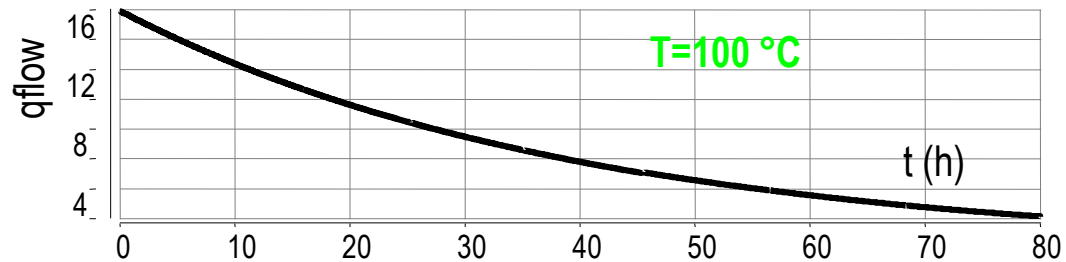
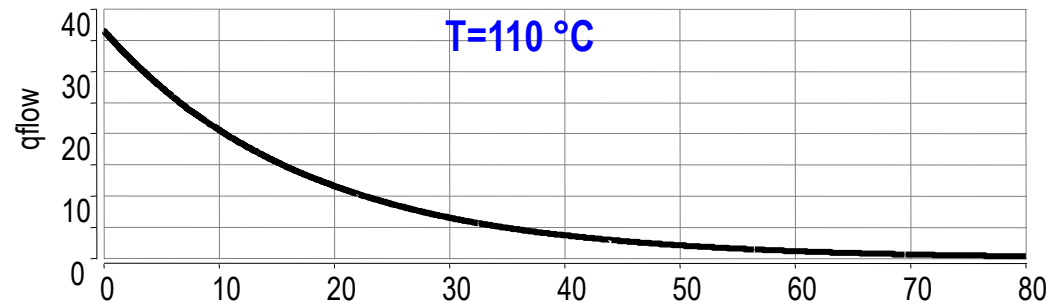
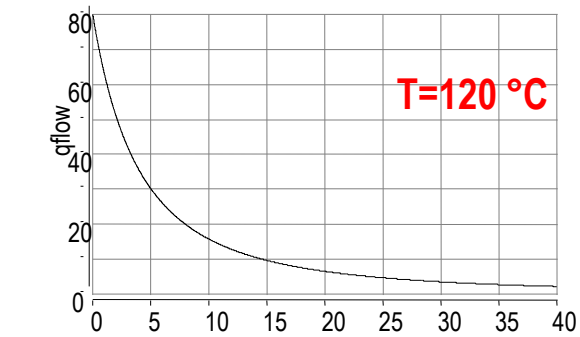
temperature (K)

$q'_{(T_0)}$

Heat release rate at  $T_0$  [W / kg]

$E_a$

Activation energy [J / mol]

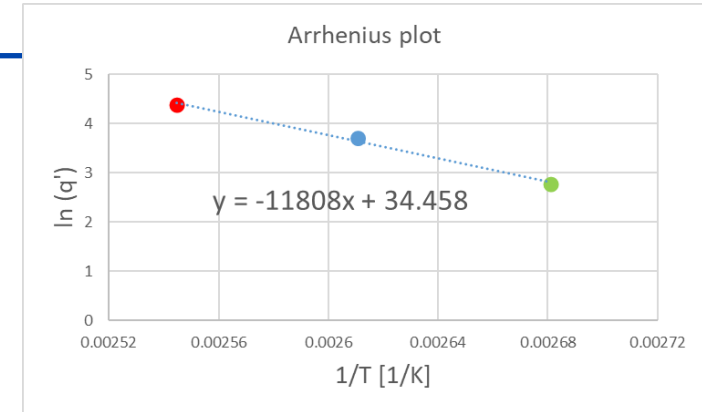


$$TMR_{ad} = \frac{c_{p'} \cdot R \cdot T_0^2}{q'_{(T_0)} \cdot E}$$

- TMRad at 100°C:
  - $q'$ : 16 W/kg
  - $E_a$ :  $11808 \times 8.314 = 98'172$  J/mol
  - $c'_p$ : estimation for an organic liquid: 1.8 kJ/(kg·K)

$$TMR_{ad} = \frac{c_{p'} \cdot R \cdot T_0^2}{q'_{(T_0)} \cdot E} = \frac{1800 \cdot 8.314 \cdot (373)^2}{16 \cdot 98172} = 1325s = 22 \text{ min}$$

- TMRad at 50°C?



## Isothermal DSC: calculation of TMRad

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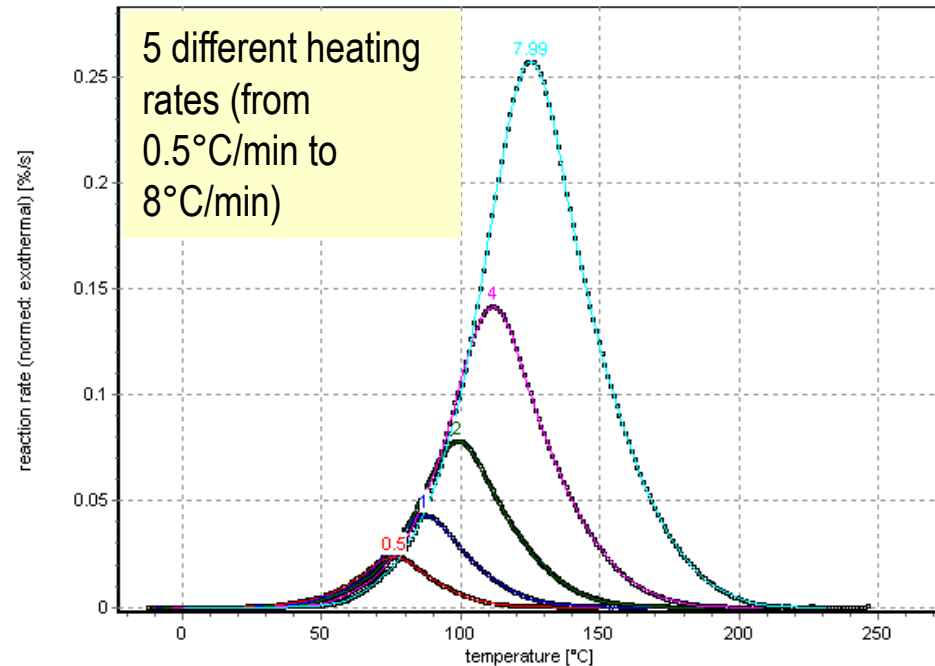
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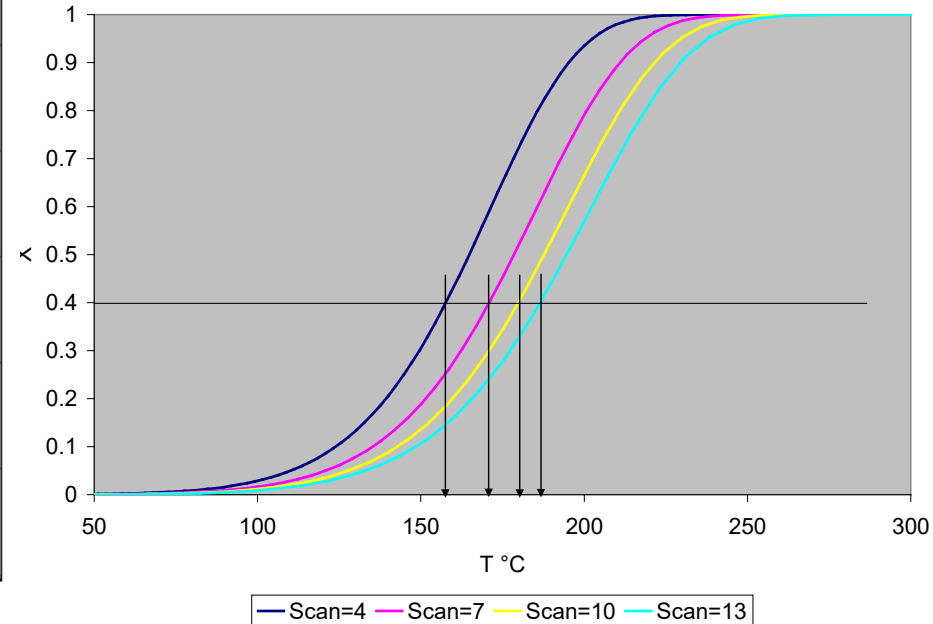
- TMRad at 50°C
  - $q'$ :? Extrapolate from isothermal measurements  $\rightarrow$  0.12 W/kg or calculate from  $q' = q'_0 \exp\left(-\frac{E}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right)\right)$
  - $E_a$ :  $11808 \times 8.314 = 98'172$  J/mol
  - $c'_p$ : estimation for an organic liquid: 1.8 kJ/(kg·K)
  - TMRad: 129'779 s  $\rightarrow$  36 hours

## Series of thermogrammes at different scan rates

Advanced Kinetic Analysis ; T-Experimental ; reaction rate(DSC) ; Confidence interval : mean value



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$$q' = \frac{dX}{dt} \cdot Q' = k_0 \cdot e^{\frac{-E}{RT}} \cdot f(X) \cdot Q'$$

$q'$ : specific heat release rate

$X$ : conversion

$t$ : time

$Q'$ : specific reaction energy

$k_0$ : pre-exponential factor

$E$ : activation energy

$R$ : gas constant

$T$ : Temperature

W/kg

-

s

J/kg

1/s

J/mol

J/(mol·K)

K

$$\frac{dX}{dt} = k_{0(X)} \cdot \exp\left\{\frac{-E_{a(X)}}{RT}\right\} \cdot f(X)$$

This part of the equation is a function of the concentrations

$$\ln\left(\frac{dX}{dt}\right) = \underbrace{\ln k_0 + \ln(f(X))}_{\text{constant for constant X}} - \frac{E_{a(X)}}{R \cdot T}$$

X: conversion

t: time

$k_{0(X)}$ : pre-exponential factor for a specific X

$E_{a(X)}$ : activation energy for a specific X

R: gas constant

T: Temperature

-

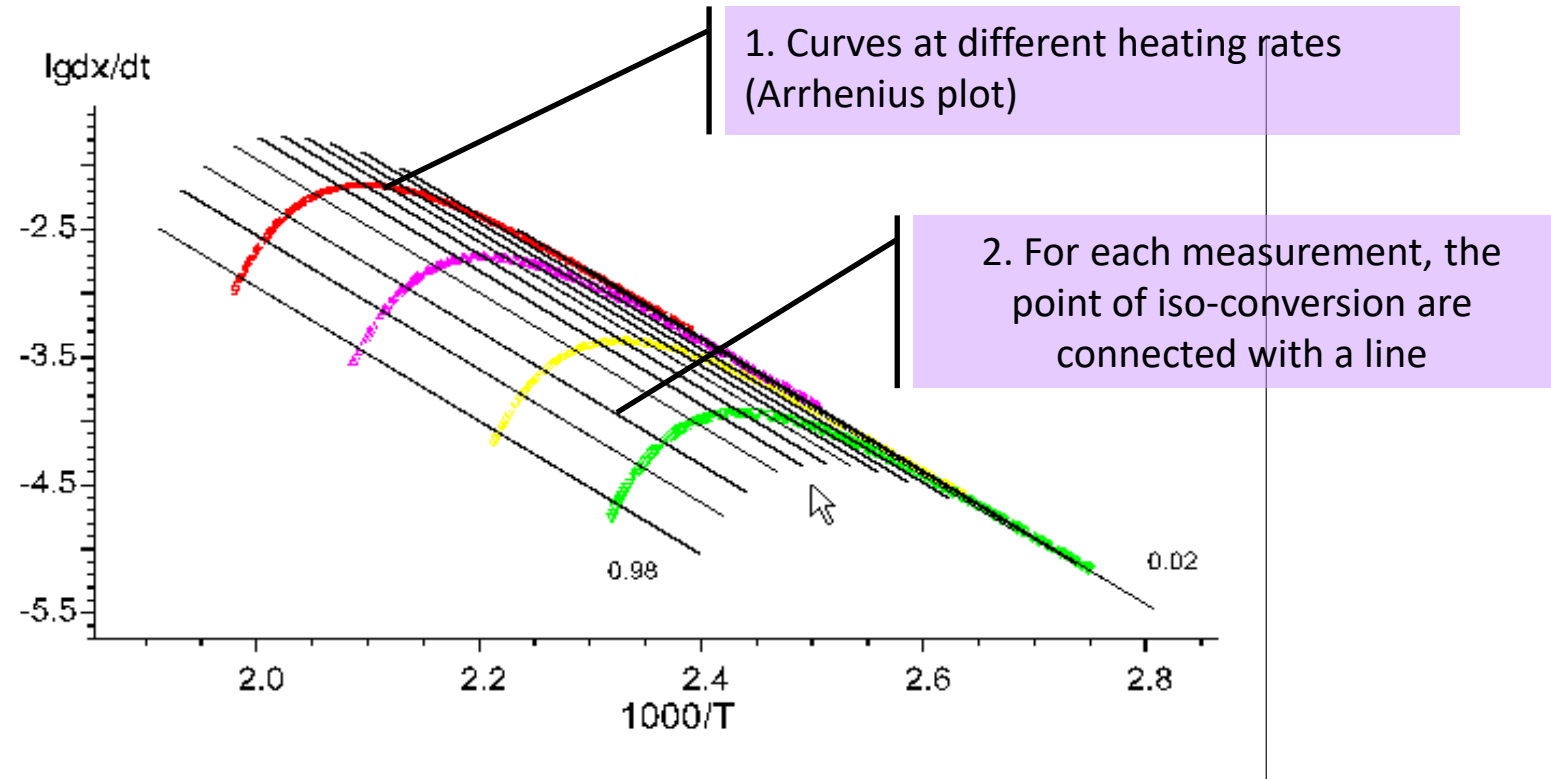
s

depends on rate law

J/mol

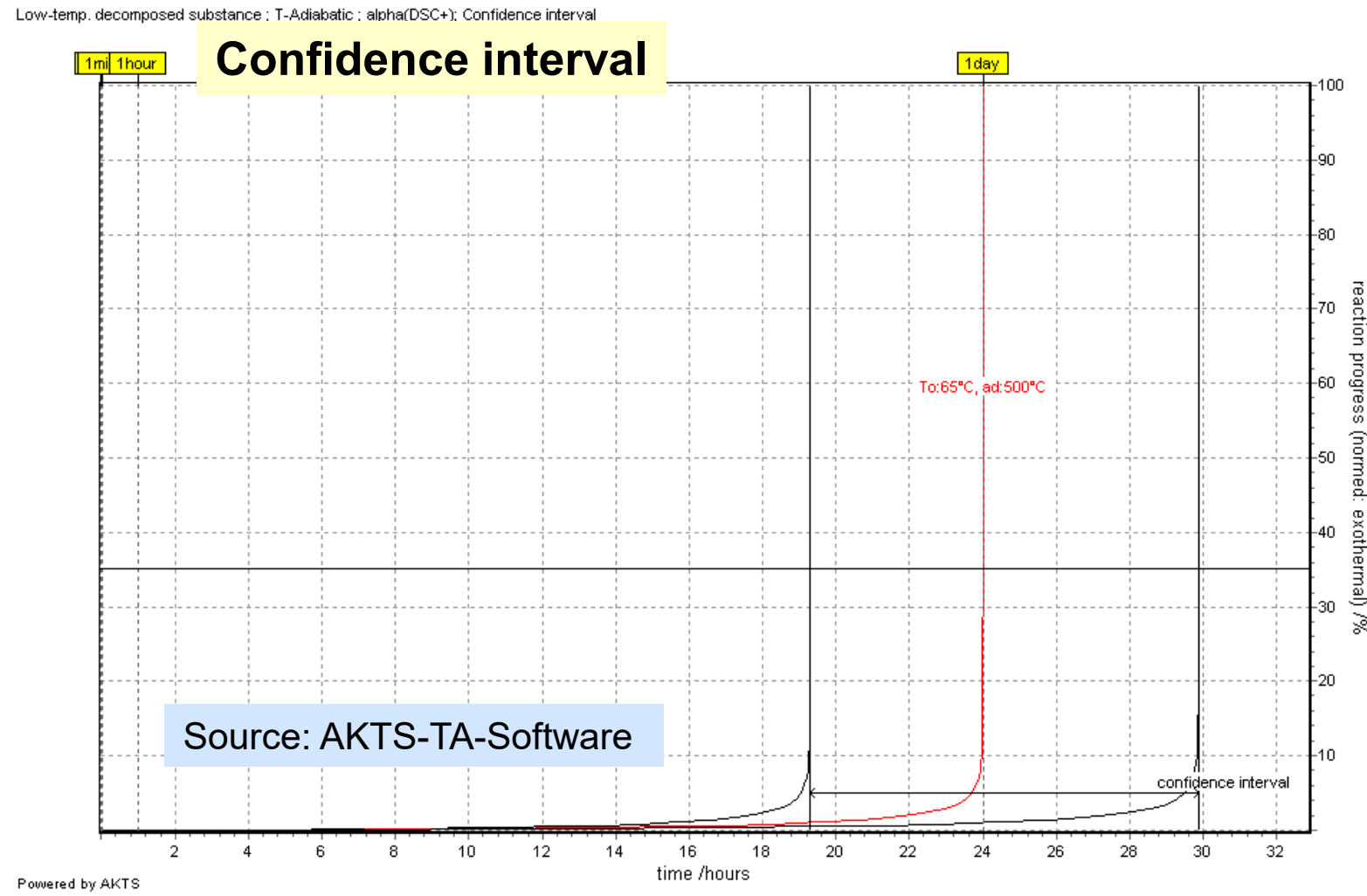
J/(mol·K)

K



Every line has an activation energy ( $E_a$ ) and an y-interception ( $\ln k_{0(X)} + \ln(f(X))$ )

$$\ln\left(\frac{dX}{dt}\right) = \ln(k_{0(X)}) + \ln(f(X)) - \frac{E_{a(X)}}{R \cdot T}$$



## On-Set (100K rule)

- 👎 Instrument specific
- 👎 No direct scale-up to plant situation
- 👎 Requires a strict guideline for scale-up

## TMRad

- 👍 Independant of laboratory instrument (not when using rule of thumbs)
- 👍 Scale-up to plant situation possible
- 👍 Based on physical chemistry (kinetics)

- Isothermal method:
  - Several isothermal measurements
  - Arrhenius plot: determination of activation energy
  - Extrapolation of heat release rate
- Isoconversional method
  - Several measurements in scan rate
  - Model free kinetics
  - Modeling decomposition
  - Problem when several decompositions
- Both methods require some time to determine TMRad (~ one week) → Need a screening method (conservative): Rule of thumb

## Rule of Thumb based on a DSC in scan mode (4°C/min)

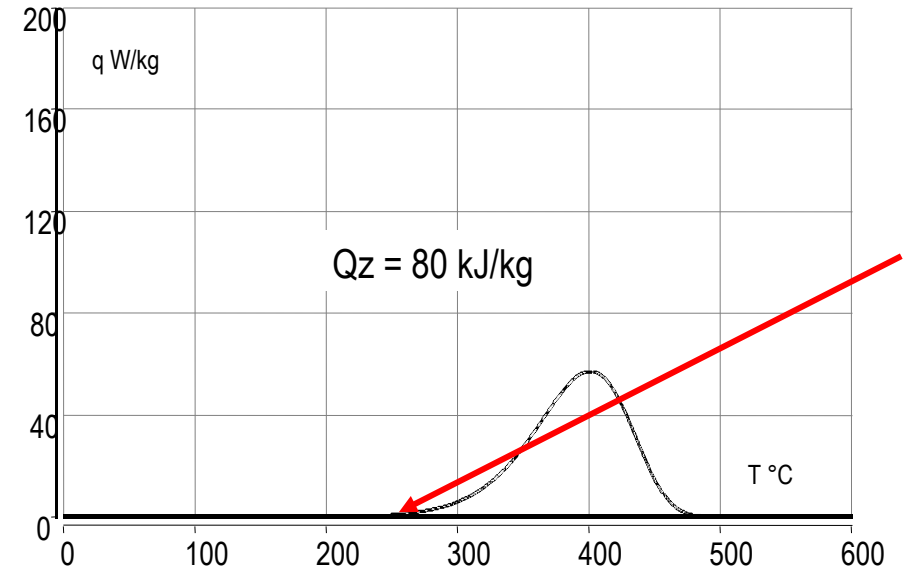
- $q_{ref} = 20$  W/kg at peak detection temperature ( $T_{ref}$ )
- Assume low Activation energy: 50 kJ/mol
- Calculate  $q = f(T)$  (0 order kinetics)

$$q'_{(T)} = q'_{(T_{ref})} \times \exp \left[ \frac{-E_a}{R} \times \left( \frac{1}{T} - \frac{1}{T_{ref}} \right) \right]$$

- Calculate  $TMR_{ad} = f(T)$  (cp for liquids 1.8, solids 1.3 kJ/kg.K)

$$TMR_{ad}(T) = \frac{c'_p R T^2}{q'_{(T)} E_a}$$

- ☹ Not valid for autocatalytic reactions (not necessarily conservative)
- ☹ Depends on instrument (on-set problematic)



Sample: 12.5 mg

Scan: 4°C / min

Gold plated high pressure crucible

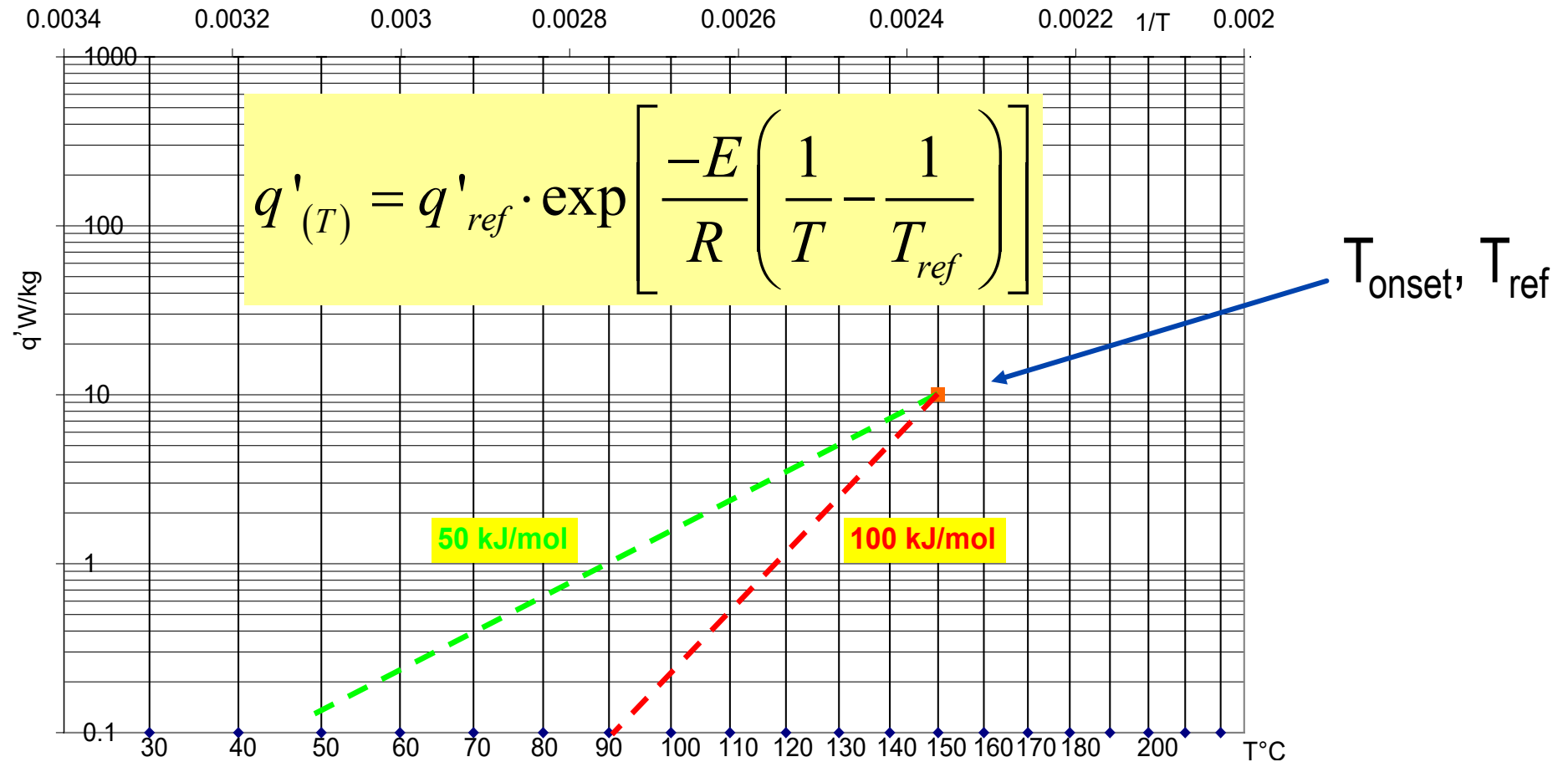
- TMRad at 100°C:
  - $q'_{\text{ref}}$ : 20 W/kg for a  $T_{\text{ref}}$  of 250°C
  - $E_a$ : 50 kJ/mol
  - $c'_p$ : estimation for an organic liquid: 1.8 kJ/(kg·K)

- TMRad at 100°C:
  - $q'_{\text{ref}}$ : 20 W/kg for a  $T_{\text{ref}}$  of 250°C
  - $E_a$ : 50 kJ/mol
  - $c'_{\text{p}}$ : estimation for an organic liquid: 1.8 kJ/(kg·K)

$$q'_{(T)} = q'_{(T_{\text{ref}})} \times \exp \left[ \frac{-E_a}{R} \times \left( \frac{1}{T} - \frac{1}{T_{\text{ref}}} \right) \right] = 20 \times \exp \left[ \frac{-50'000}{8.314} \times \left( \frac{1}{373} - \frac{1}{523} \right) \right] = 0.2 W / kg$$

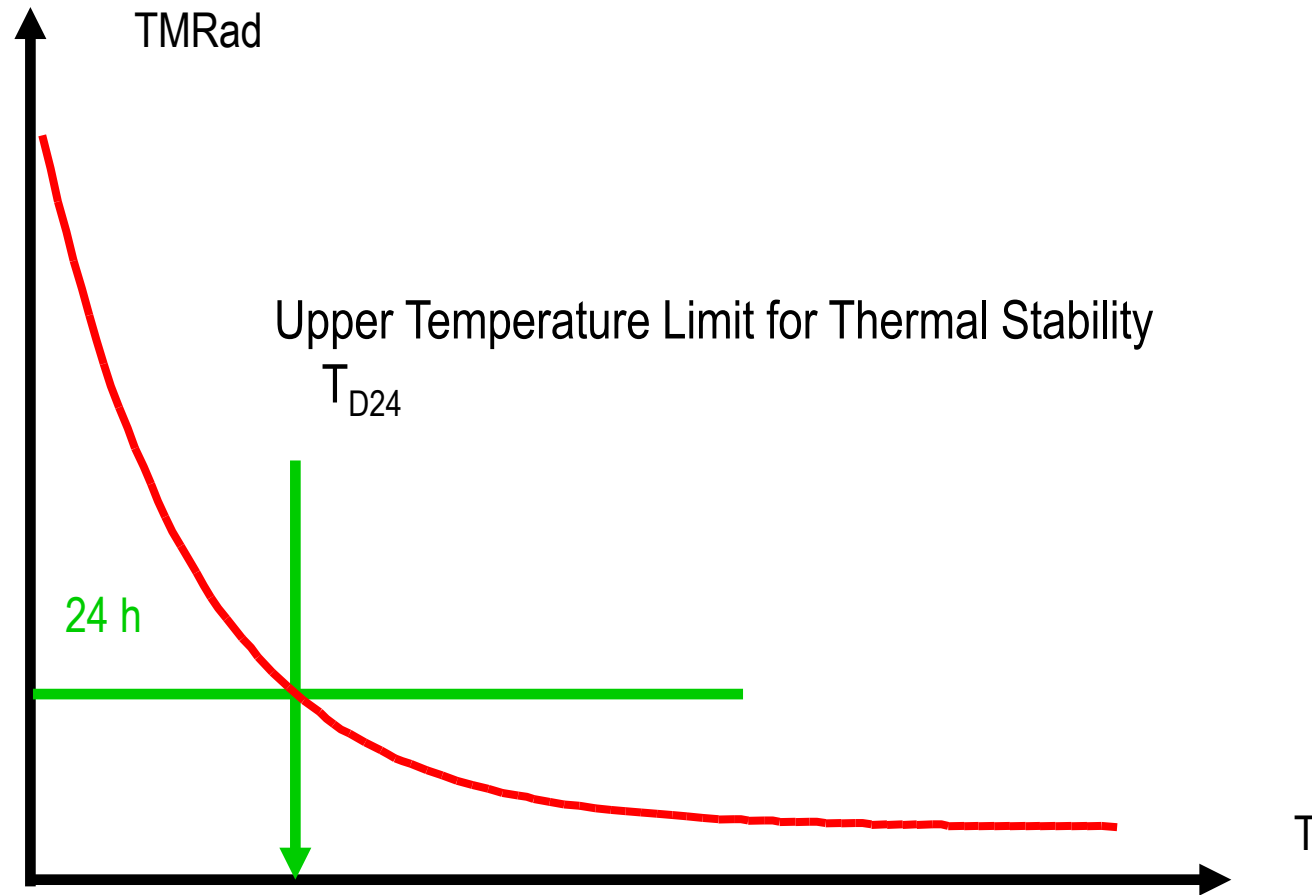
$$TMR_{ad} = \frac{c_{p'} \cdot R \cdot T_0^2}{q'_{(T_0)} \cdot E} = \frac{1800 \cdot 8.314 \cdot (373)^2}{0.2 \cdot 50'000} = 2 \cdot 10^5 = 58h$$

- Extrapolation from one reference point, why is 50 kJ/mol a conservative activation energy?



# TMRad as a Function of Temperature

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# Definitions

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- $T_{D24}$ : Temperature at which TMRad = 24 h
- $T_{D8}$  : Temperature at which TMRad = 8 h

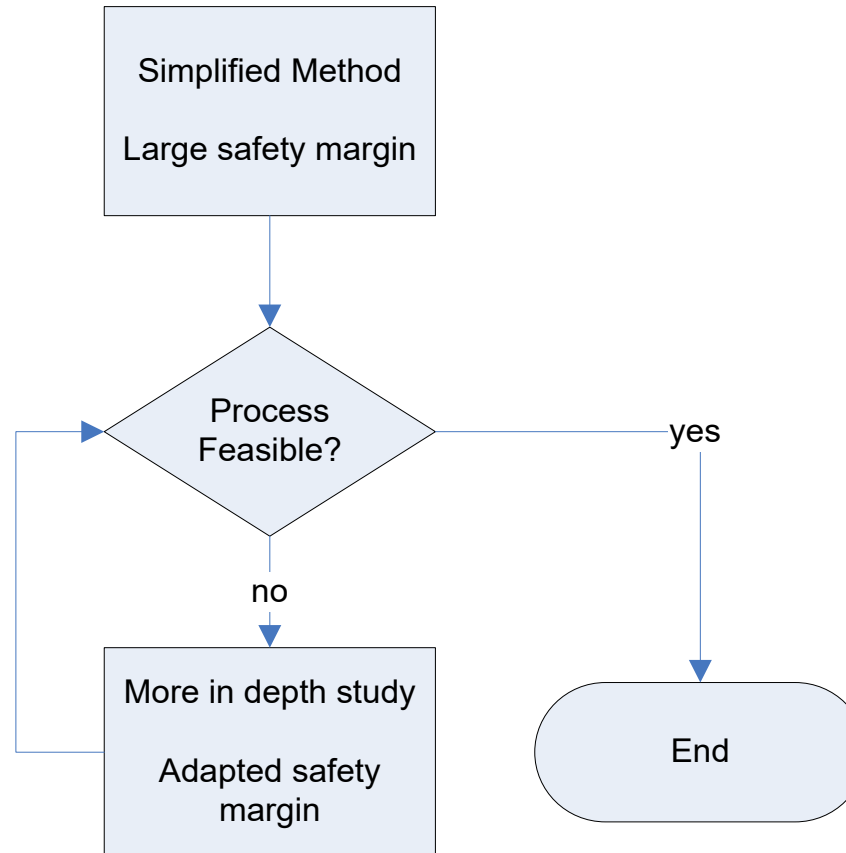
Rule of thumb / Order of magnitude:

- |                          |                |
|--------------------------|----------------|
| • Detection limit in DSC | TMRad = 1hr    |
| • For 1 W/kg             | TMRad = 8 hrs  |
| • For 0.3 W/kg           | TMRad = 24 hrs |

Which method should we use?

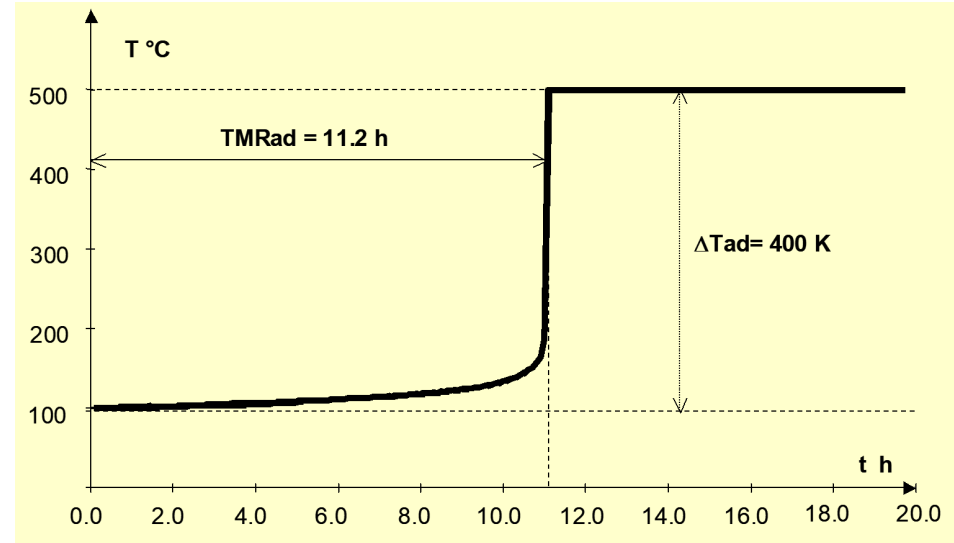
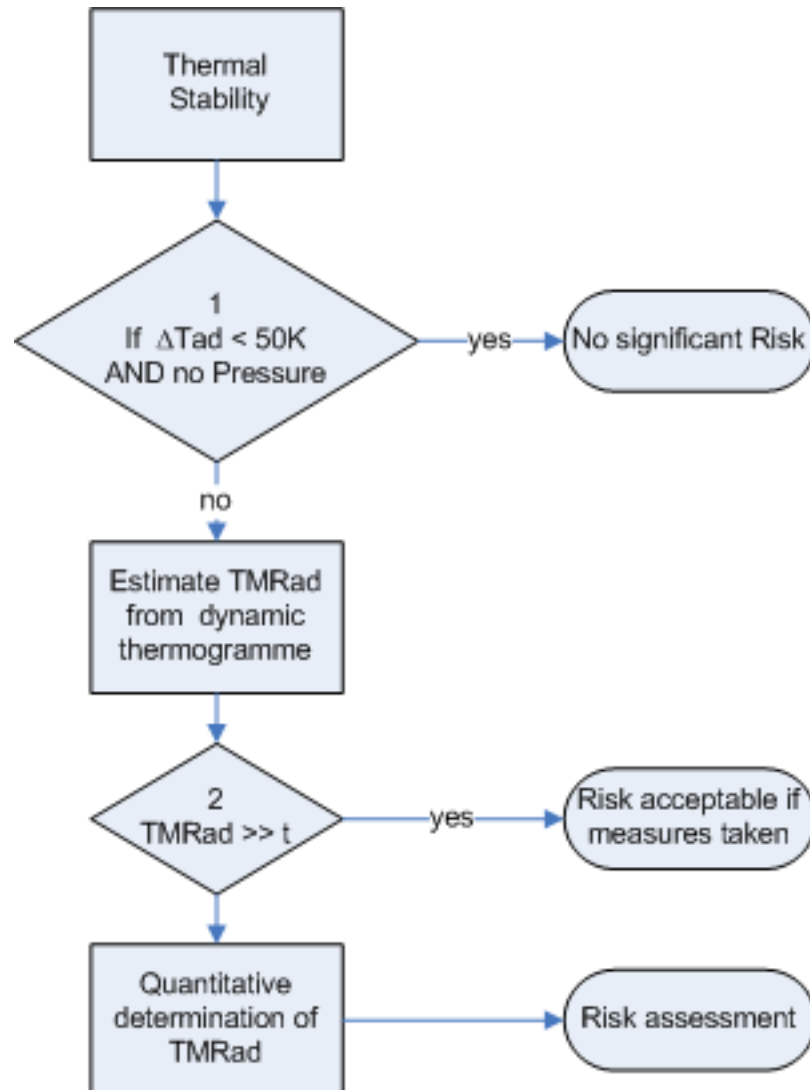
- **KISS**-Principle:

**K**eep **I**t **S**imple and **S**afe



# TMR<sub>ad</sub> and Risk Assessment

## Characterisation of secondary reactions



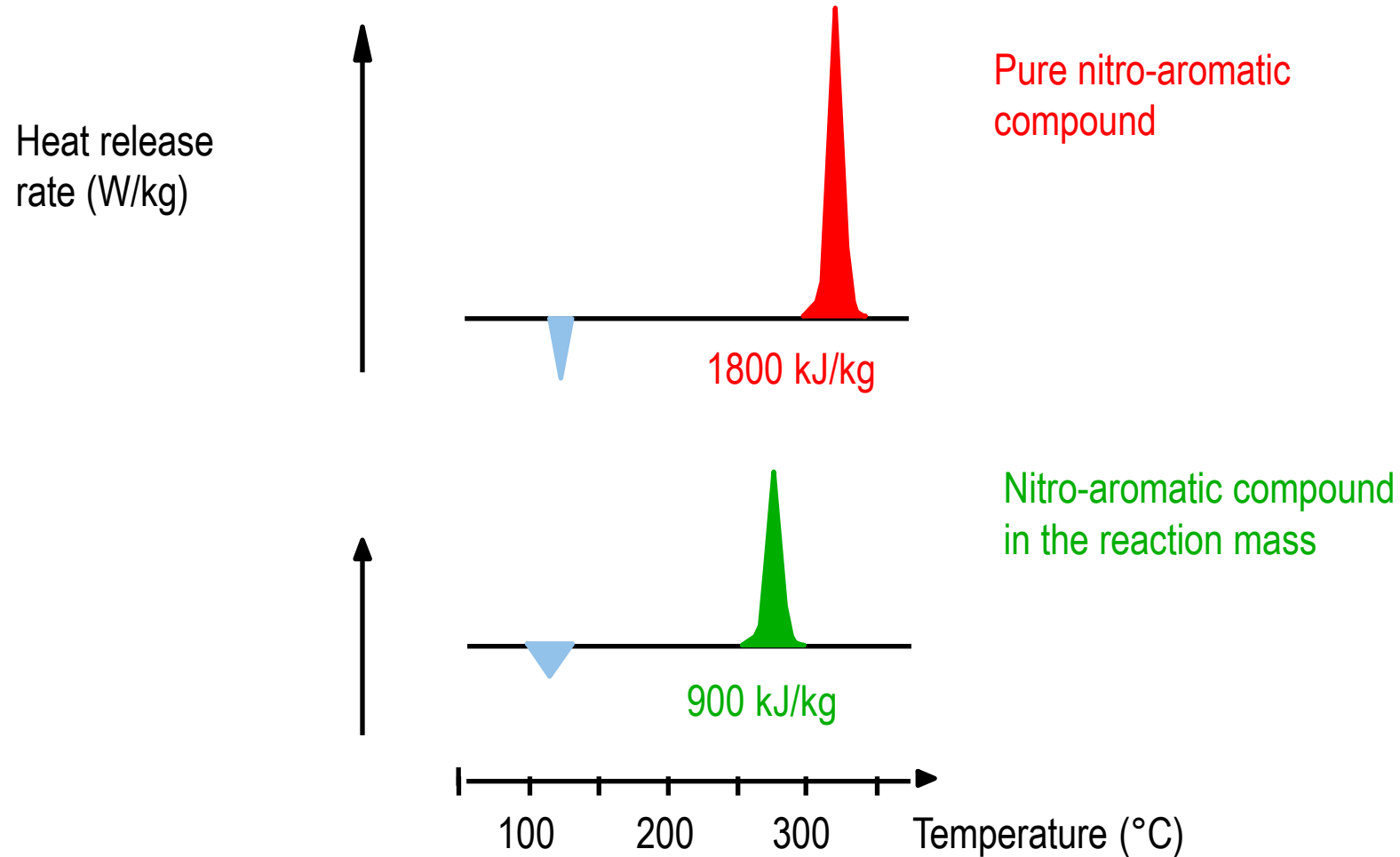
- Risk assessment
  - Severity:  
Energy, temperature, pressure
  - Probability of triggering TMR<sub>ad</sub>, time for  
applying measures

# Decomposition Reactions

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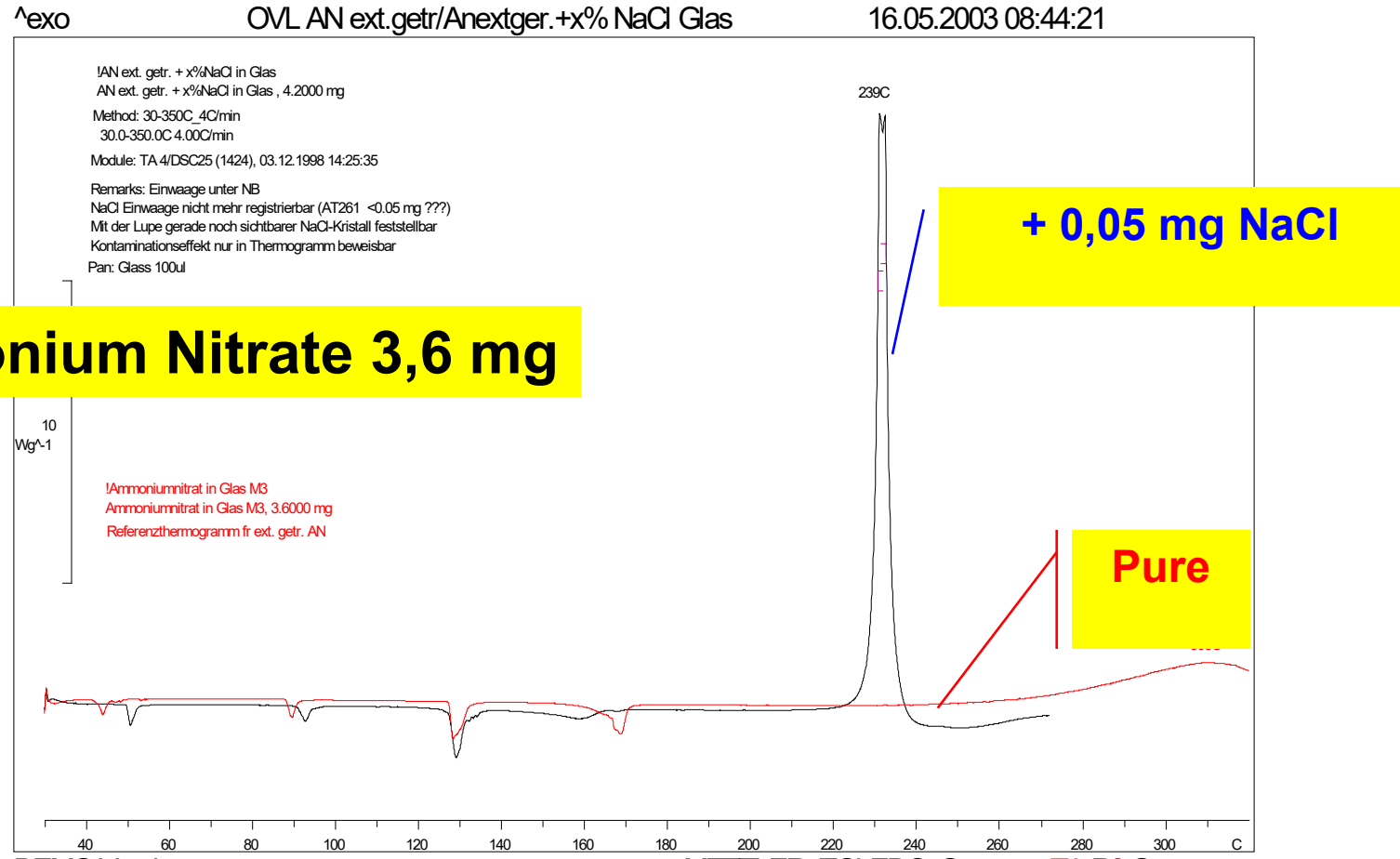
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# DSC: Hydrogenation of a Nitro-Aromatic Compound



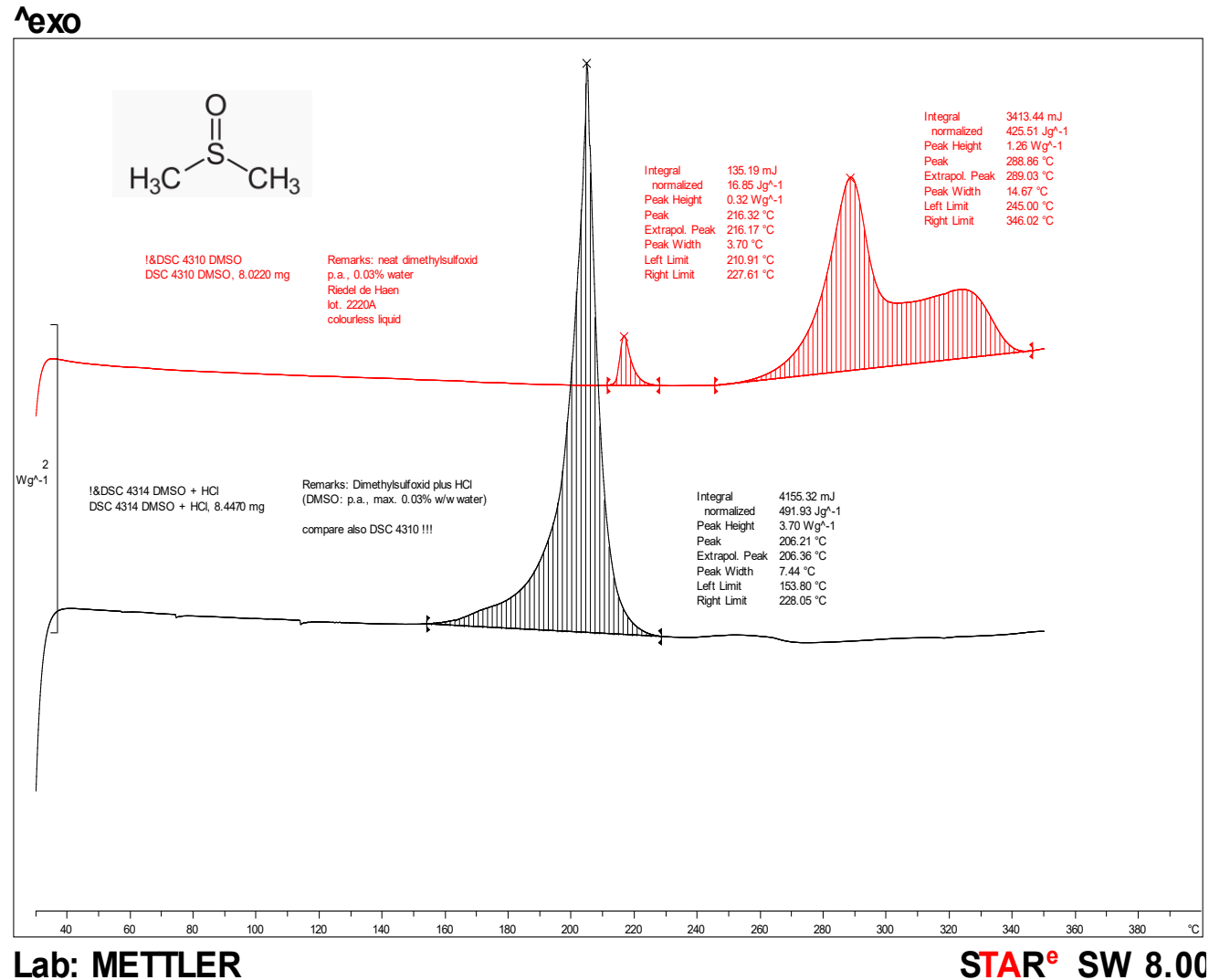
**Conclusion:** measure the stability of a representative sample → as it will be present in the process

# Contamination by impurities



**Conclusion:** impurities can have a tremendous effect on the stability. Test foreseeable impurities

# Effects of contaminants on DMSO



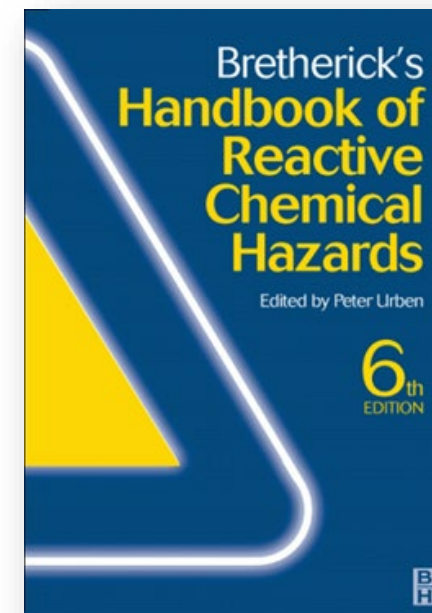
**Conclusion:** impurities can have a tremendous effect on the stability. Test foreseeable impurities

**Bretherick:**

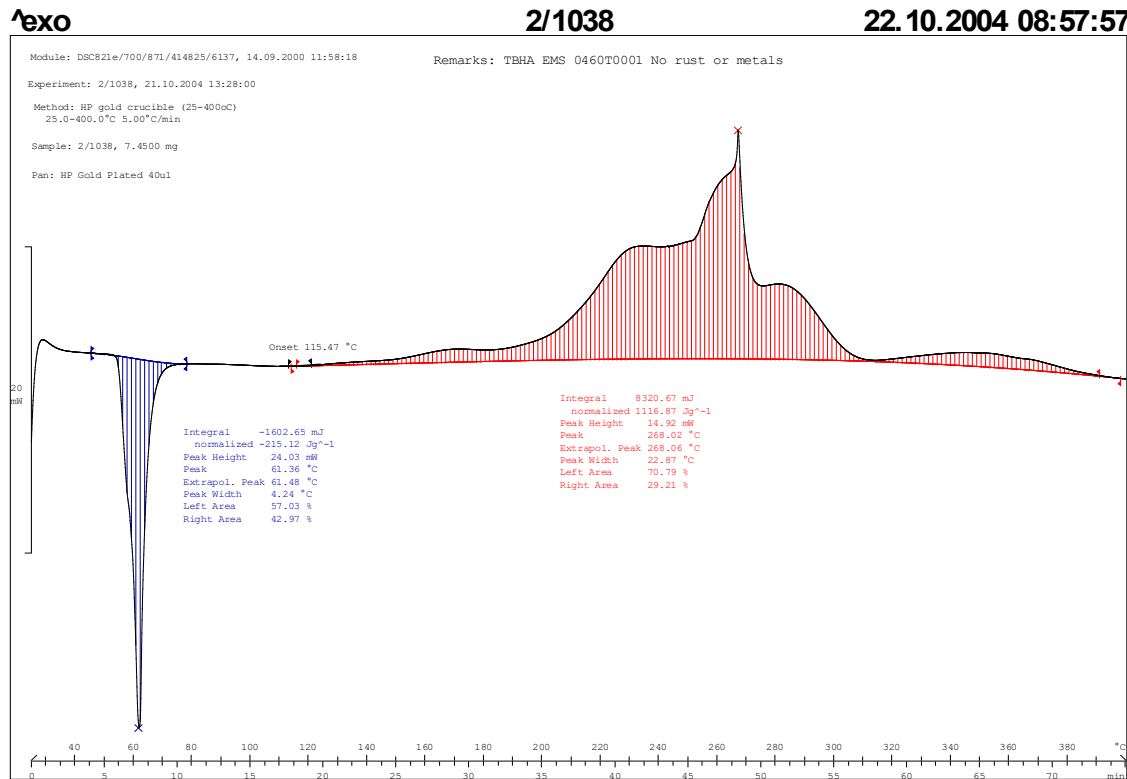
... Two instances of used DMSO decomposing exothermally while being kept at 150°C prior to recovery by vacuum distillation were investigated. Traces of alkyl bromides lead to a delayed, vigorous and strongly exothermic reaction ( $Q = 850 \text{ J/gm}$ ) at 180°C ...

### Named compatibility issues with 30 compounds or classes:

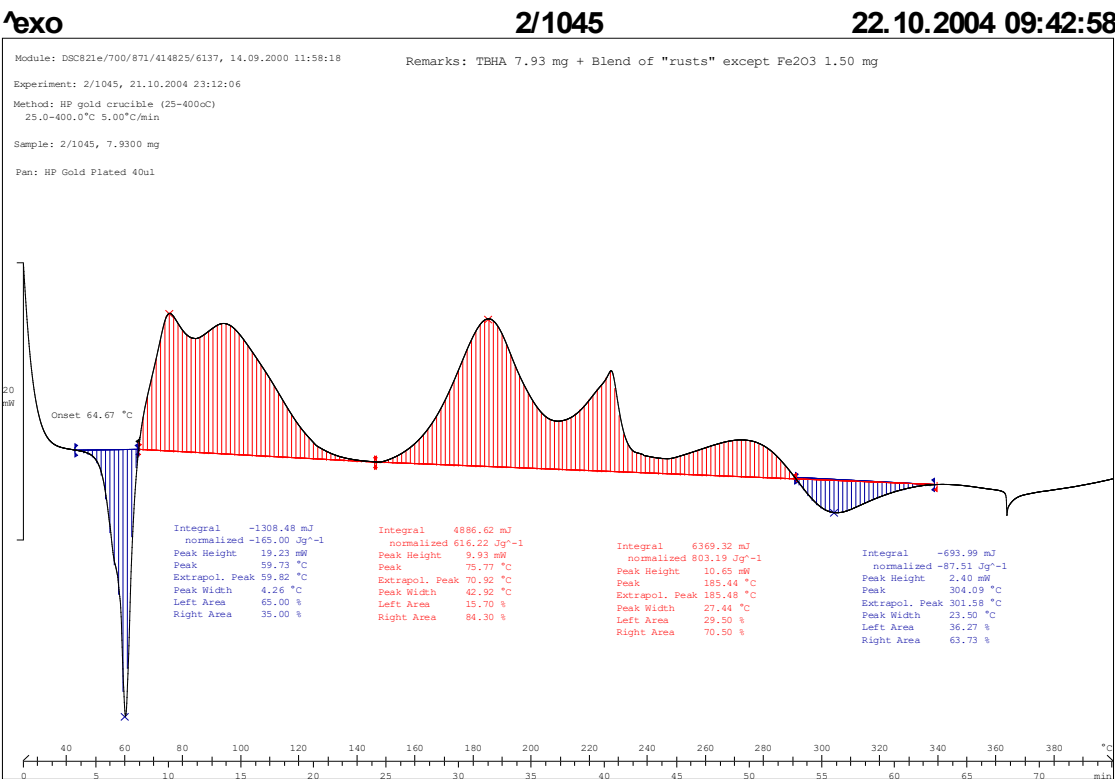
Acid anhydrides - Acids, or Bases - Acyl halides, or Non-metal halides - Allyl trifluoromethanesulfonates - Boron compounds  
 Bromides - 4(4'-Bromobenzoyl)acetanilide – Bromomethane - Carbonyl diisothiocyanate - per, Trichloroacetic acid -  
 Dichloromethane, Perchloric acid - Dinitrogen tetroxide – Hexachlorocyclotriphosphazine - Iodine pentafluoride  
 Magnesium perchlorate - Metal alkoxides - Metal oxosalts - Nitric acid - Non-metal halides - Other reactants  
 Perchloric acid - Periodic acid - Phosphorus(III) oxide – Potassium - Potassium permanganate  
 Silver difluoride – Sodium - Sodium hydride - Sulfur trioxide - Trifluoroacetic anhydride

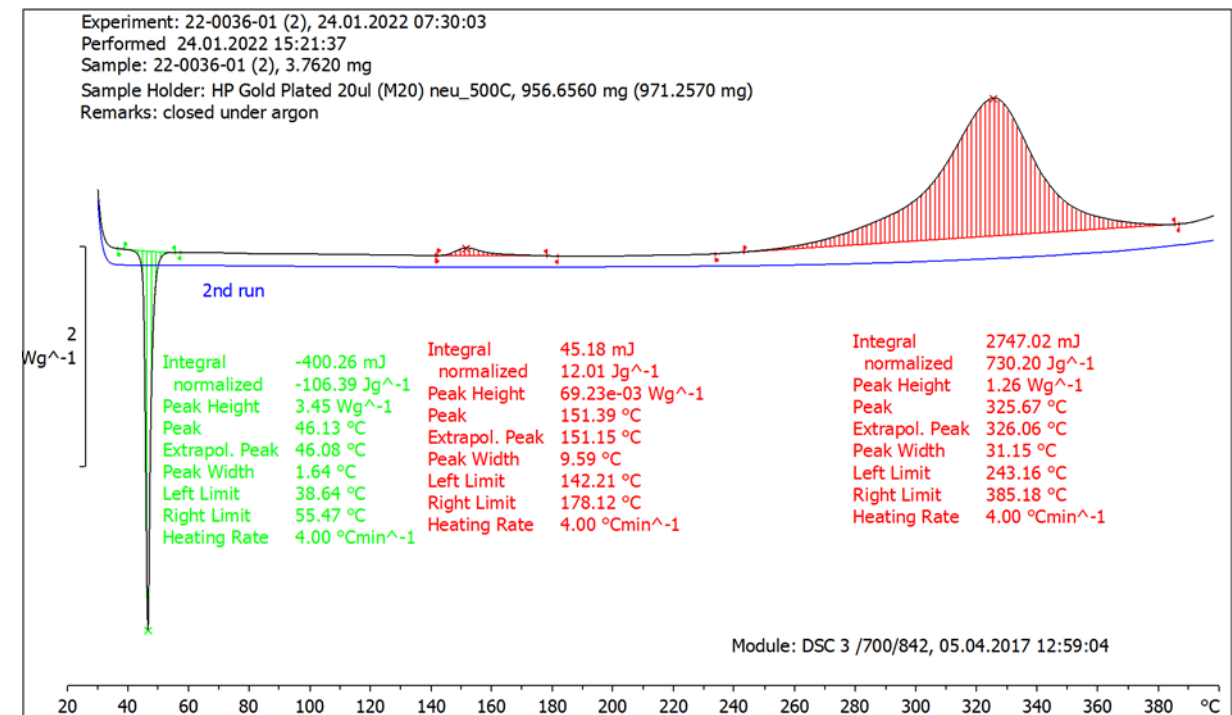
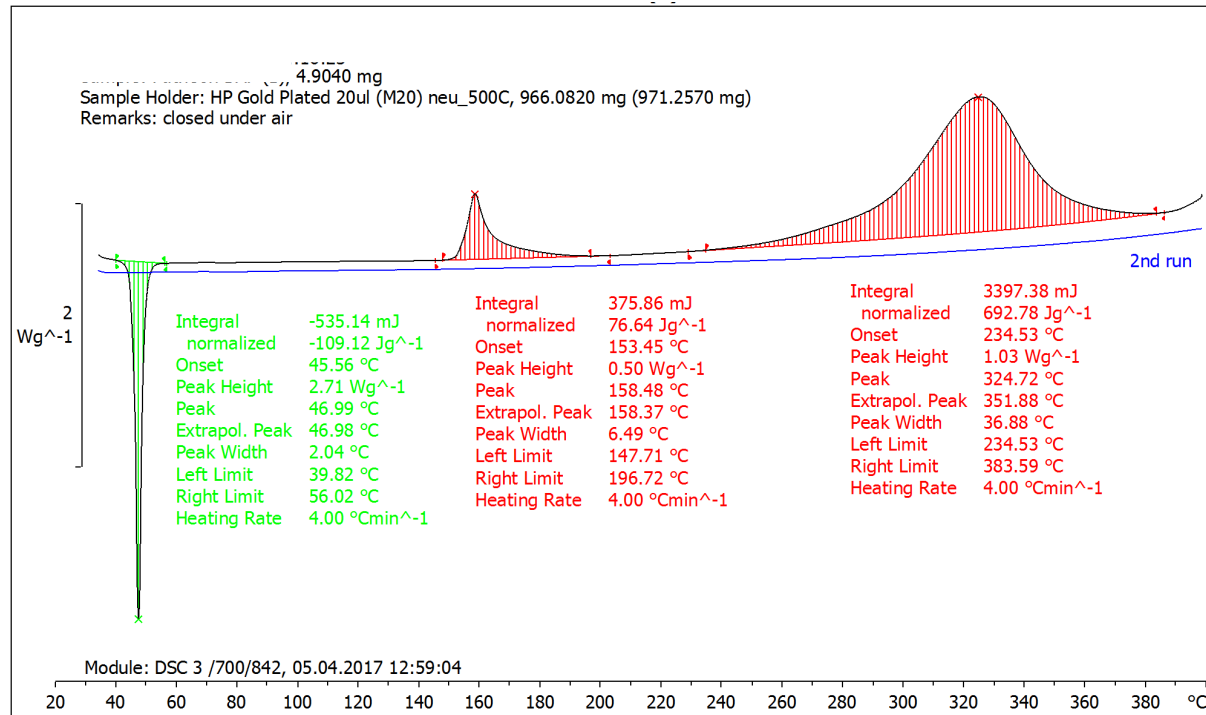


neat

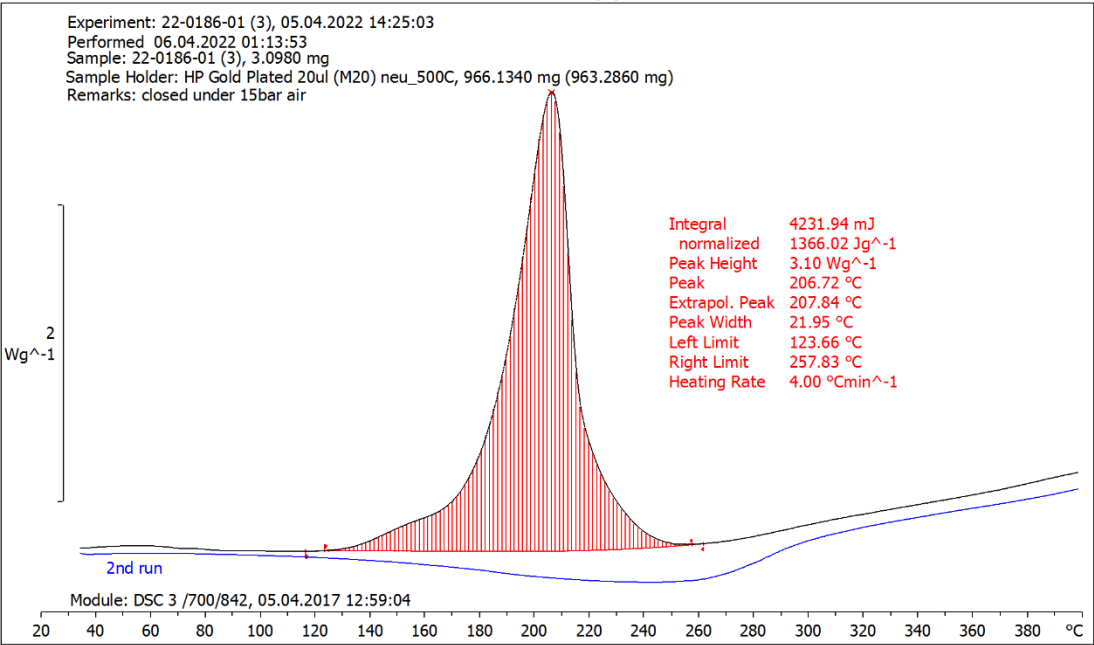
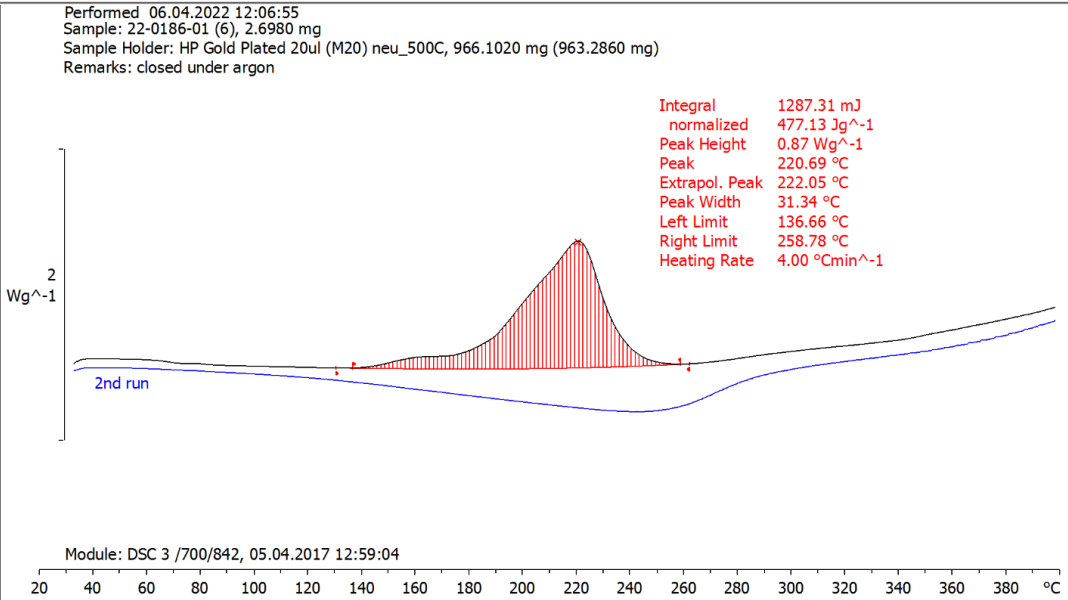
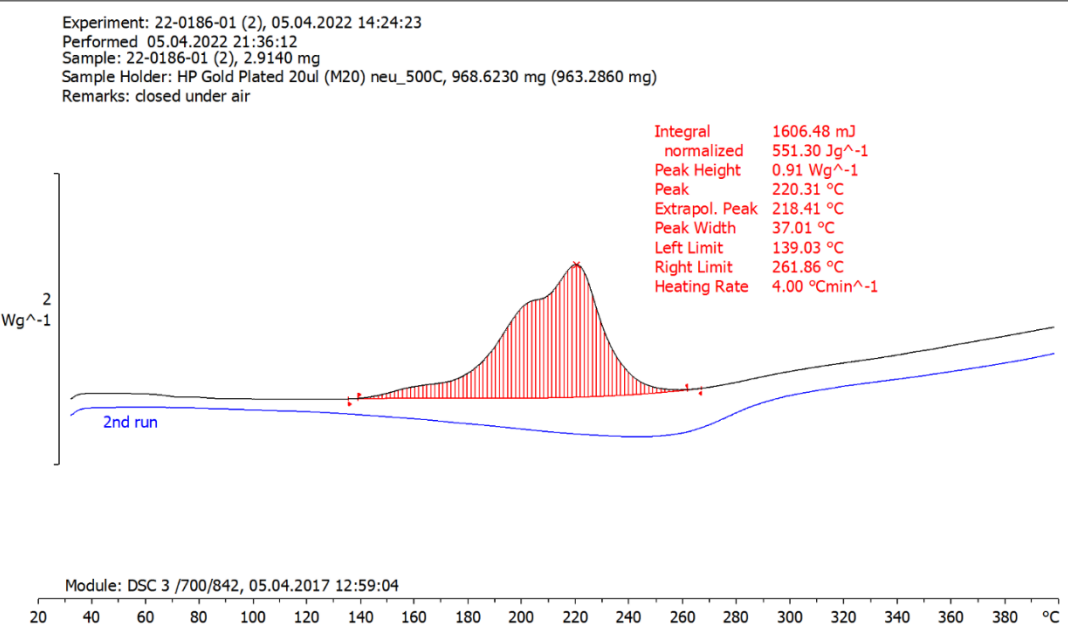


contaminated





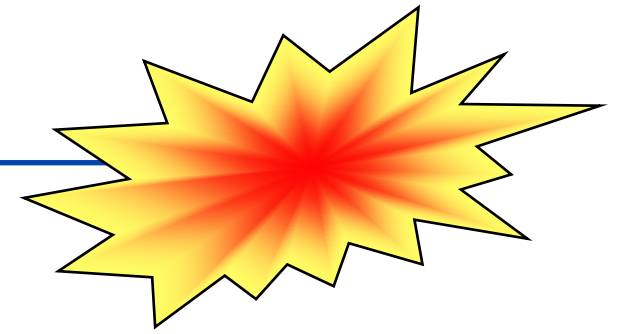
**Conclusion:** crucibles under air might show a little oxidation. However the amount of oxygen present in the crucible is low  
→ if the decomposition is problematic, make a measurement under argon



# Decomposition Reactions

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- What are decomposition reactions?
- Characterisation of secondary reaction
  - Energy of decomposition
  - Onset and Safety Margin
  - Determination of  $\text{TMR}_{\text{ad}}$
- Examples
- Highly energetic molecules



- Substances that undergo decomposition or combustion with great rapidity, evolving much heat and producing a large volume of gas.
- ... are
  - Impact sensitive
  - Friction sensitive
  - Heat sensitive

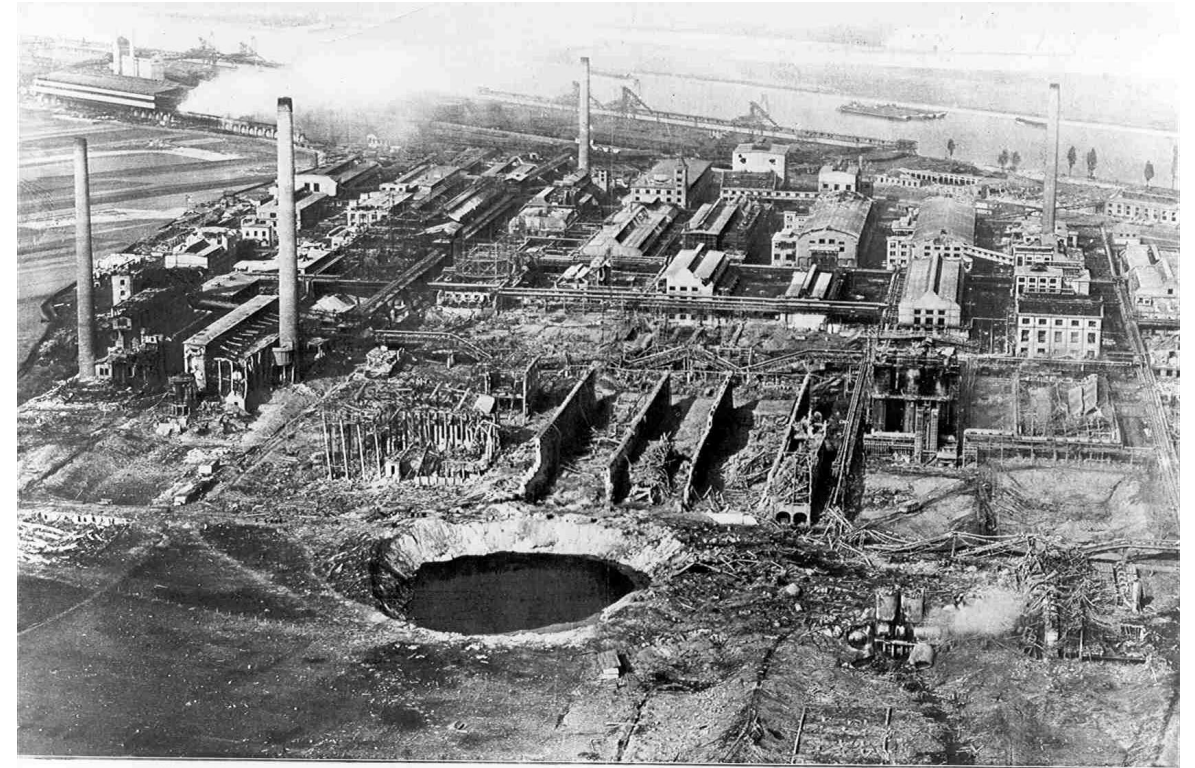
## Consequences of a detonation

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- 1 gram:
  - Serious injury to a person holding the explosive
- 10 gram:
  - Very serious injury to a person close to the explosive
- 100 gram:
  - Almost certain death of persons in very close proximity (e.g. holding the material)

# Explosion in condensed phase (liquid/solid)

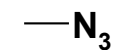
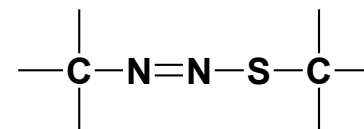
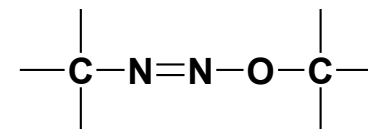
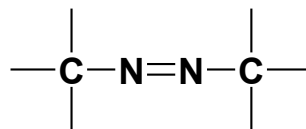
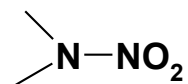
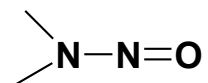
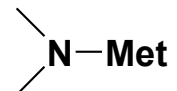
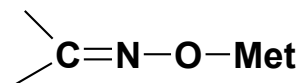
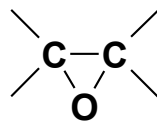
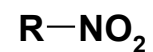
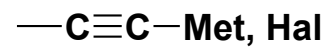
- Oppau - September 21<sup>st</sup>, 1921
- Ammonium nitrate
- Mass: 4500 t
- Damages:
  - 561 fatalities
  - 1997 injured
  - structural damages within a radius of 6 km



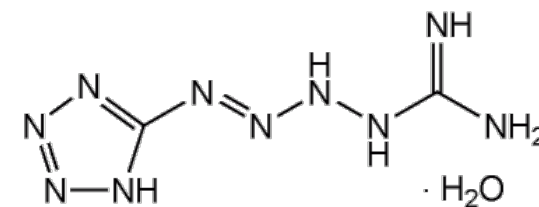
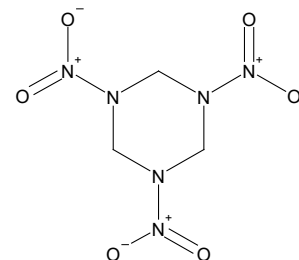
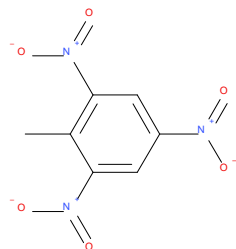
VUE AÉRIENNE DE L'USINE DE LA « BADISCHE ANILIN UND SODA FABRIK » A OPPAU, APRÈS LA FORMIDABLE EXPLOSION DU 21 SEPTEMBRE  
Au premier plan, le cratère formé par la mystérieuse déflagration et à demi rempli d'eau par les canalisations rompues et par les infiltrations souterraines; au delà, les bâtiments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

# Structures known to be hazardous

55



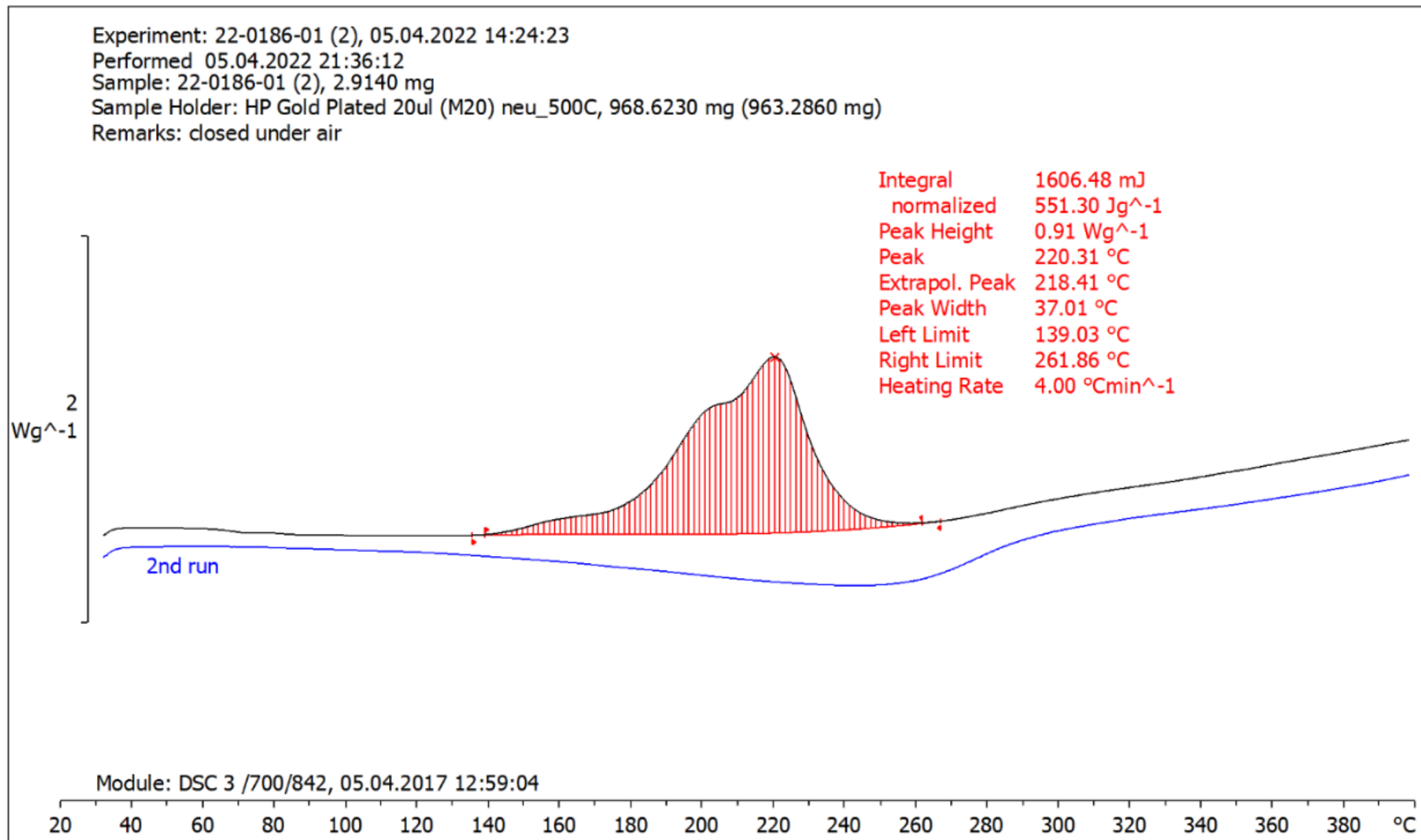
**Military Explosives:**



# Questions

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- What equipment are used to assess thermal stability?
- New substance and you need to assess whether you can handle it safely
  - What do you do



# Question

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# Question

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- Isothermal measurements in DSC

| Temperature | Heat release rate (W/kg) |
|-------------|--------------------------|
| 150°C       | 15                       |
| 160°C       | 28                       |
| 170°C       | 51                       |
| 180°C       | 90                       |

# Summary

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- Take a few minutes to write the main points concerning thermal stability and TMRad