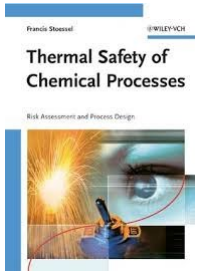
Autocatalytic reactions

Module 4
ENG 431: Safety Chemical Processes

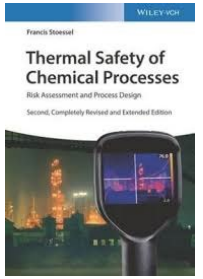
Annik Nanchen

Autocatalytic Decomposition Reactions

- Autocatalytic reactions
- Mechanisms
- Characterization
- Practical safety aspects



Chapter 12



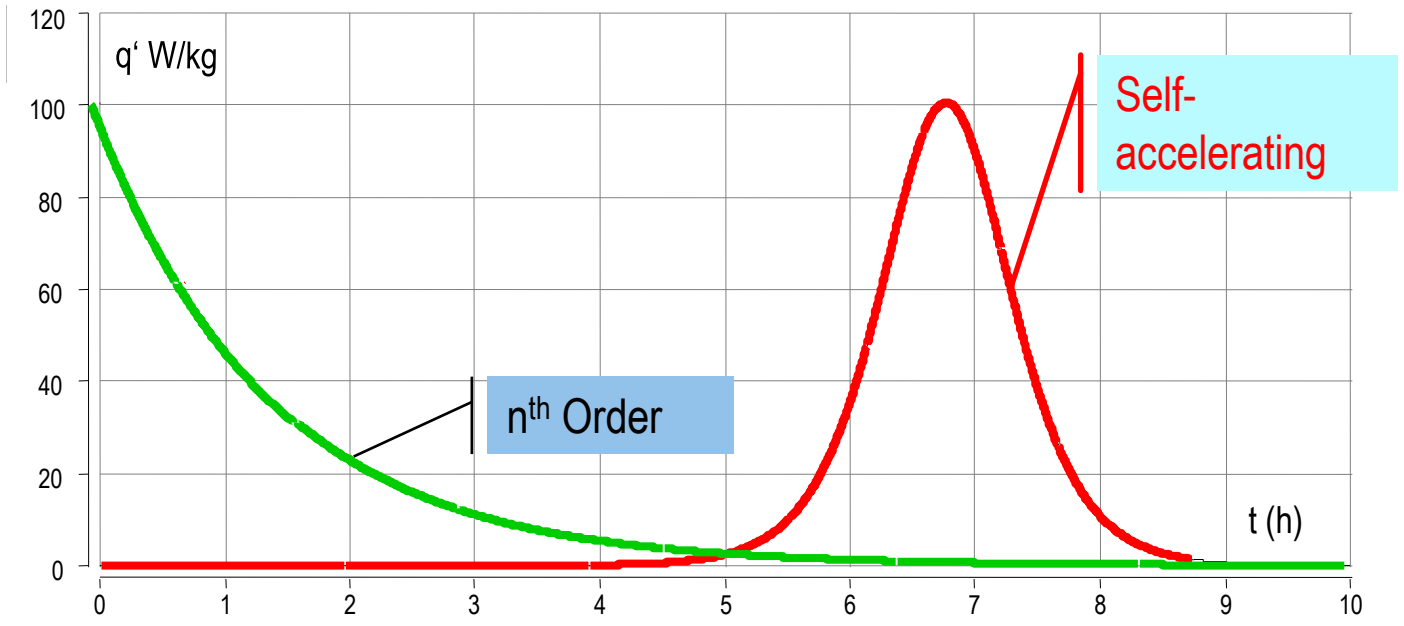
Chapter 11

Definition

- Reaction for which a product acts as a catalyst on the reaction course
- The reaction rate increases with time from its initial value, even at constant temperature
- Reaction rate is proportional to the concentration of a product.
- Self-accelerating

Self-accelerating reactions

Comparison n^{th} order with self-accelerating reaction under Isothermal conditions

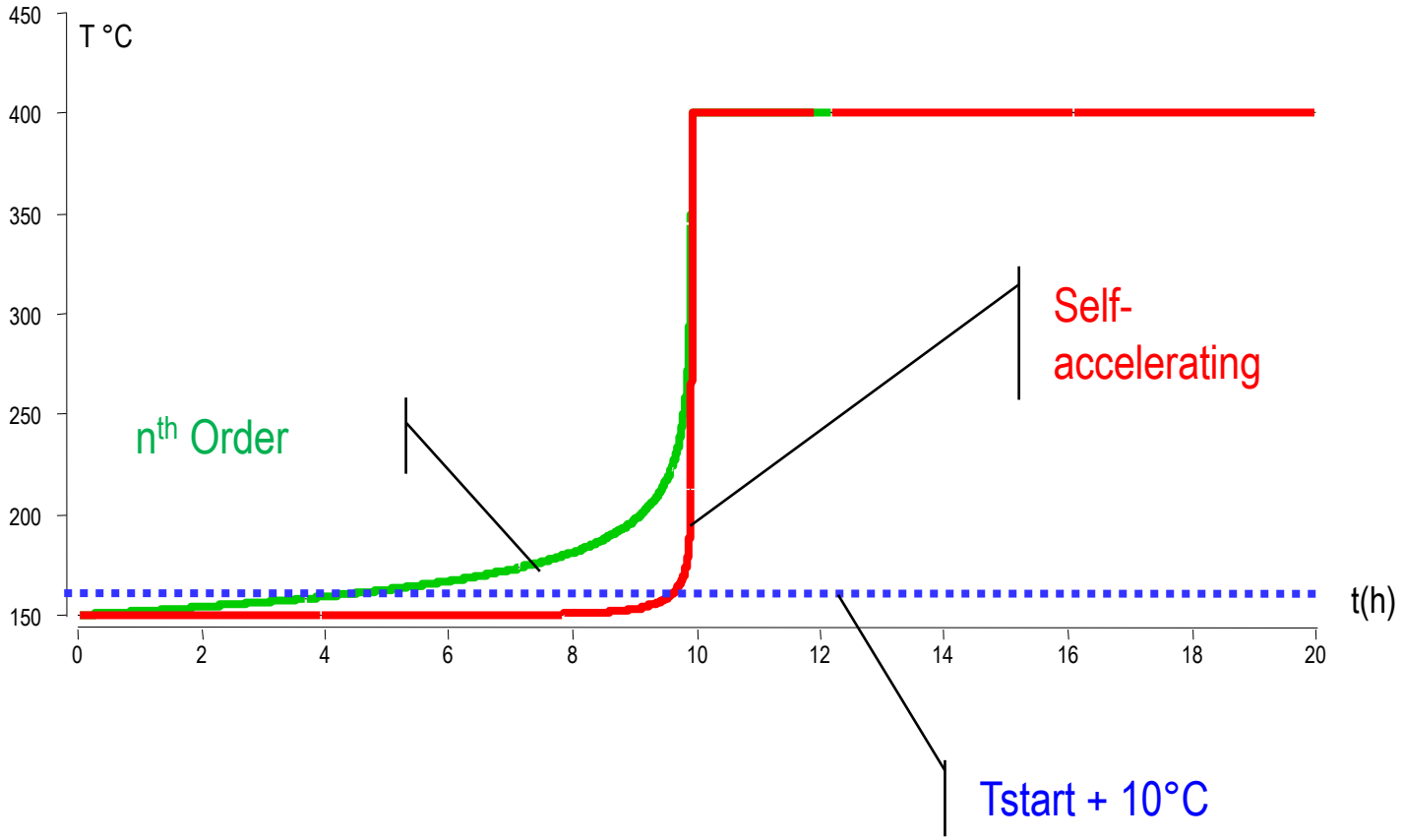


Conclusion:

Under isothermal conditions, heat release maximum at the beginning for the n^{th} order reaction.

For a self-accelerating reaction, max. heat release rate is measured after a delay (induction time).
This induction time is also T dependent (higher T = shorter induction time)

Adiabatic conditions



Conclusion:

Under adiabatic conditions, T increases slowly for the n^{th} order reaction. For a self-accelerating reaction, does not measure any temperature increase until the sharp temperature increase (induction time)

→ Temperature alarm cannot be used (not enough time for counter measures)

Autocatalytic Decomposition Reactions

- Autocatalytic reactions
- Mechanisms
- Characterization
- Practical safety aspects

Mechanisms

- Prout-Tompkins

$$A + B \xrightarrow{k} 2B$$

$$-r_A = k \cdot C_A \cdot C_B$$

- Benito-Perez

$$A \xrightarrow{k_1} B$$

$$A + B \xrightarrow{k_2} 2B$$

$$-r_A = k_1 C_A + k_2 C_A C_B$$

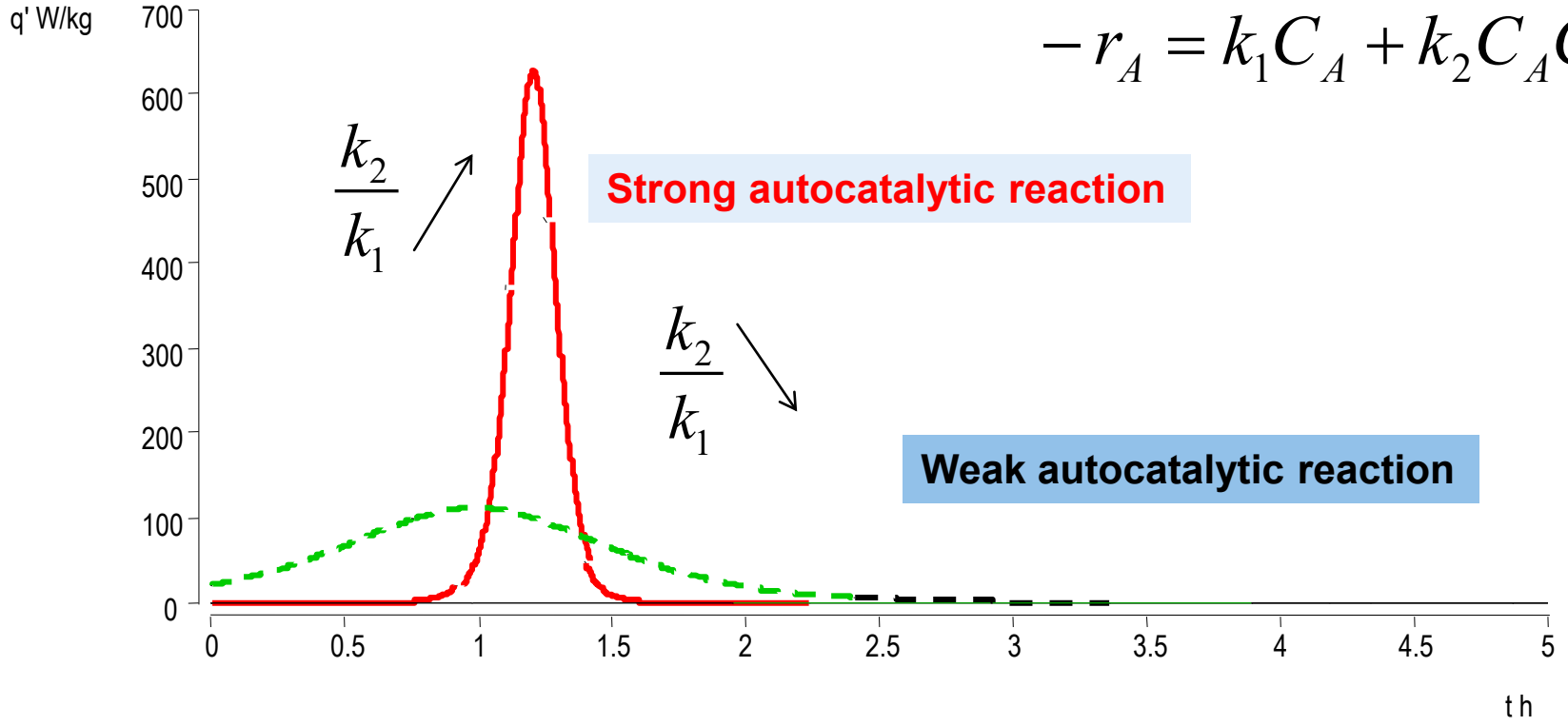
Conclusion:
Benito-Perez model, enables to describe different degrees of autocatalytic reactions

“Degree” of autocatalysis

$$A \xrightarrow{k_1} B$$

$$A + B \xrightarrow{k_2} 2B$$

$$-r_A = k_1 C_A + k_2 C_A C_B$$



Autocatalytic Decomposition

Benito-Perez:

$$A \xrightarrow{k_1} B$$

$$A + B \xrightarrow{k_2} 2B$$

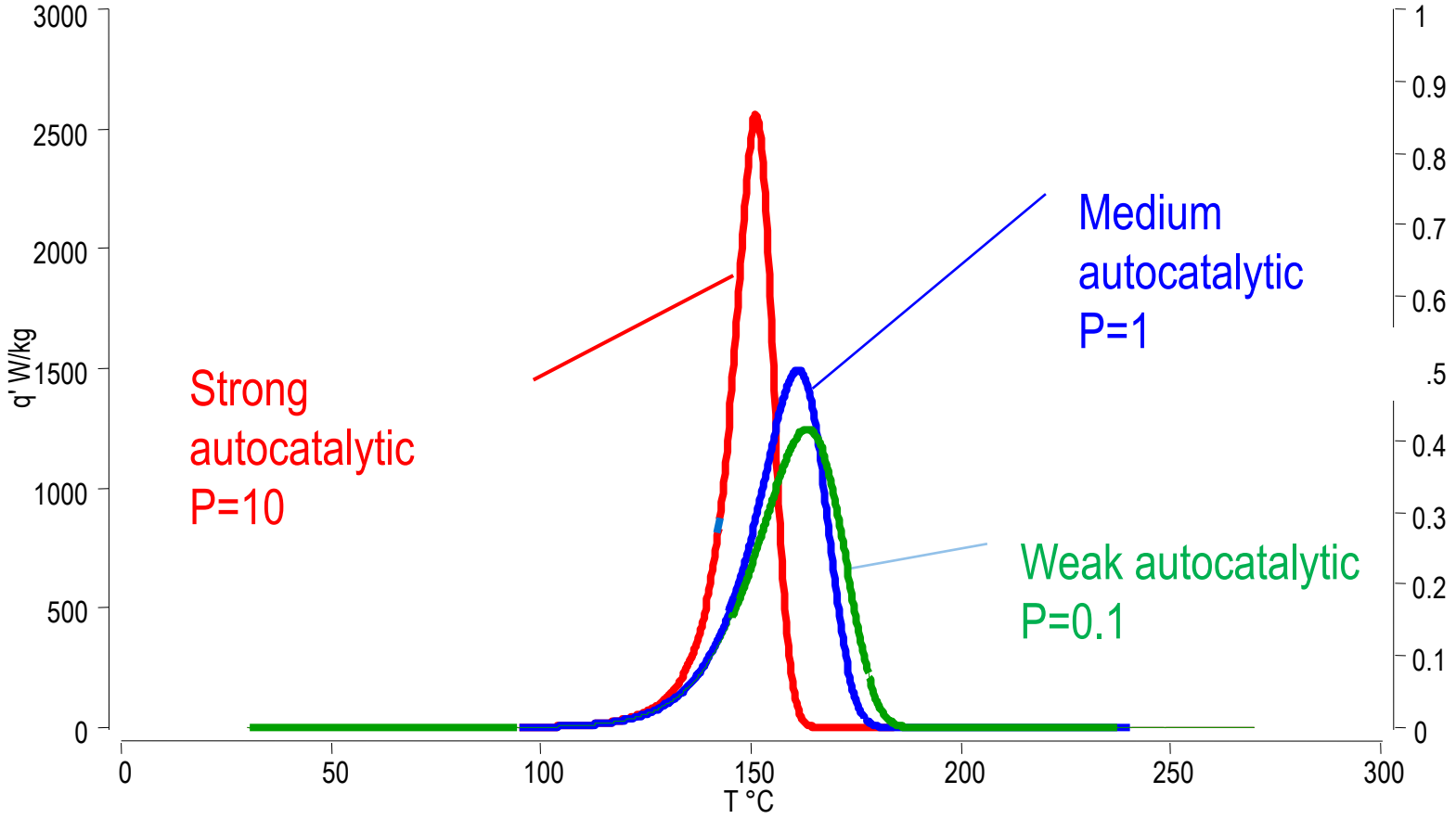
$$-r_A = k_1 C_A + k_2 C_A C_B$$

Reaction rate: (Grewer)

$$\begin{cases} \dfrac{dX}{dt} = k_1 (1 + PX)(1 - X) \\ P = \dfrac{k_2 C_{A0}}{k_1} \end{cases}$$

Autocatalytic Factor

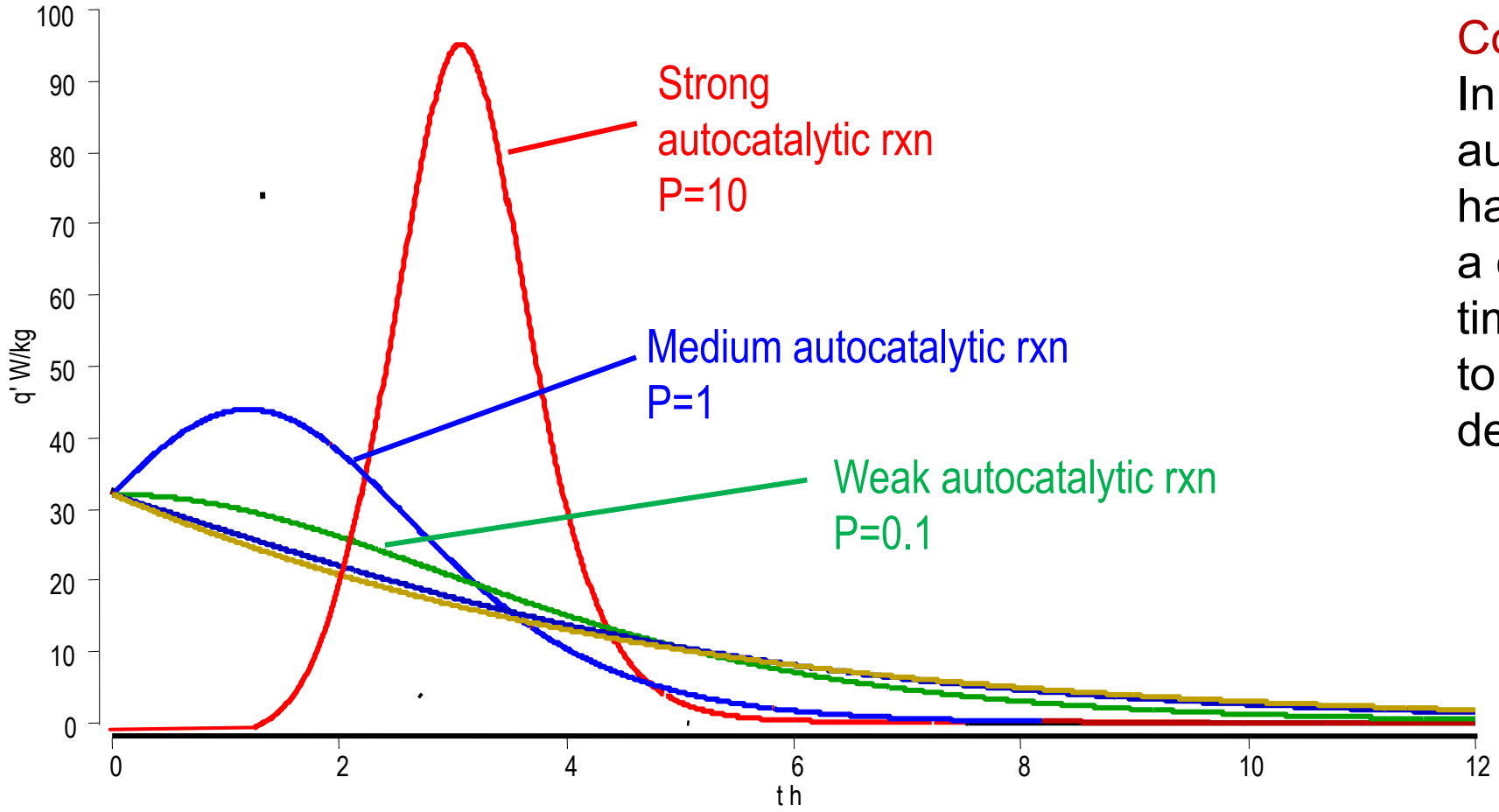
Effect of increasing autocatalytic character on dynamic DSC Thermogramm



Conclusion:

In a dynamic DSC (screening method), strong autocatalytic reactions will have narrow peaks with high heat release rates

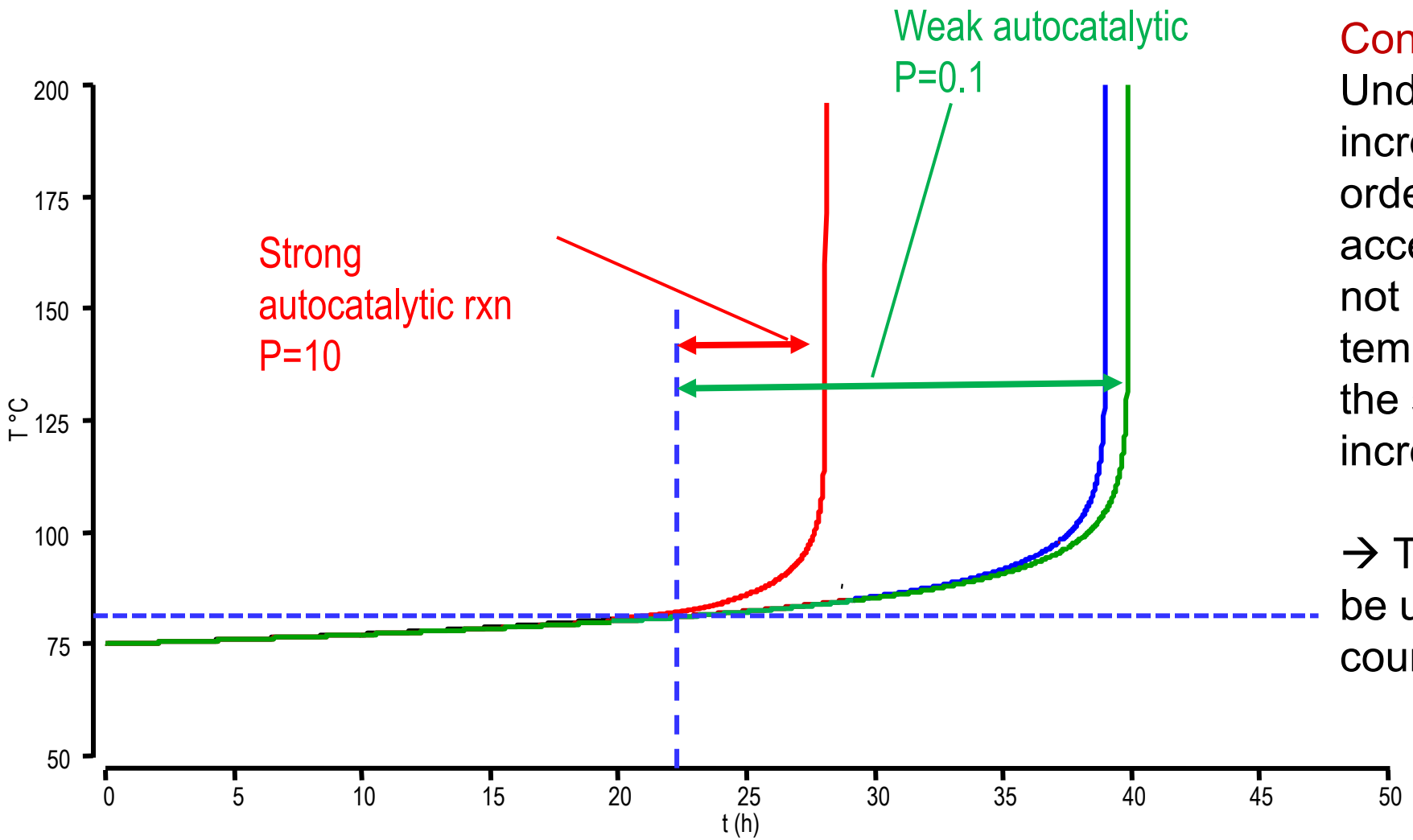
Effect of increasing autocatalytic character on isothermal DSC Thermogramm



Conclusion:

In an isothermal DSC, strong autocatalytic reactions will have no heat release rate for a certain time (induction time) and then it will increase to a maximum. Maximum is delayed.

Effect of increasing autocatalytic Character on Runaway under adiabatic conditions



Conclusion:

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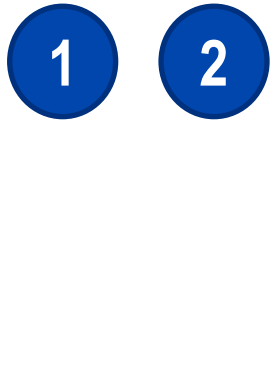
→ Temperature alarm cannot be used (not enough time for counter measures)

Autocatalytic Decomposition Reactions

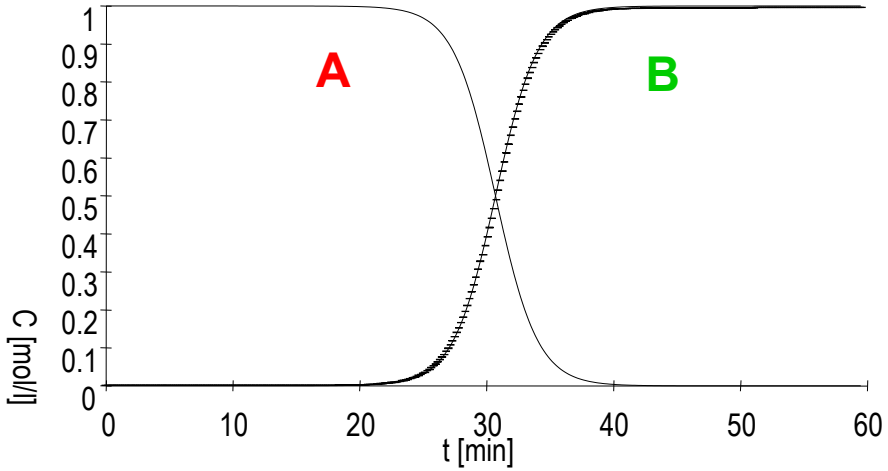
- Autocatalytic reactions
- Mechanisms
- Characterization methods
    1. Identification of autocatalysis from peak shape
    2. Zero order evaluation from scan and isothermal DSCs
    3. Kinetic evaluation
    4. Isoconversional evaluation



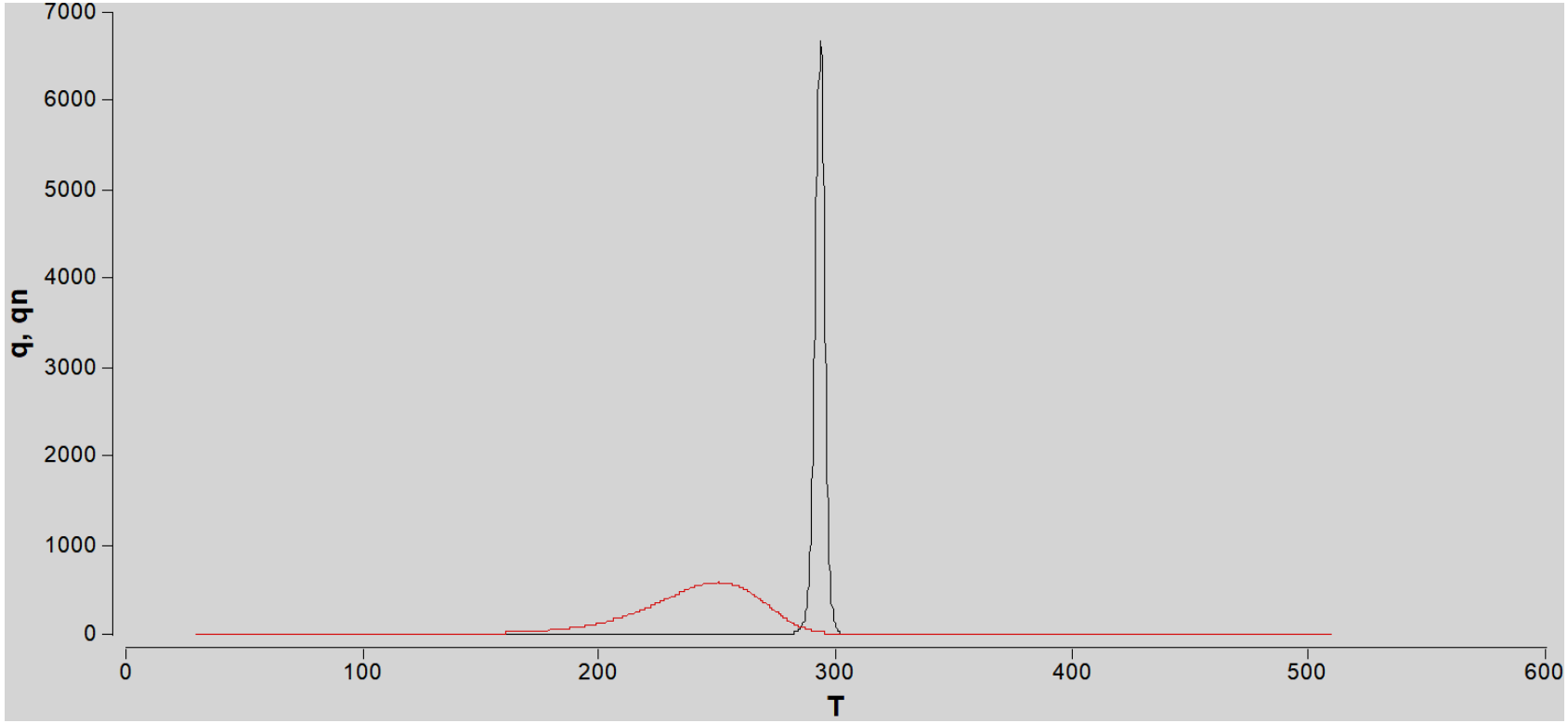
- Practical safety aspects

Chemical Characterization

- Aromatic nitro compounds
- Monomers
- Chlorinated aromatic amines
- DMSO
- Cyanuric chloride (hydrolysis)



Characterization by dynamic DSC



Conclusion:

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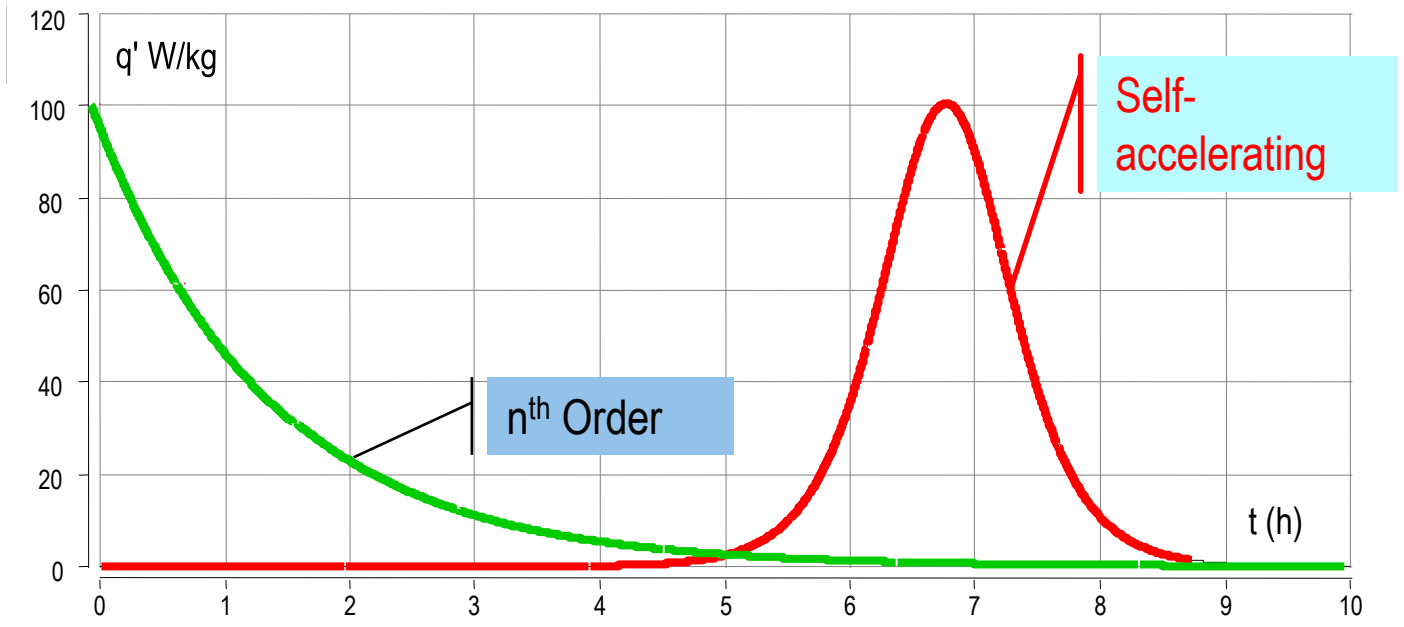
Self-accelerating reactions

Comparison n^{th} order with self-accelerating reaction under Isothermal conditions



Conclusion:
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This induction time is also T dependent (higher T = shorter induction time)

Estimation of T_{D24}

1

Rule of Thumb

- q'_{ref} =20 W/kg at peak detection temperature (T_{ref})
- Assume low Activation energy: 50 kJ/mol
- Calculate q = f (T)

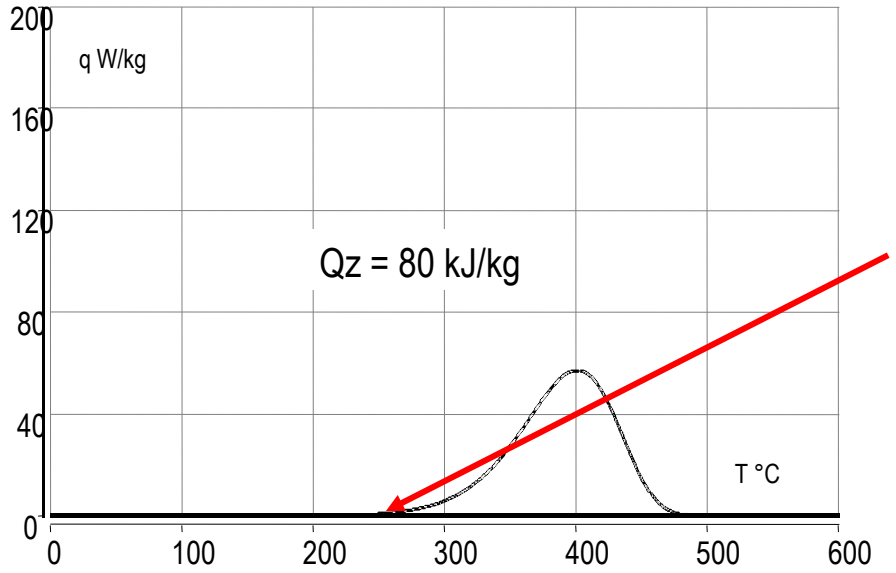
$$q'_{(T)} = q'_{(Tref)} \times \exp\left[\frac{-E_a}{R} \times \left(\frac{1}{T} - \frac{1}{T_{ref}}\right)\right]$$

- Calculate TMRad = 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**), ok for TD24 or long TMRad

☹ Depends on instrument



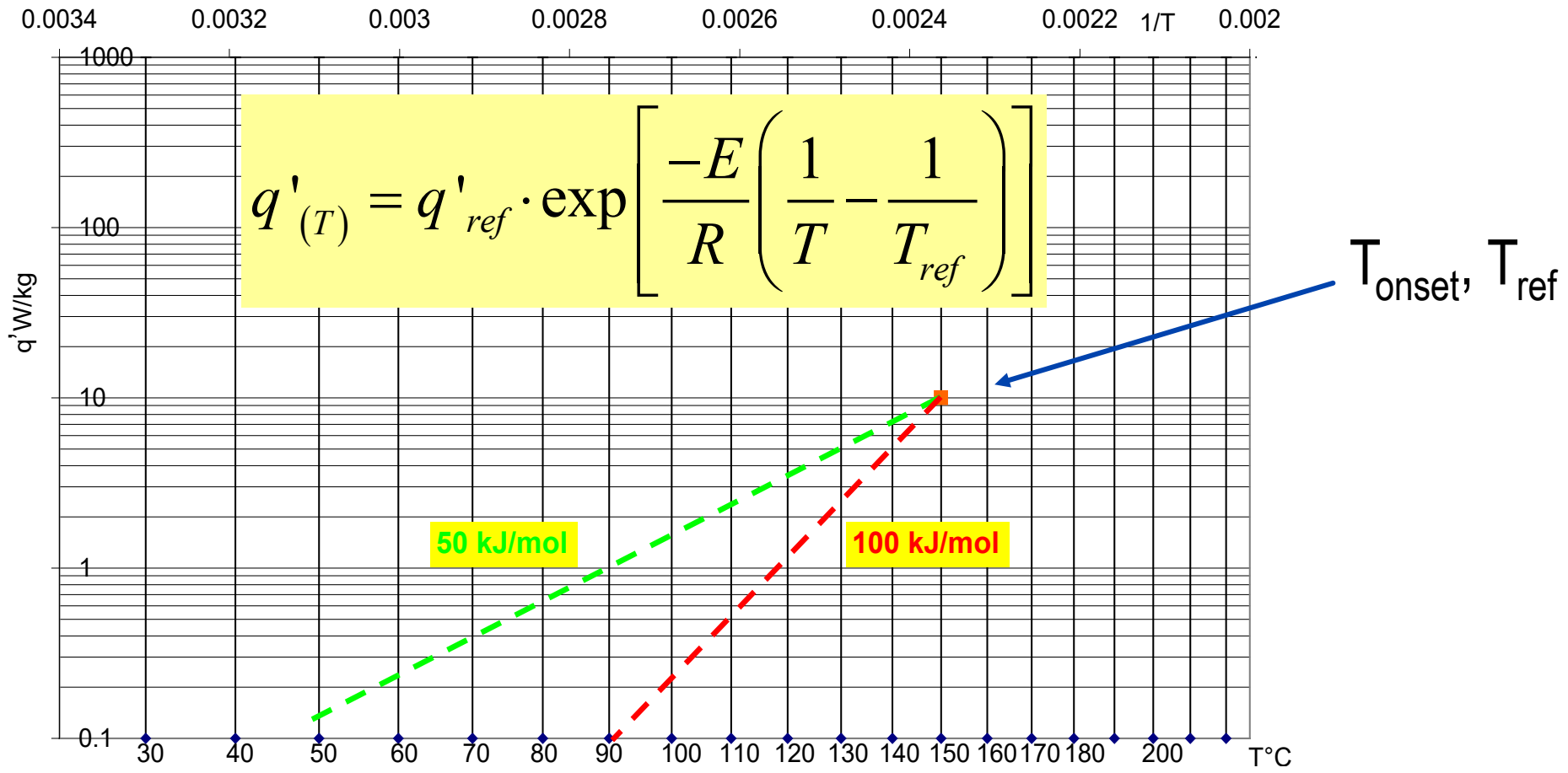
Sample: 12.5 mg

Zero order kinetics

Scan: 4°C / min
Gold plated high pressure crucible

Arrhenius diagram

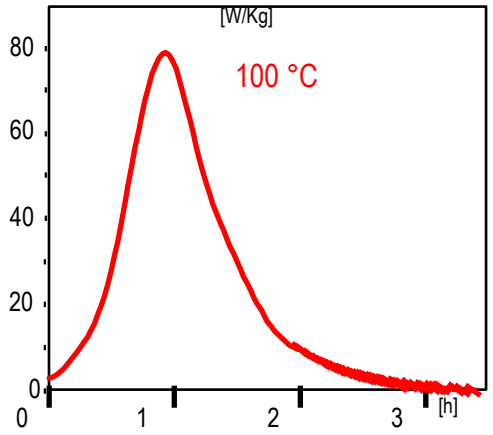
- Extrapolation from one reference point, why is 50 kJ/mol a conservative activation energy?

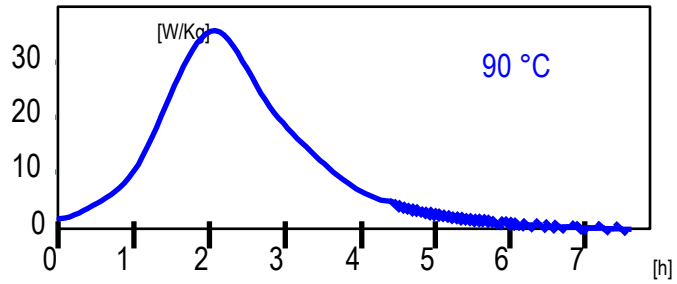


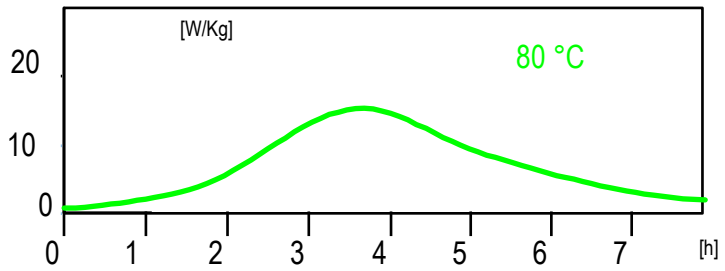
Determination of Time to Maximum Rate

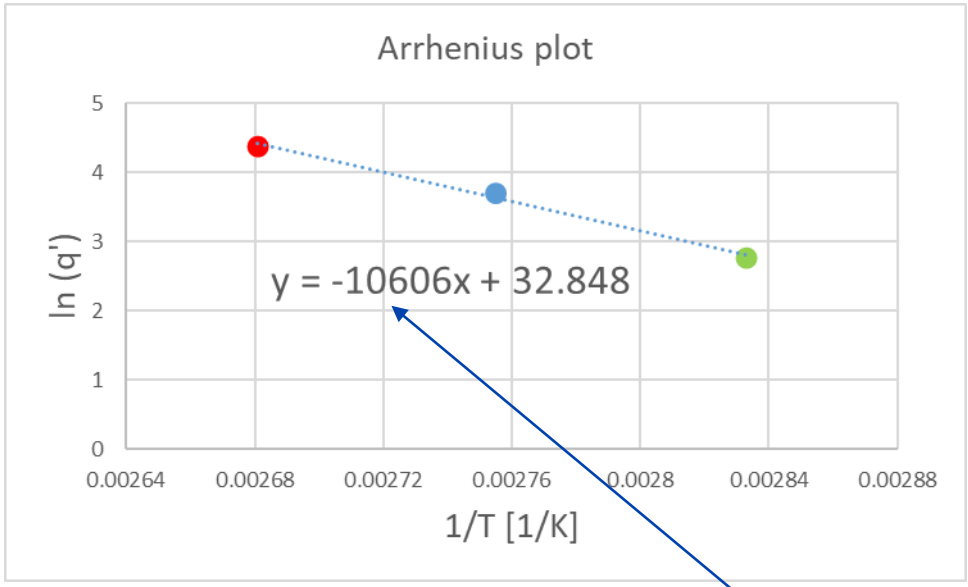
2

Isothermal Calorimetry







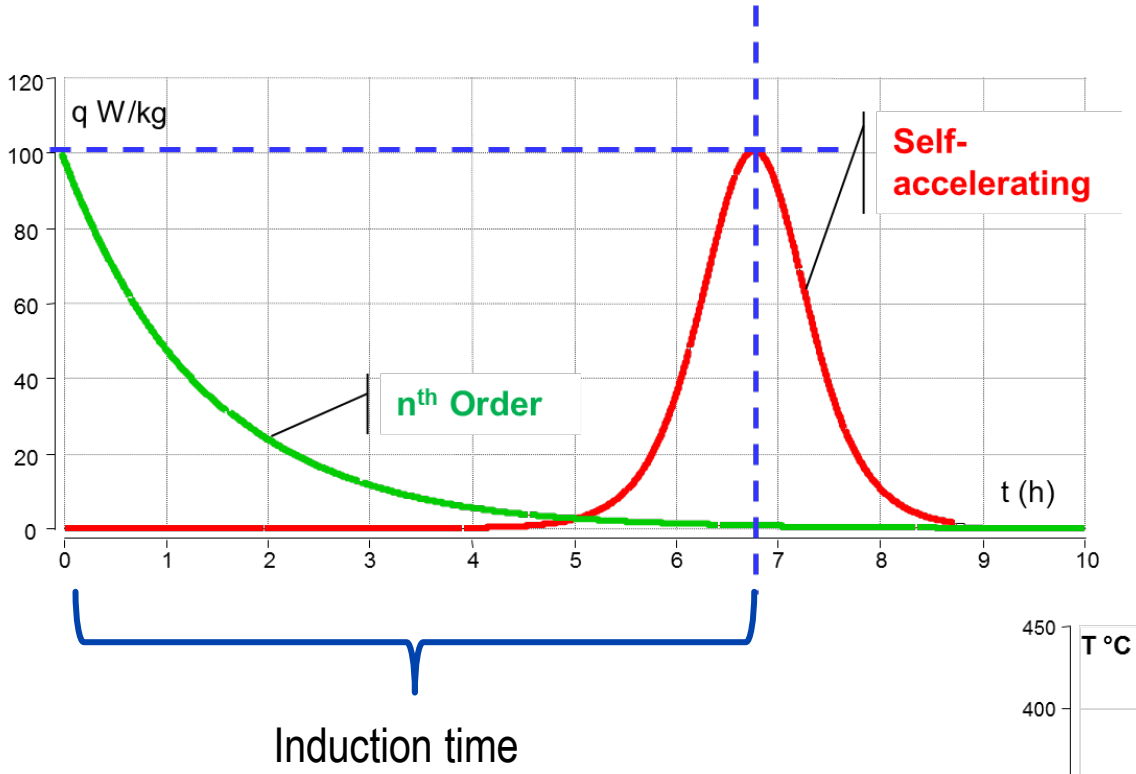


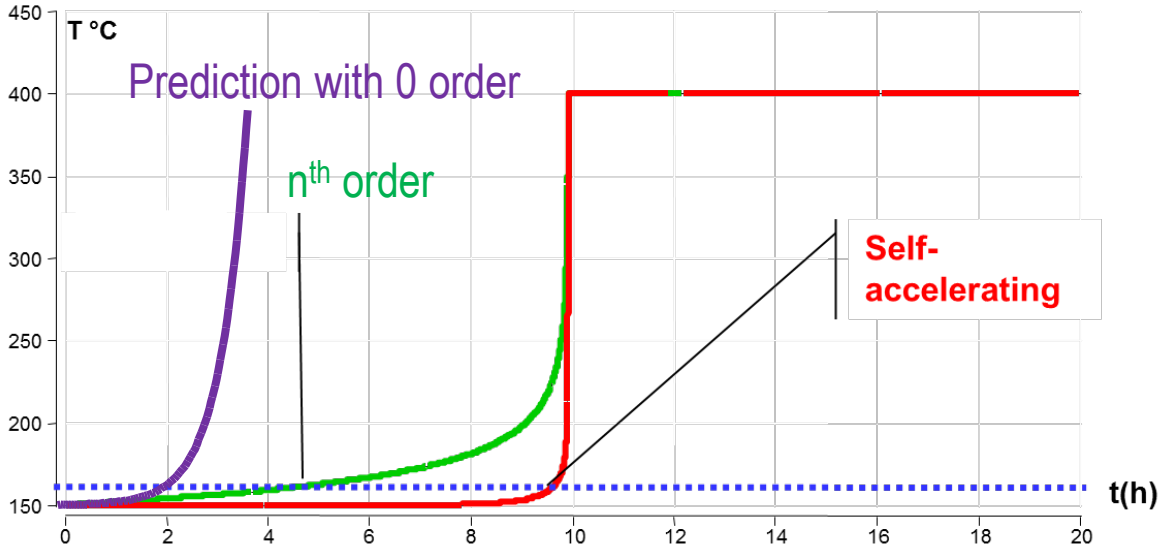
Slope = -Ea/R

$$TMR_{ad} = \frac{c'_P R T_0^2}{q'_0 E_a}$$

Zero order kinetics

Zero order Approximation

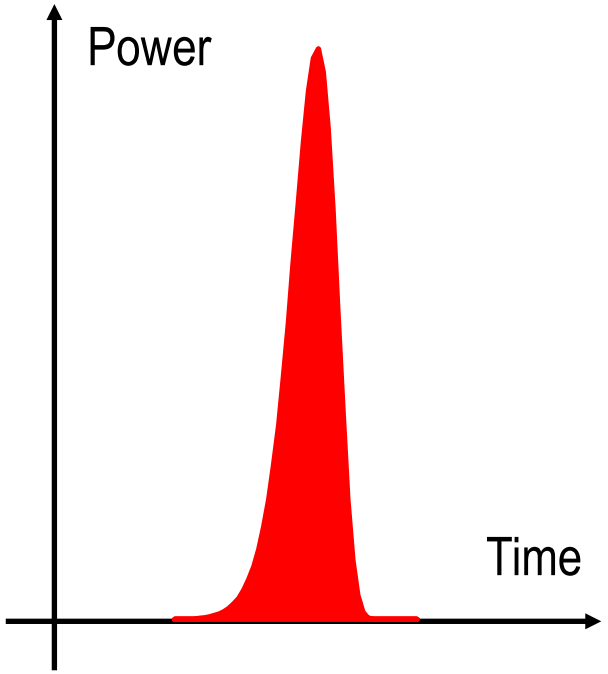




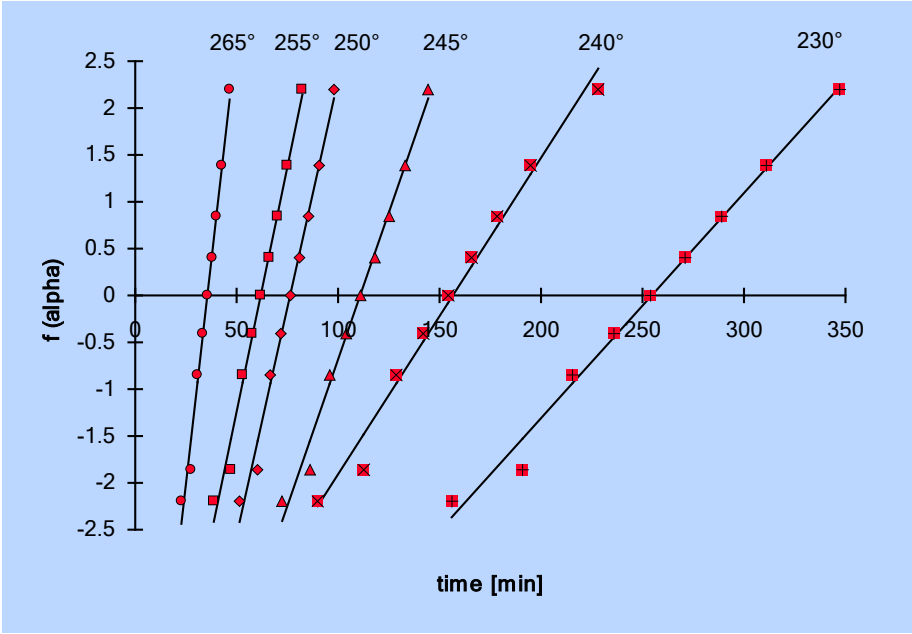
Determination of kinetic parameters

3a

High degree
of autocatalysis
(no initial power)



$$\ln\left[\frac{X}{1-X}\right] = \ln\left(\frac{k_1}{k_2 C_{A0}}\right) + k_2 C_{A0} \cdot t$$



$$A \xrightarrow{k_1} B$$

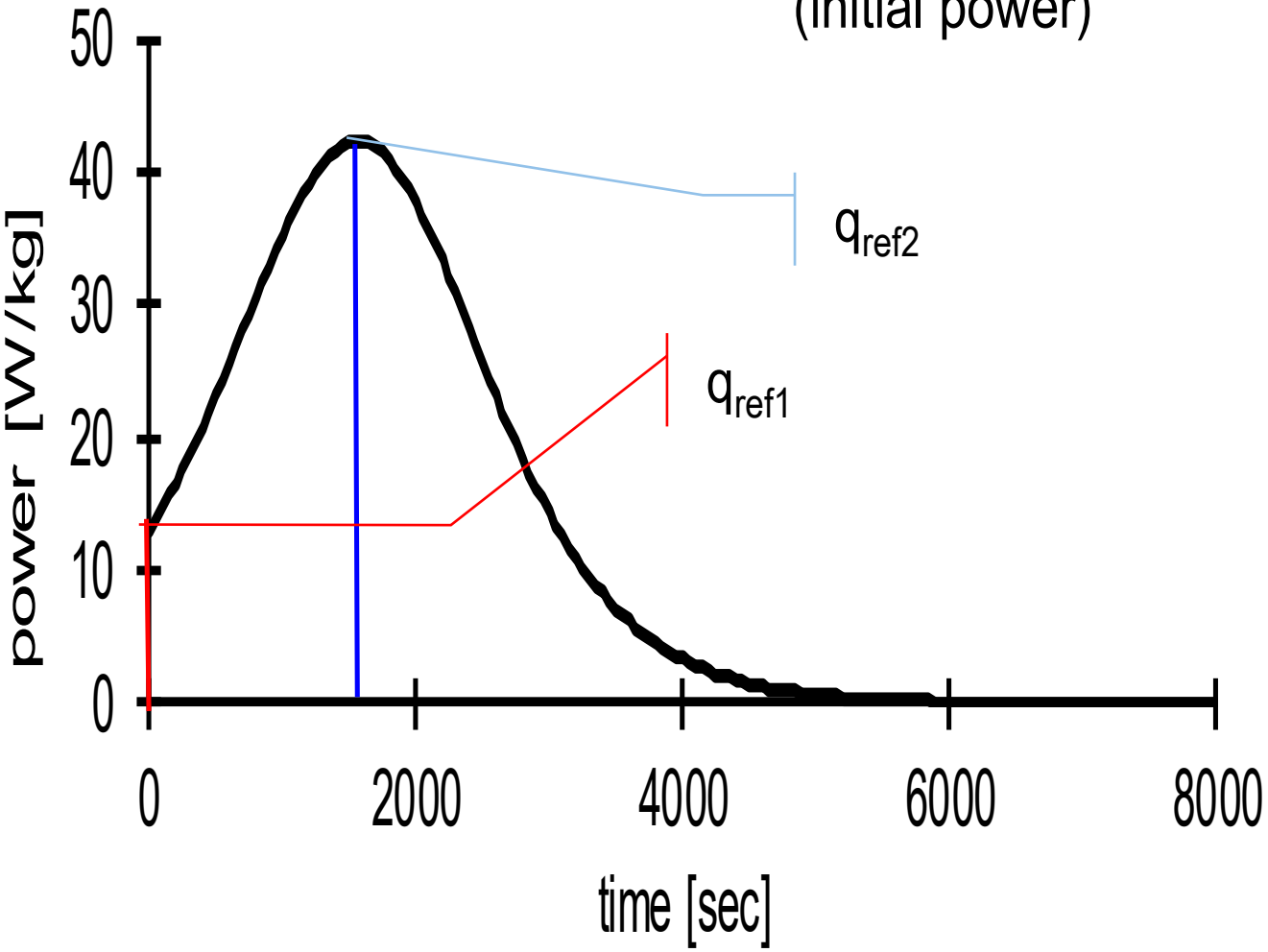
$$A + B \xrightarrow{k_2} 2B$$

$$-r_A = k_1 C_A + k_2 C_A C_B$$

Determination of kinetic parameters

3b

Low degree
of autocatalysis
(initial power)



$$A \xrightarrow{k_1} B$$

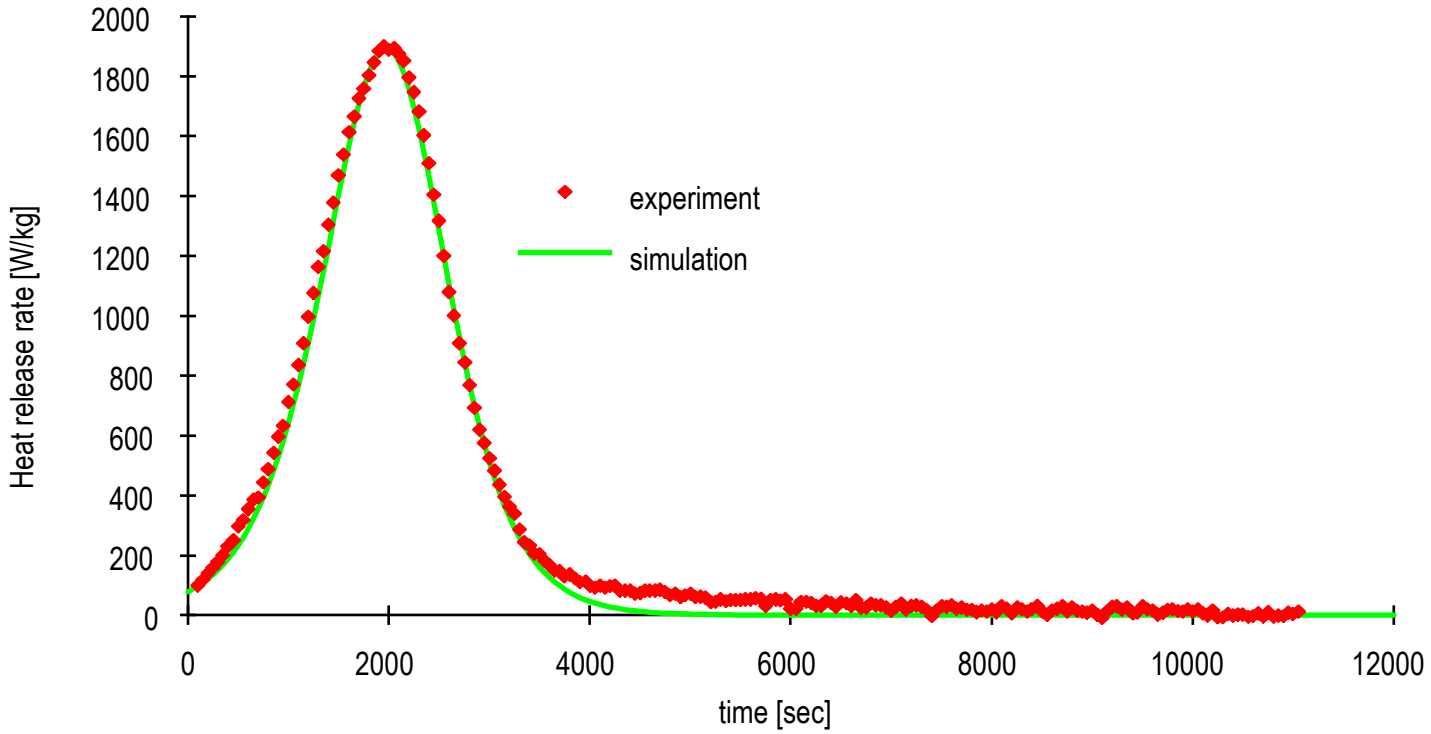
$$A + B \xrightarrow{k_2} 2B$$

$$-r_A = k_1 C_A + k_2 C_A C_B$$

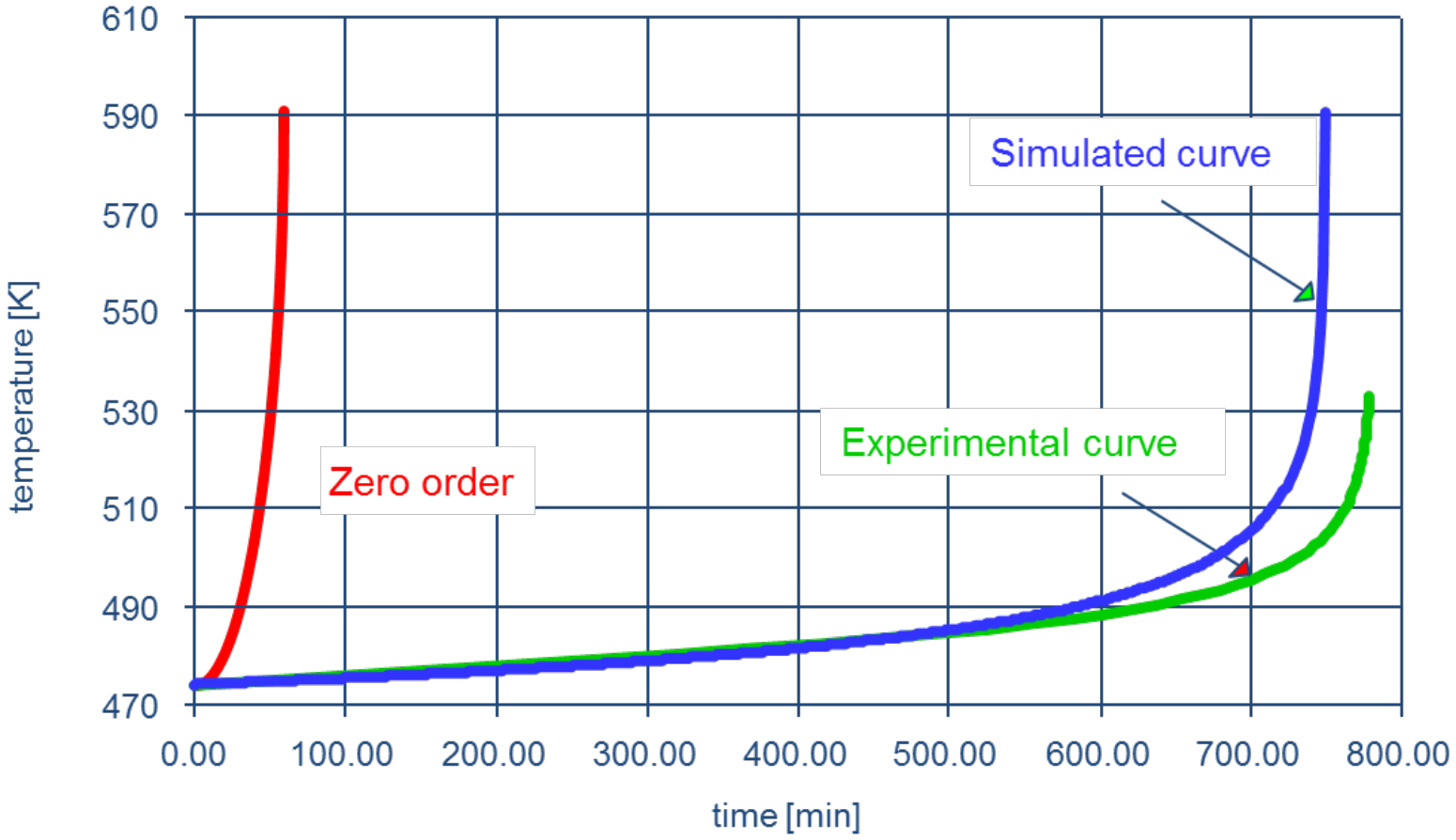
$$k_1 = \frac{q'_{ref\,1}}{Q'_r}$$

$$k_2 = \frac{4 \cdot q'_{ref\,2}}{Q'_r \cdot C_{A0}}$$

Simulation of isothermal experiment

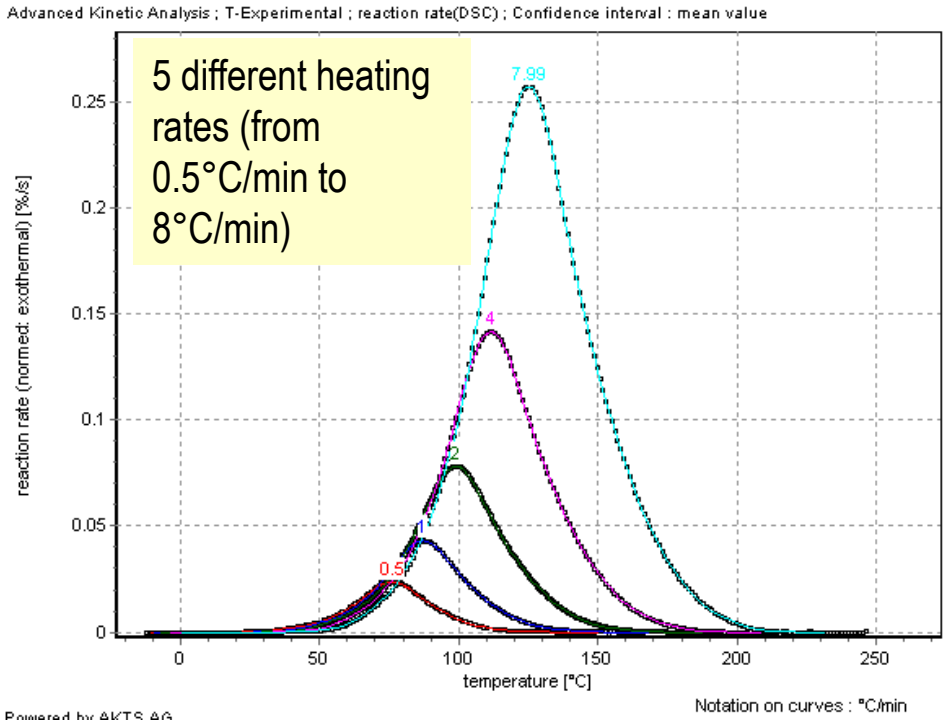


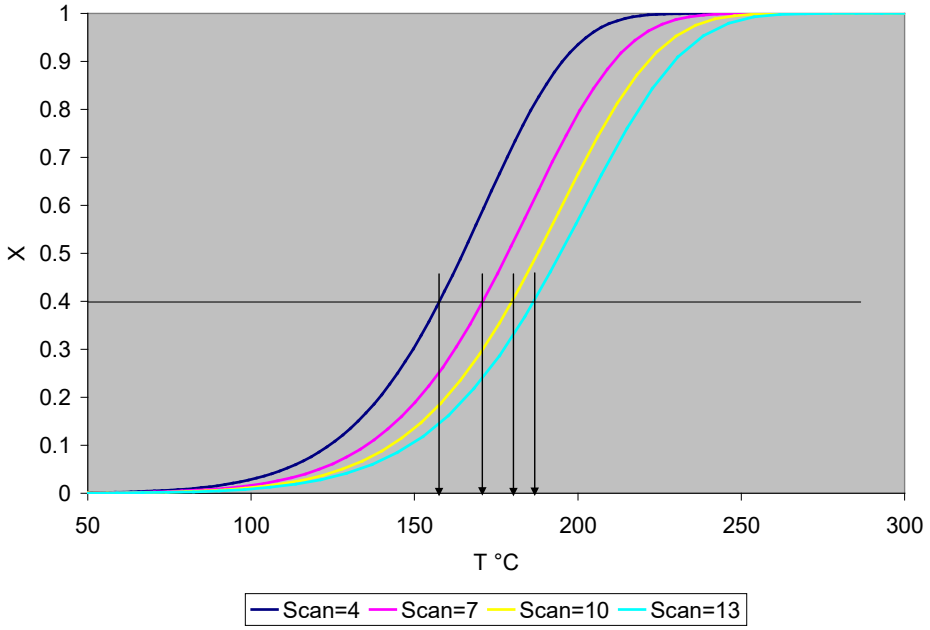
Simulation of Adiabatic Temperature Course



Isoconversional methods

Series of thermogrammes at different scan rates

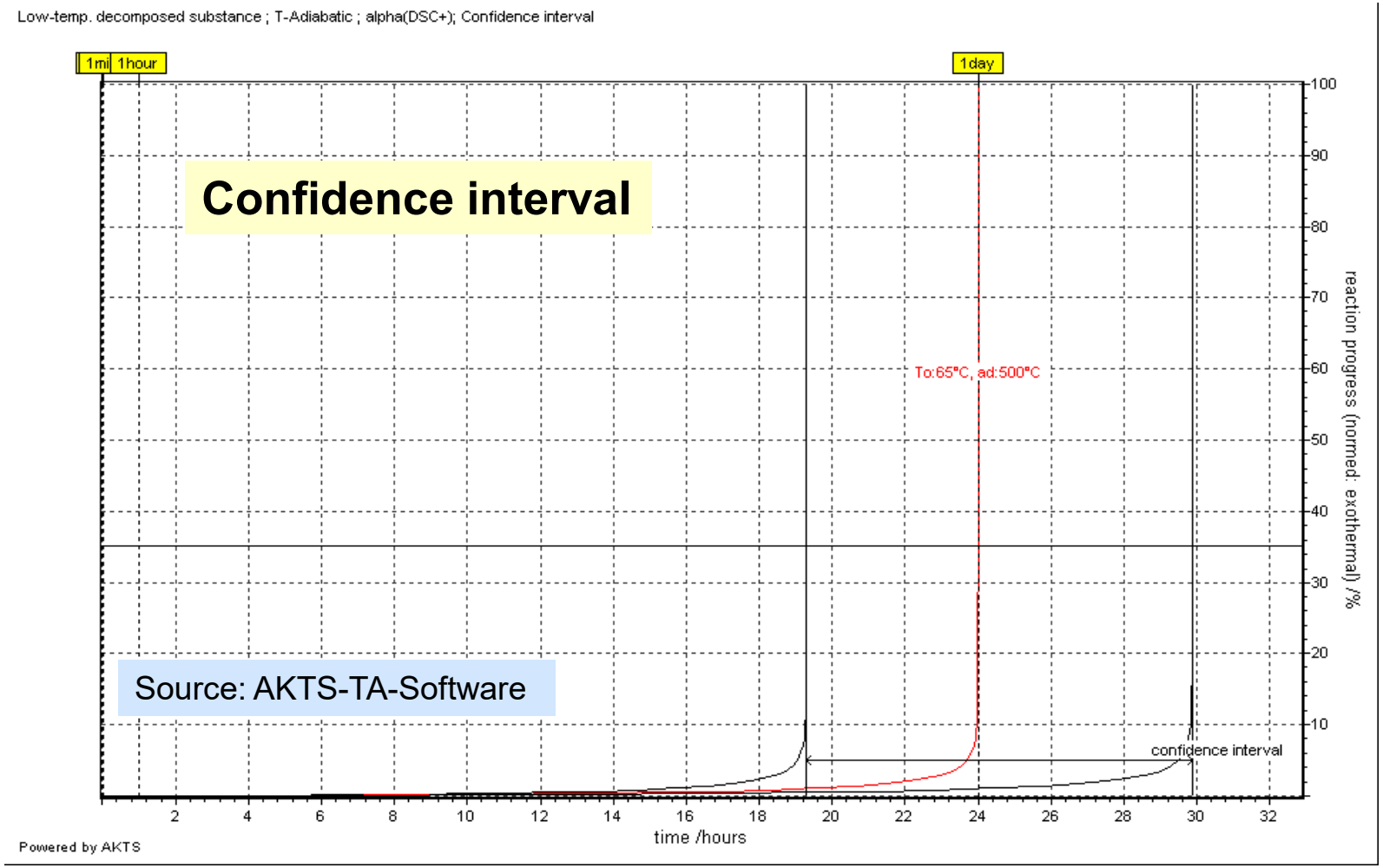




$$q' = \frac{dX}{dt} \cdot Q' = k_0 \cdot e^{\frac{-E}{RT}} \cdot f(X) \cdot Q'$$

q': specific heat release rate	W/kg
X: conversion	-
t: time	s
Q': specific reaction energy	J/kg
k_0: pre-exponential factor	1/s
E: activation energy	J/mol
R: gas constant	J/(mol·K)
T: Temperature	K

Kinetics and Safety Margins



Methods of TMRad determination for autocatalytic reactions

#	Method	Hypothesis	Advantages	Disadvantages
1	Rule of thumb: 1 DSC scan mode	0 order 20 W/kg at onset Ea: 50 kJ/mol	Simple	Not conservative estimation of q'ref → only conservative if extrapolation to low T (TD24 is the limit
2	Isothermal DSC	0 order	Estimation of Ea Measurement of q'ref	Very conservative (neglects induction time). TMRad are more conservative than with rule of thumb Long
3	Kinetic model with isothermal DSC (either strong or weak autocatalysis)		Takes induction time into account	No safety margins Long
4	Isoconversional method with dynamic DSC		Takes induction time into account	No kinetics, only model. Is the extrapolation valid? Need to validate the model. No safety margins Long

Autocatalytic Decomposition Reactions

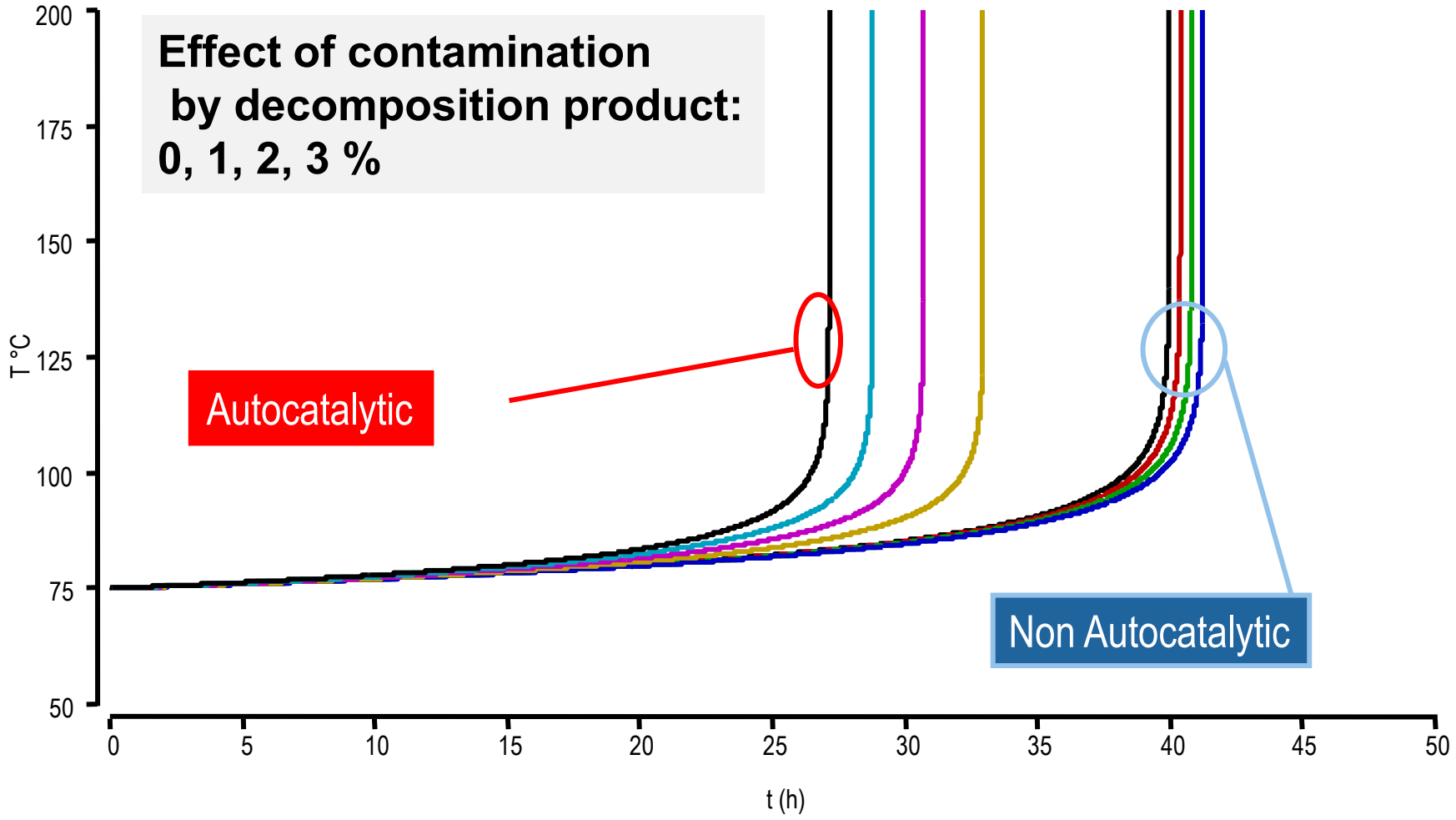
- Autocatalytic reactions
- Mechanisms
- Characterization
- Practical safety aspects

Specific aspects of autocatalytic reactions

Sensitivity to:

- Initial concentration of product
- Thermal history
- Impurities
- Product quality

Autocatalytic Decomposition



Thermal history for “normal” reactions

Situation	Isothermal Exposure T	Exposure t	TMRad 130°C
1	-	-	24 h
2	130°C	4 h	
3	130°C	20 h	
4	135°C	4 h	
5	140°C	4 h	

Thermal history for autocatalytic reactions

Situation	Isothermal Exposure T	Exposure t	TMRad 130°C
1	-	-	24 h
2	130°C	4 h	
3	130°C	20 h	
4	135°C	4 h	
5	140°C	4 h	

Thermal history for autocatalytic reactions

Situation	Isothermal Exposure T	Exposure t	Cool down	TMRad 130°C without cooling	TMRad 130°C with cooling
1	-	-	-	24 h	24 h
2	130°C	4 h	Leave 2 weeks at room T (25°C)	20 h	
3	130°C	20 h		4 h	
4	135°C	4 h		5.5 h	
5	140°C	4 h		1 h	

Testing Procedure

- First use zero order kinetics

- If critical check following points
  - Can contamination be excluded?
  - Do analytical specifications exist ?
  - Is it impossible to mix stressed material with fresh ?
  - Do isothermal measurements from the past exist
  - Was induction time constant ?

- Then use kinetic model

Specific Measures

Testing

- Repeat testing with different qualities
- Control thermal history of samples

Plant

- Control thermal history
  - Limitation of exposure
  - Time limit
  - Temperature limit
- Do not rely on temperature alarm
- Specify quality
  - Avoid contamination
  - Avoid corrosion

Summary

Batch distillation

Process

- Batch distillation at the end of the process (product removed at the top of the column)
- Several batches per campaign

- Sump (distillation residues) shows autocatalytic decomposition behavior (isothermal measurement performed on sump from laboratory distillation)

Recommendations:

- Think about 3-5 recommendations you could make

Batch distillation

Process

- Batch distillation at the end of the process (product removed at the top of the column)
- Several batches per campaign

- DSC from sump measured in scan mode and estimation of TMRad with rule of thumb: 4h.
- Suspicion of autocatalysis

Recommendations:
- What could you recommend concerning further measurements?