Determination of SADT and TMRad by Advanced Kinetic Elaboration of DSC Data

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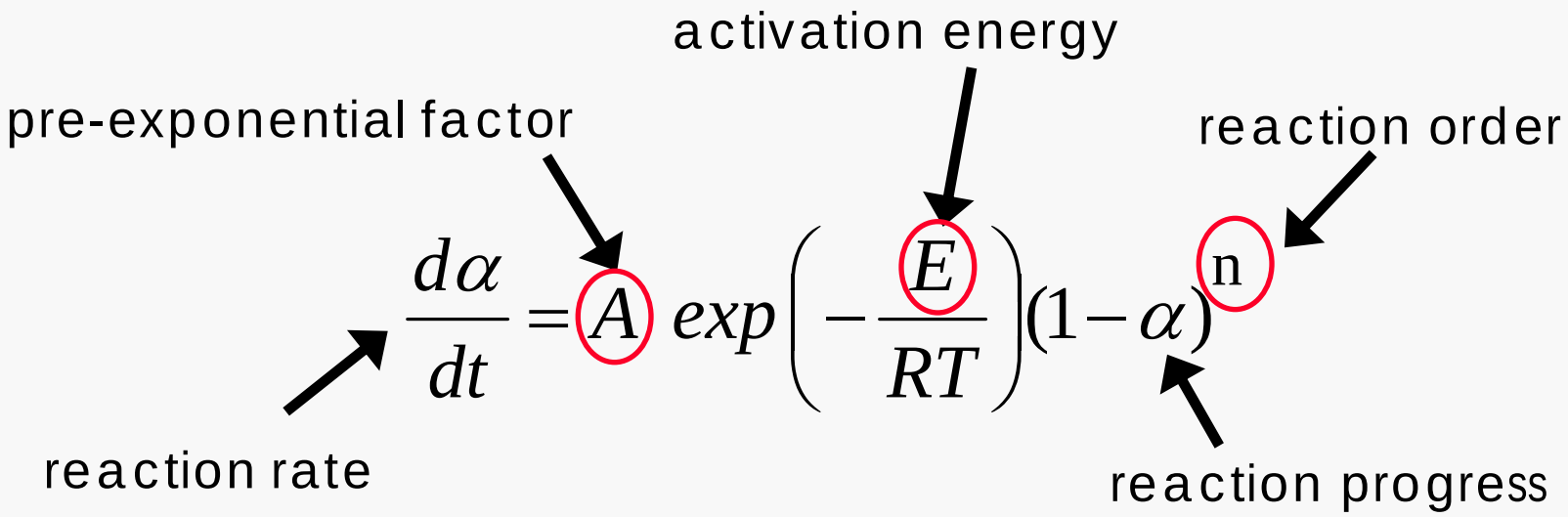
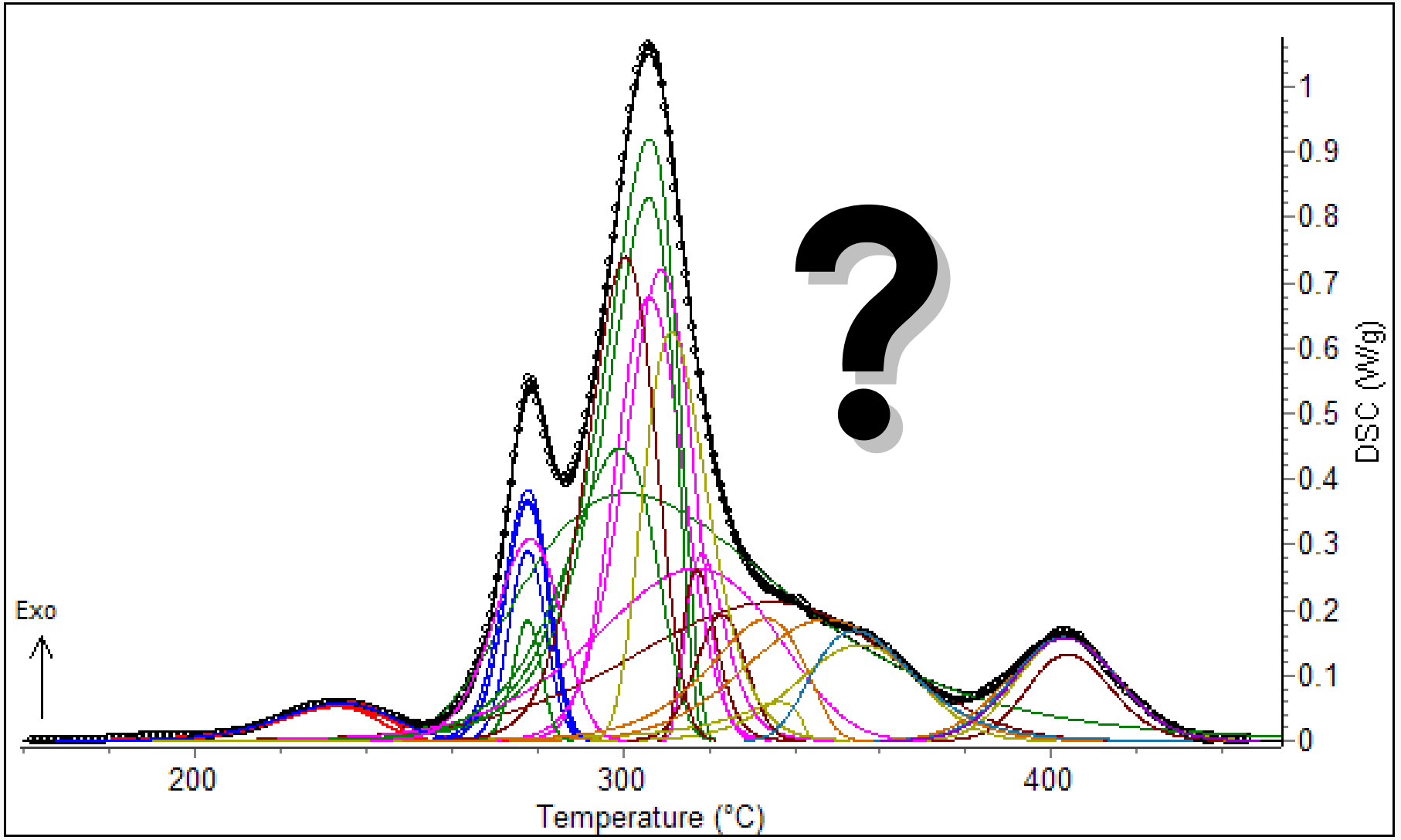
Still commonly used simplification:

‘ Let‘s assume that the reaction is of n-th order ‘



E = constant
Simplified model f(a) = $(1-a)^n$
Where n-reaction order is assumed to be 0, 1 or 2

Determination of the kinetic characteristics



Problem of interpretation of an observation

What do you see ?

- Isoconversional methods (model free):
  - There are 3 main modifications of isoconversional method:
  - - Differential (Friedman)
  - - Integral (Flynn-Ozawa-Wall)
  - - Advanced integral based on non-linear procedure (Vyazovkin)

Differential isoconversional method of Friedman

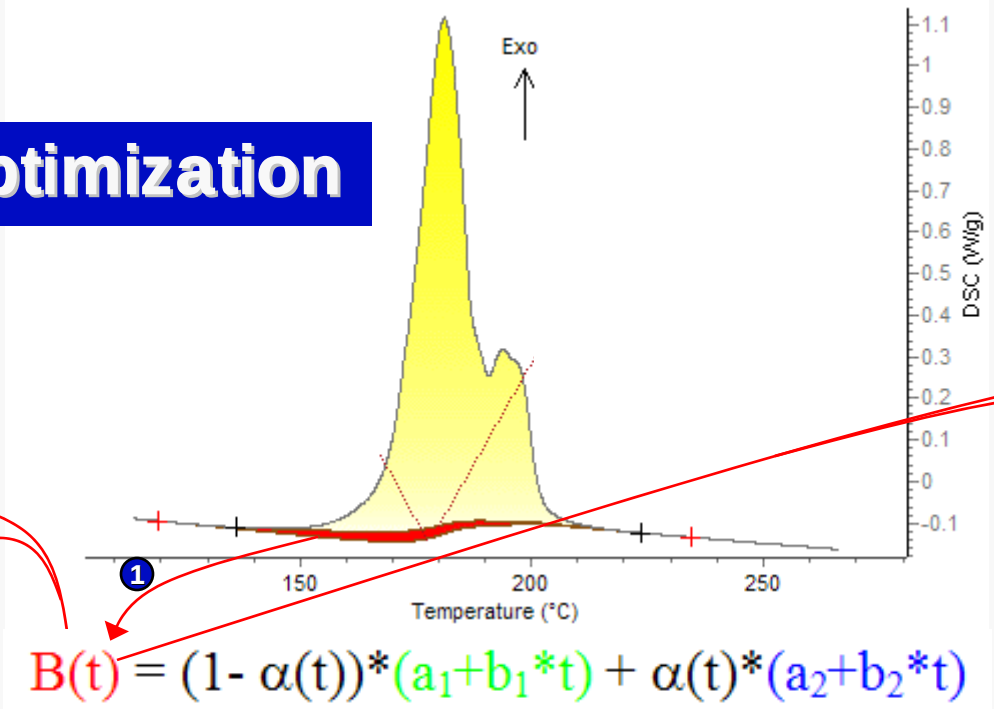
Rate of the reaction is expressed by the Arrhenius equation

$$\frac{d\alpha}{dt} = A \ exp\left(-\frac{E}{RT}\right) f(\alpha)$$

$$\ln\left(\frac{d\alpha}{dt}\right)_{\alpha} = Const - \frac{E_{\alpha}}{R}\frac{1}{T}$$

Differential isoconversional method of Friedman

Baseline optimization



$$\frac{d\alpha}{dt} = \frac{(S(t) - B(t))}{\int_{to}^{tend} (S(t) - B(t))dt}$$

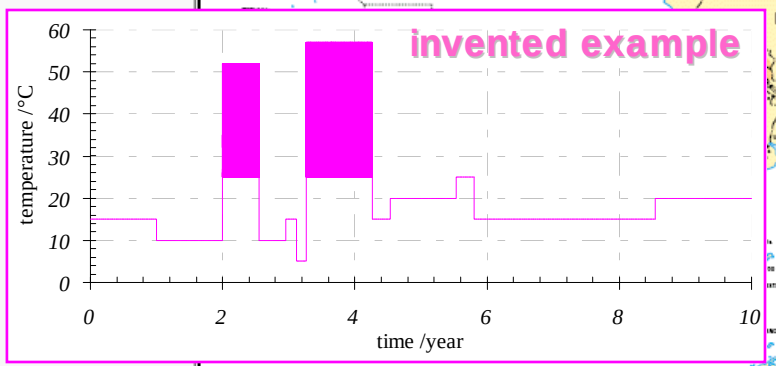
$$B(t) = (1 - \alpha(t))*(a_1 + b_1*t) + \alpha(t)*(a_2 + b_2*t)$$

$$\alpha(t) = \frac{\int_{to}^{t} (S(t) - B(t))dt}{\int_{to}^{tend} (S(t) - B(t))dt}$$

$$\ln\left(\frac{d\alpha}{dt}\right)_{\alpha} = Const - \frac{E_{\alpha}}{R}\frac{1}{T}$$

STANAG 2895 – climatic categories

$$\frac{d\alpha}{dt_\alpha} = \{A_\alpha \; f(\alpha)\} exp\left(-\frac{E_\alpha}{RT(t_\alpha)}\right)$$



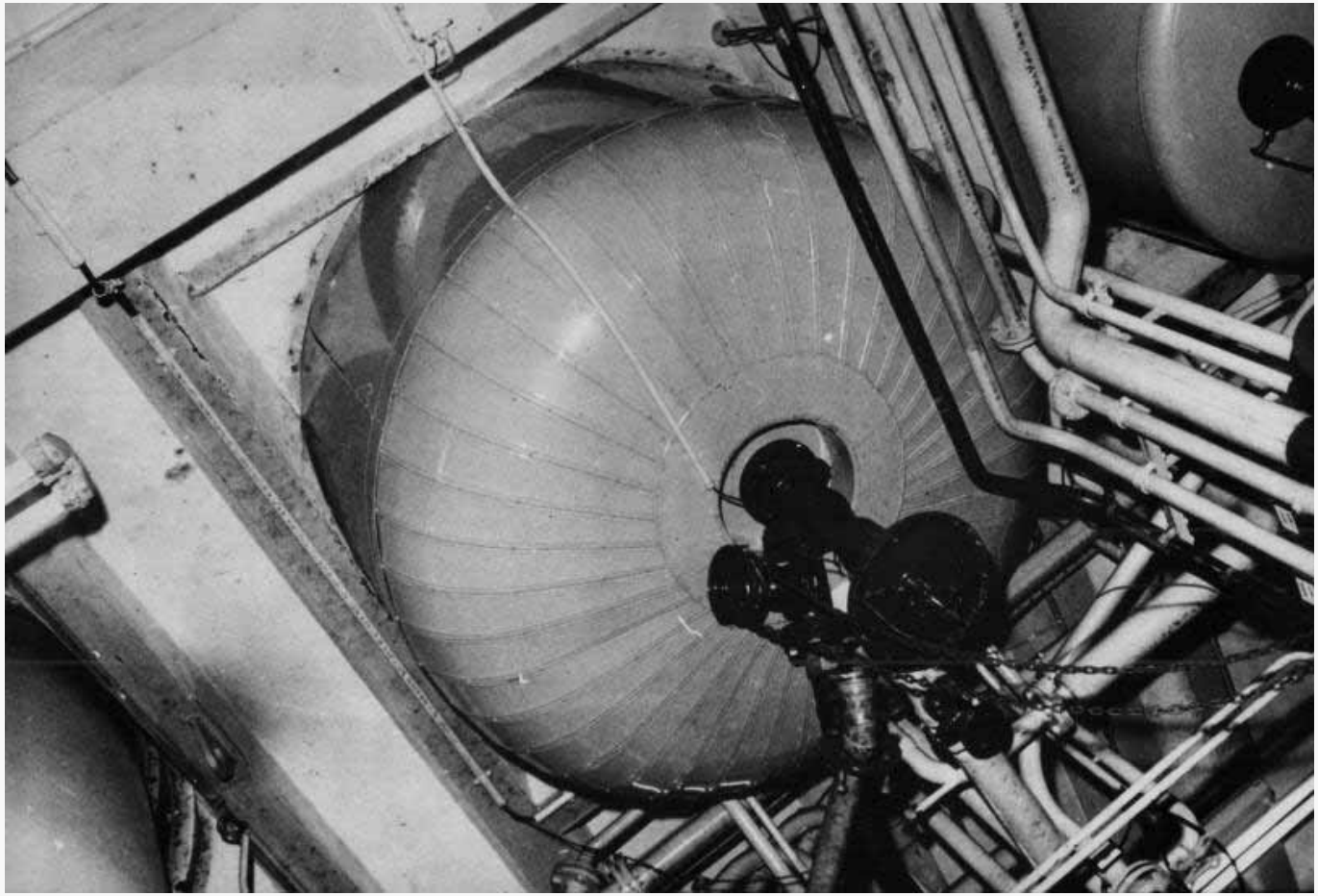
Beijing

STANAG 2895
A2 (Hot dry)

Up-scaling

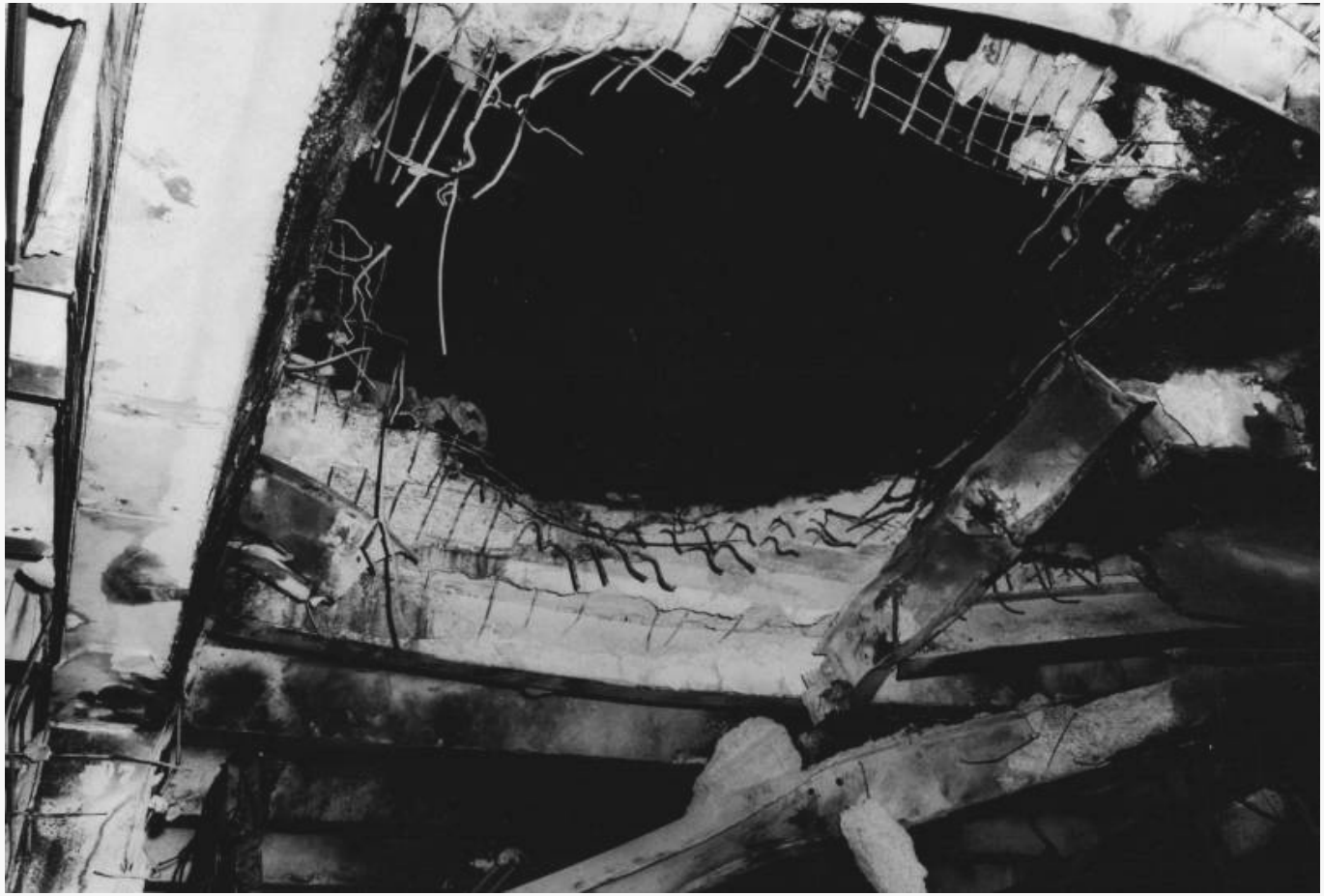
Example of adiabatic runaway scenario

Before :

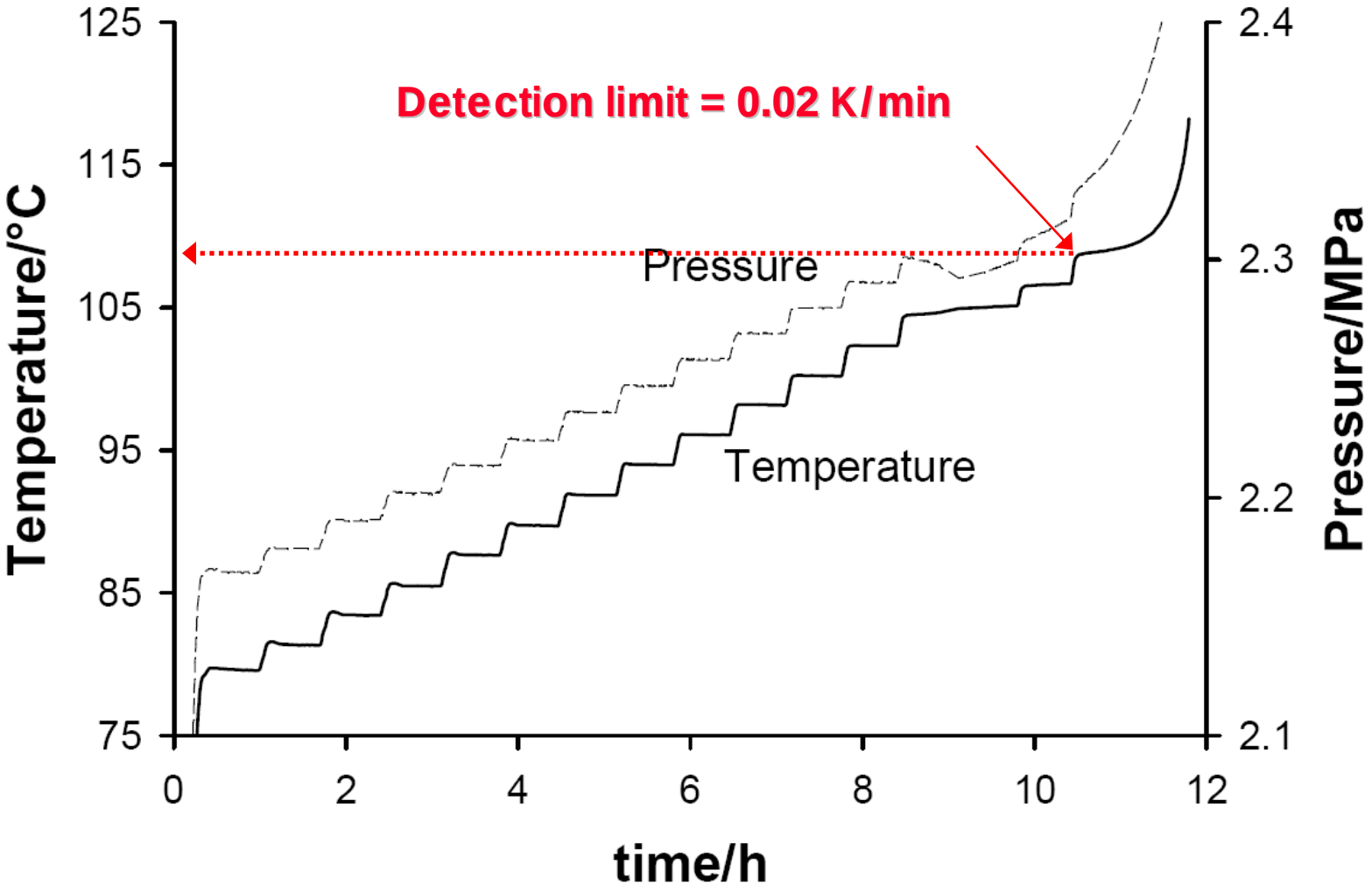


Example of adiabatic runaway scenario

After :



Temperature and pressure dependence on time recorded during ARC HWS experiment at air pressure of 1.8 MPa



Determination of time to maximum rate under adiabatic conditions (TMRad)

$$\begin{cases} \dfrac{d\alpha}{dt} = \{A_\alpha\, f(\alpha)\} exp\left(-\dfrac{E_\alpha}{RT(t)}\right) \\ M_s C_{p,s} \dfrac{dT_s}{dt} + M_c C_{p,c} \dfrac{dT_c}{dt} = \boxed{U}A(T_{env} - T_c) + M_s \Delta H \dfrac{d\alpha}{dt} \end{cases}$$

adiabatic conditions

Or $(T_{env} = T_c)$

$U = 0$

$$\Rightarrow \quad \frac{dT}{dt} = \frac{M_s C_{p,s}}{M_c C_{p,c} + M_s C_{p,s}} \frac{\Delta H}{C_{p,s}} \frac{d\alpha}{dt}$$

$$\Rightarrow \quad \frac{dT}{dt} = \frac{1}{\Phi} \frac{\Delta H}{C_{p,s}} \frac{d\alpha}{dt}$$

$\Phi = 1$ $\quad$ $\frac{\Delta H}{C_{p,s}} = \Delta T_{ad}$

From DSC

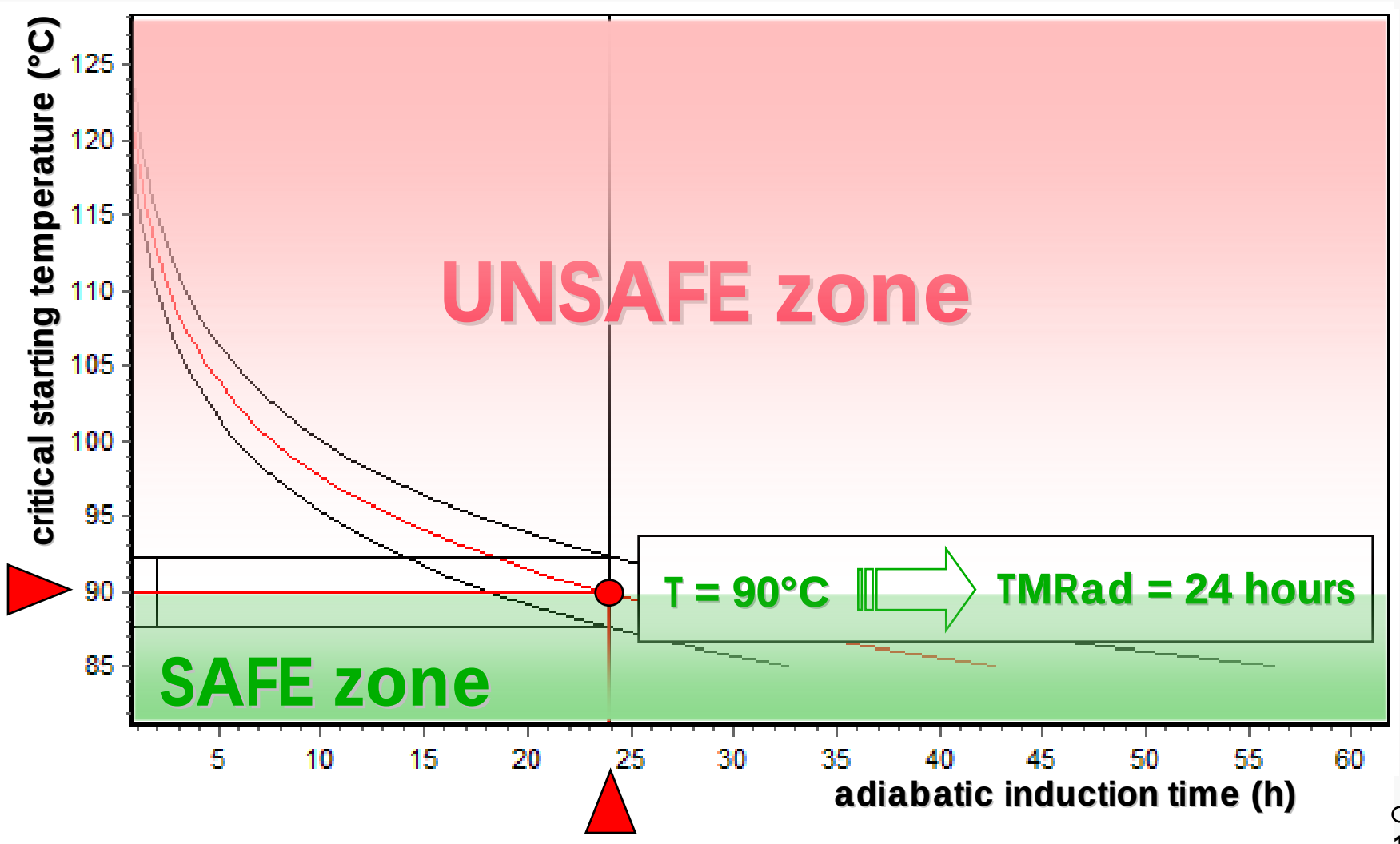
> 1000 kg

Thermal safety diagram: Dependence of TMRad on starting temperature

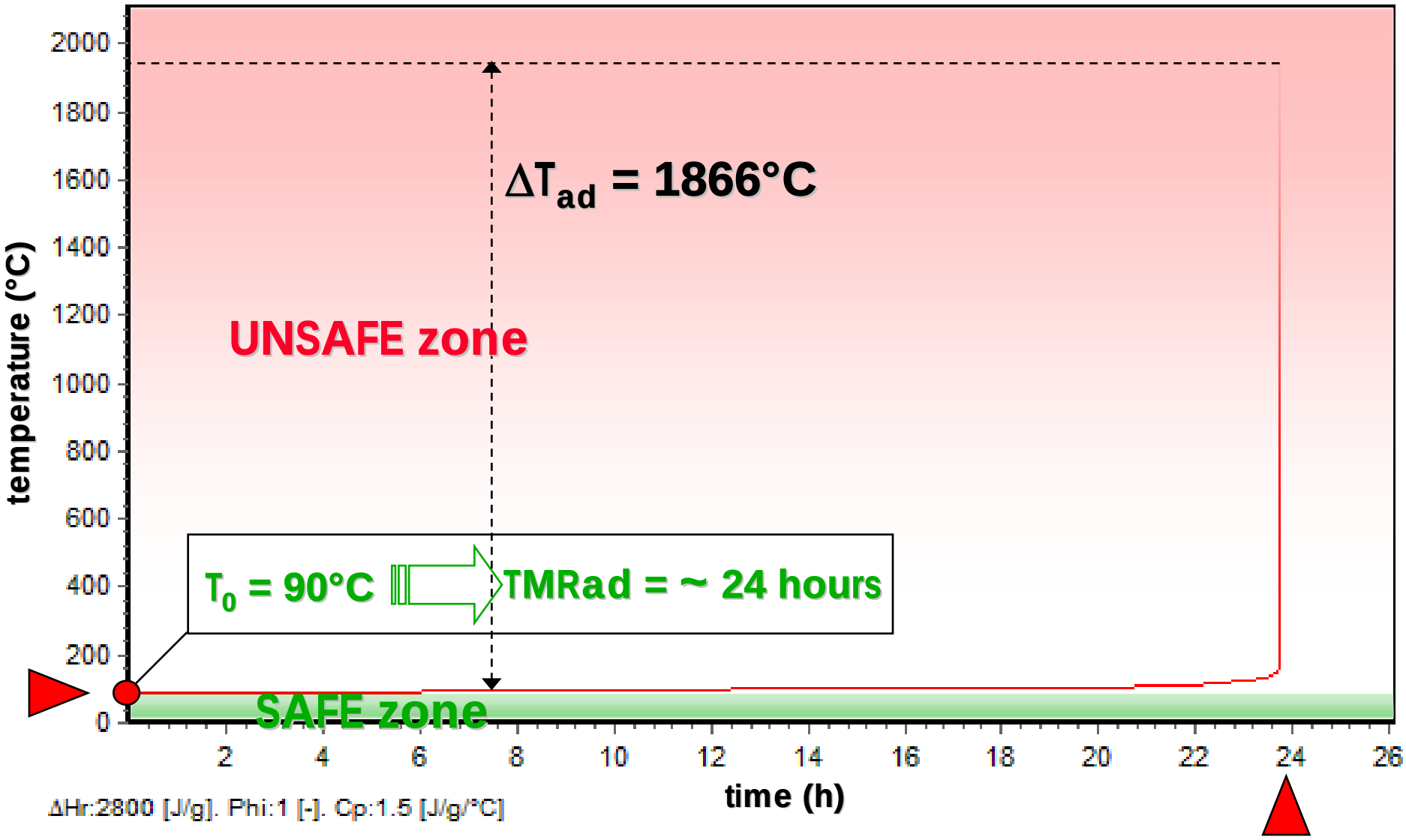
With U =0

Or

$(T_{env} = T_c)$



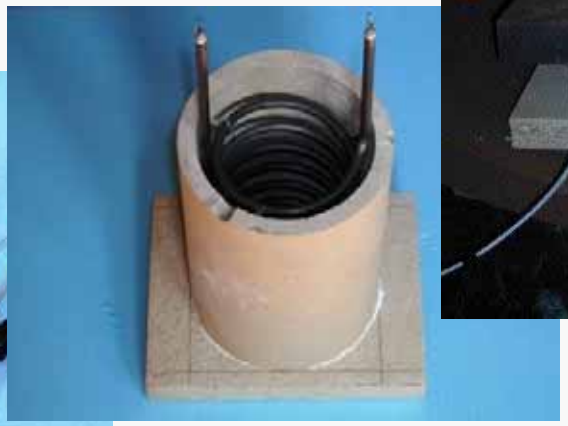
Adiabatic runaway scenario: Time to Maximum Rate under adiabatic conditions

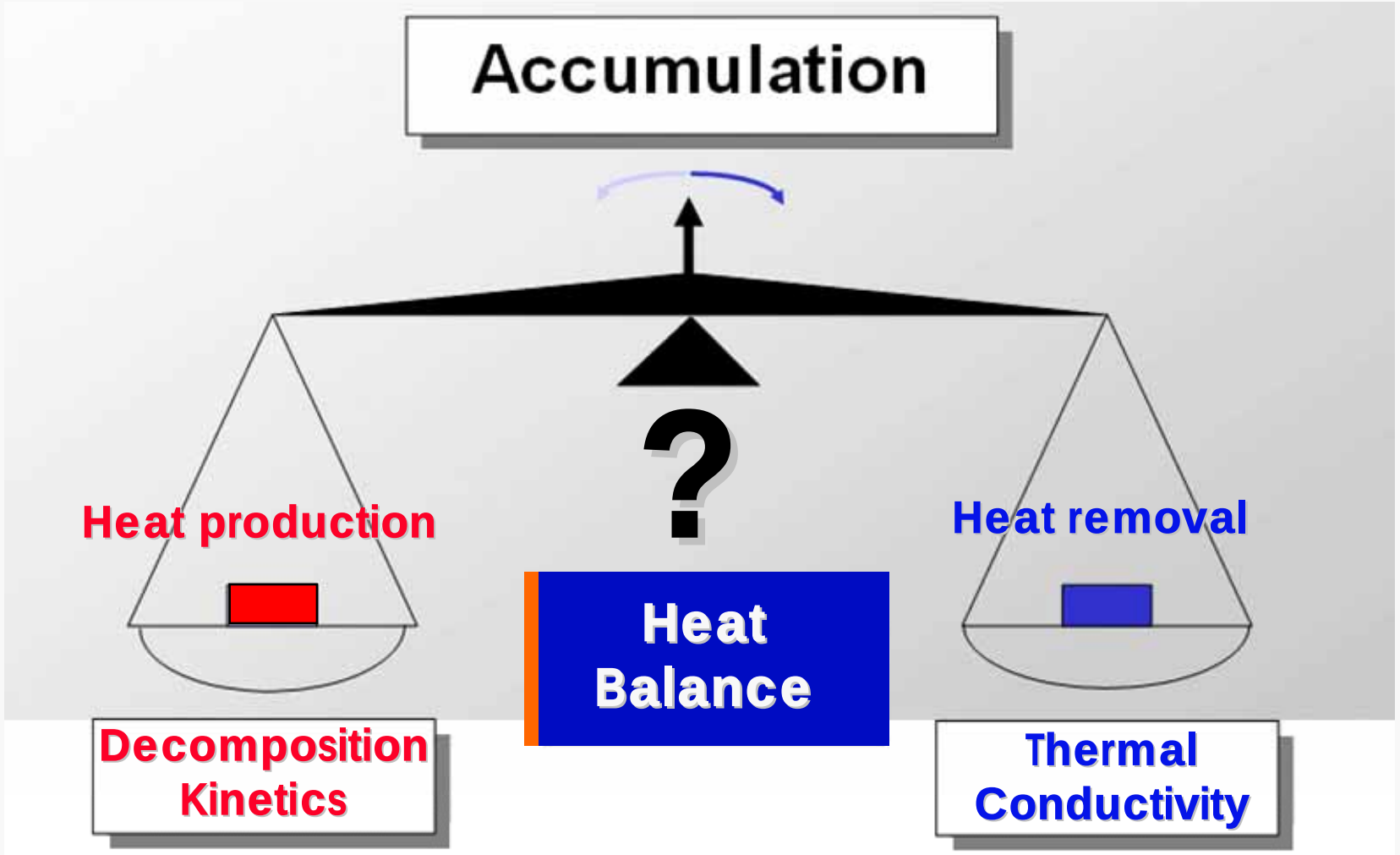


Example of cook-off experiment

After :

Before :



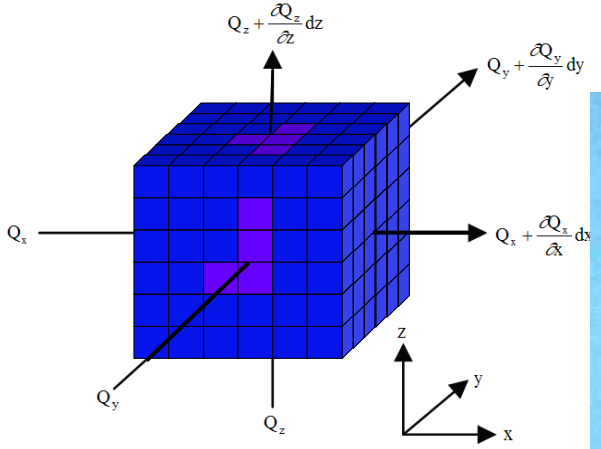

Accumulation
?
Heat production
Heat removal
Heat Balance
Decomposition Kinetics
Thermal Conductivity
DSC
?

Heat balance under non-adiabatic conditions

input = reaction + output + accumulation

- input: heat conducted in
- reaction: heat generated within
- output: heat conducted out
- accumulation: change in energy stored within

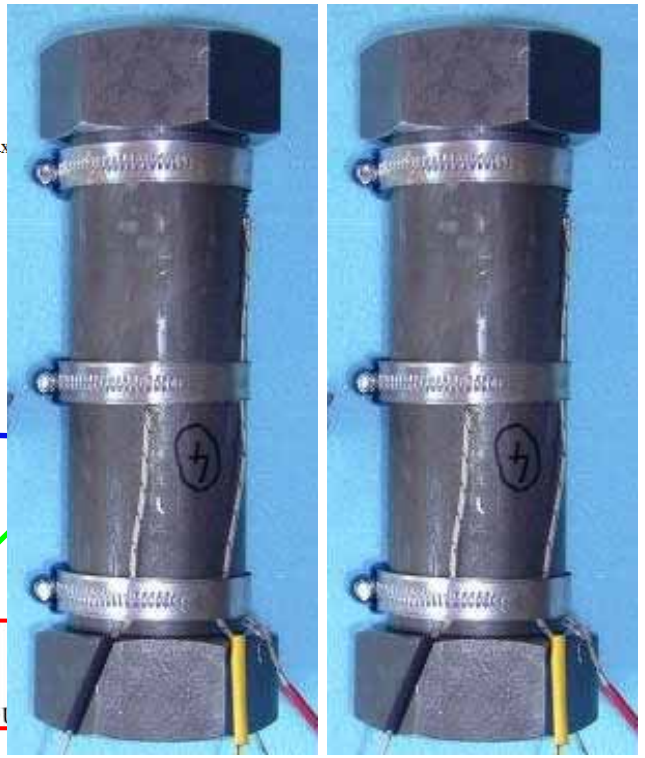
$$\frac{\partial T}{\partial t} = \frac{\lambda}{\rho C_P}\left(\frac{\partial^2 T}{\partial r^2} + \frac{J}{r}\frac{\partial T}{\partial r}\right) + \Delta T_{ad}\frac{d\alpha}{dt}$$



$$\lambda \left.\frac{\partial T}{\partial x}\right|_U = h(T_s - T_\infty)$$ **wall**

$$\left.\frac{\partial T}{\partial x}\right|_U = 0 \text{ (if perfect insulation)}$$ **center**

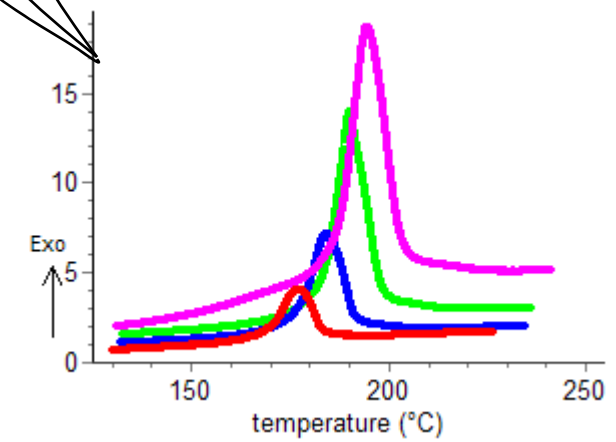
$$\lambda_{Layer_U} \left.\frac{\partial T}{\partial x}\right|_U = \lambda_{Layer_{U+1}} \left.\frac{\partial T}{\partial x}\right|_U$$



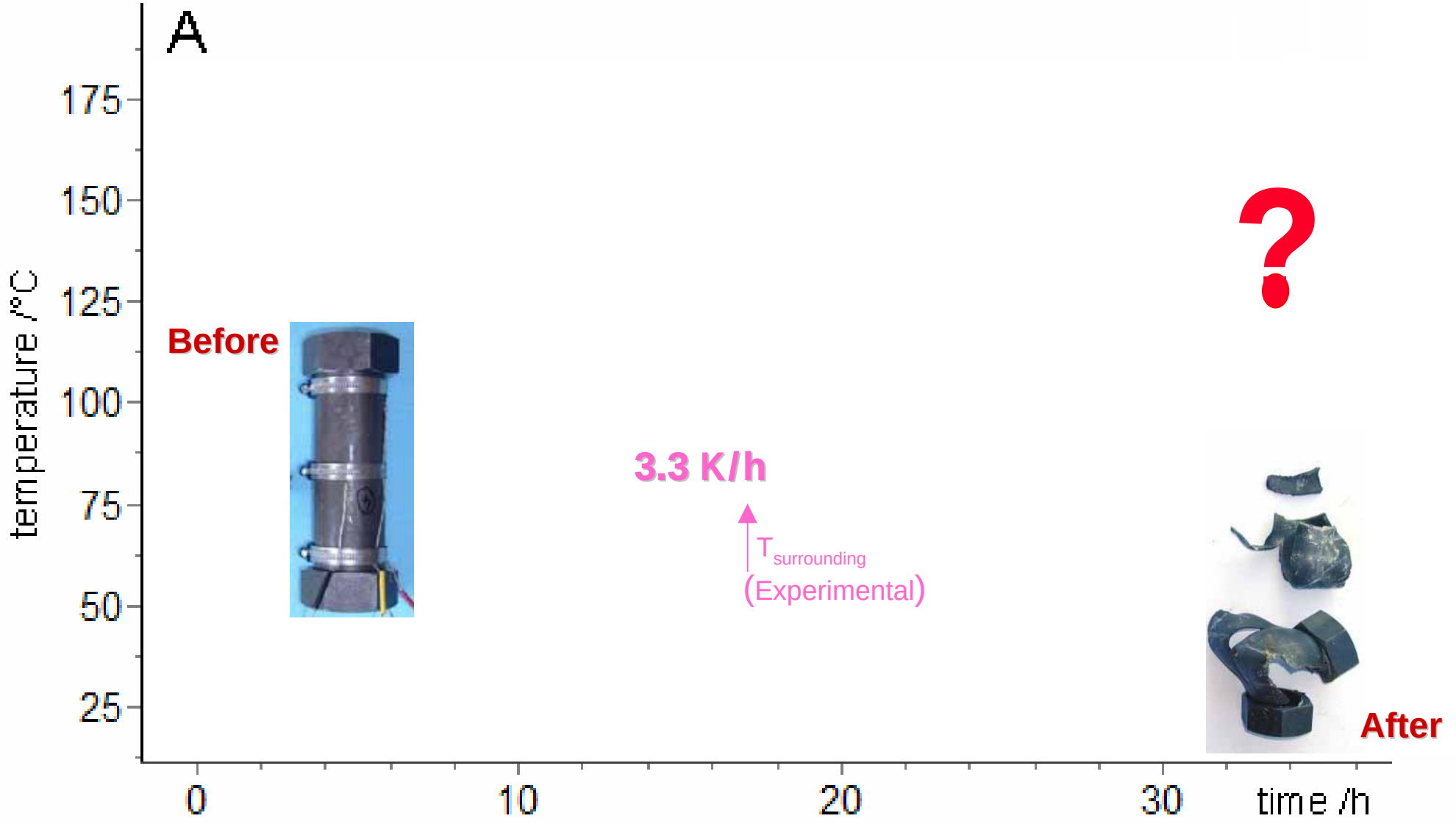
$$\frac{d\alpha}{dt} = A(\alpha)\exp\left(\frac{-E(\alpha)}{RT(t)}\right) f(\alpha)$$

$$\Delta T_{ad} = \frac{\Delta H}{C_P}$$

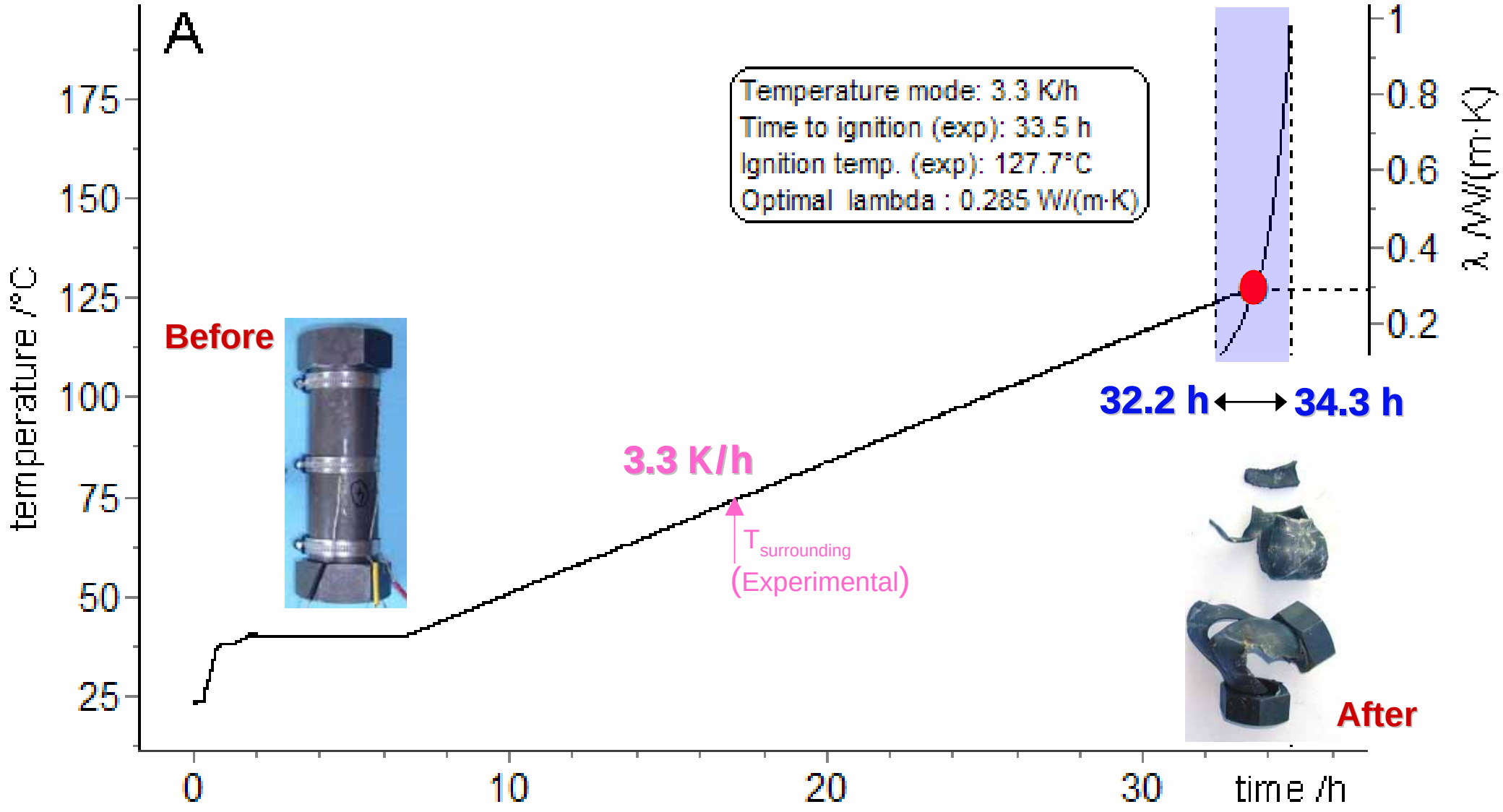
Kinetics / DSC



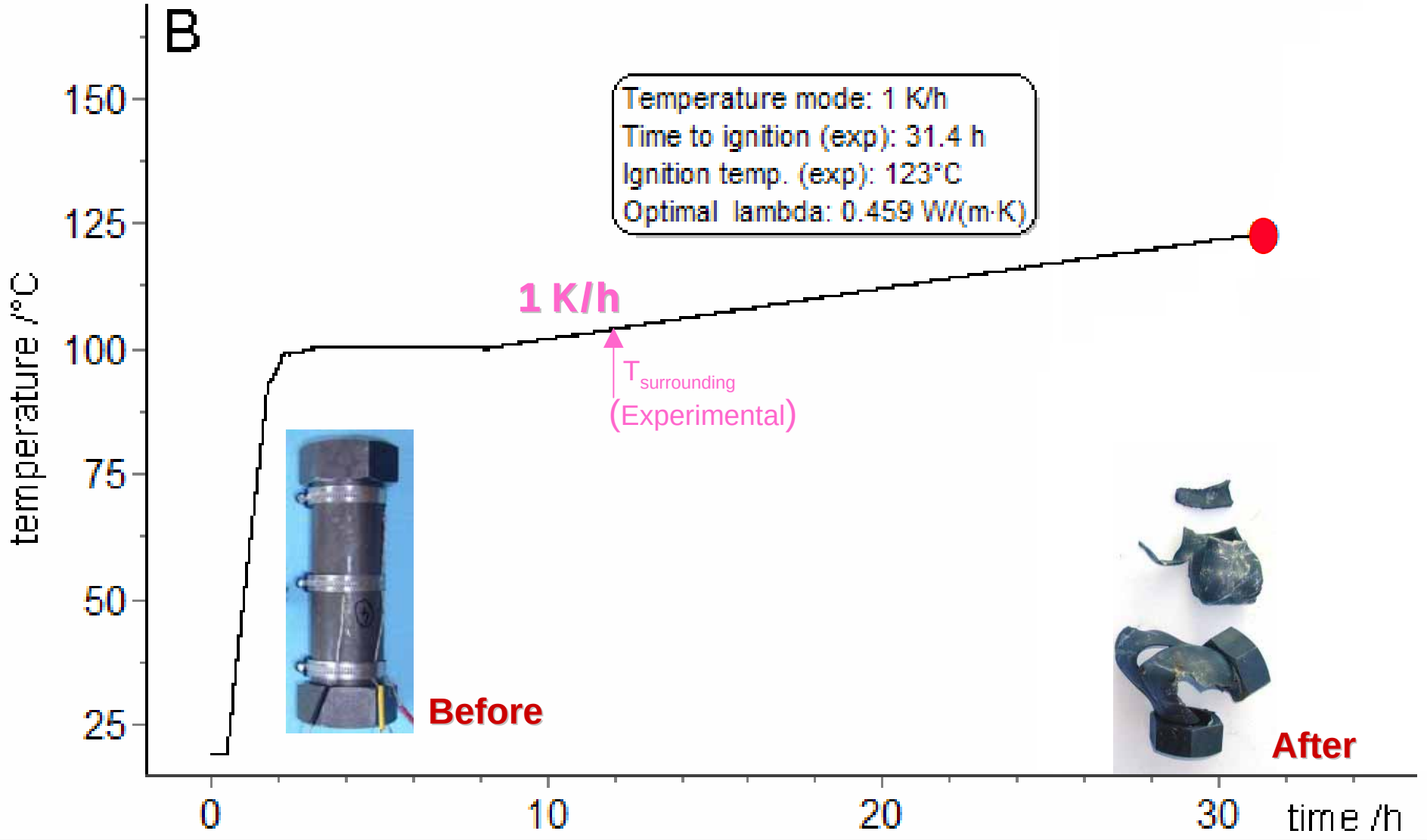
Cook-off experiment



Simulation of time to ignition for 0.1 < λ < 1 W(m· K)



Cook-off experiment



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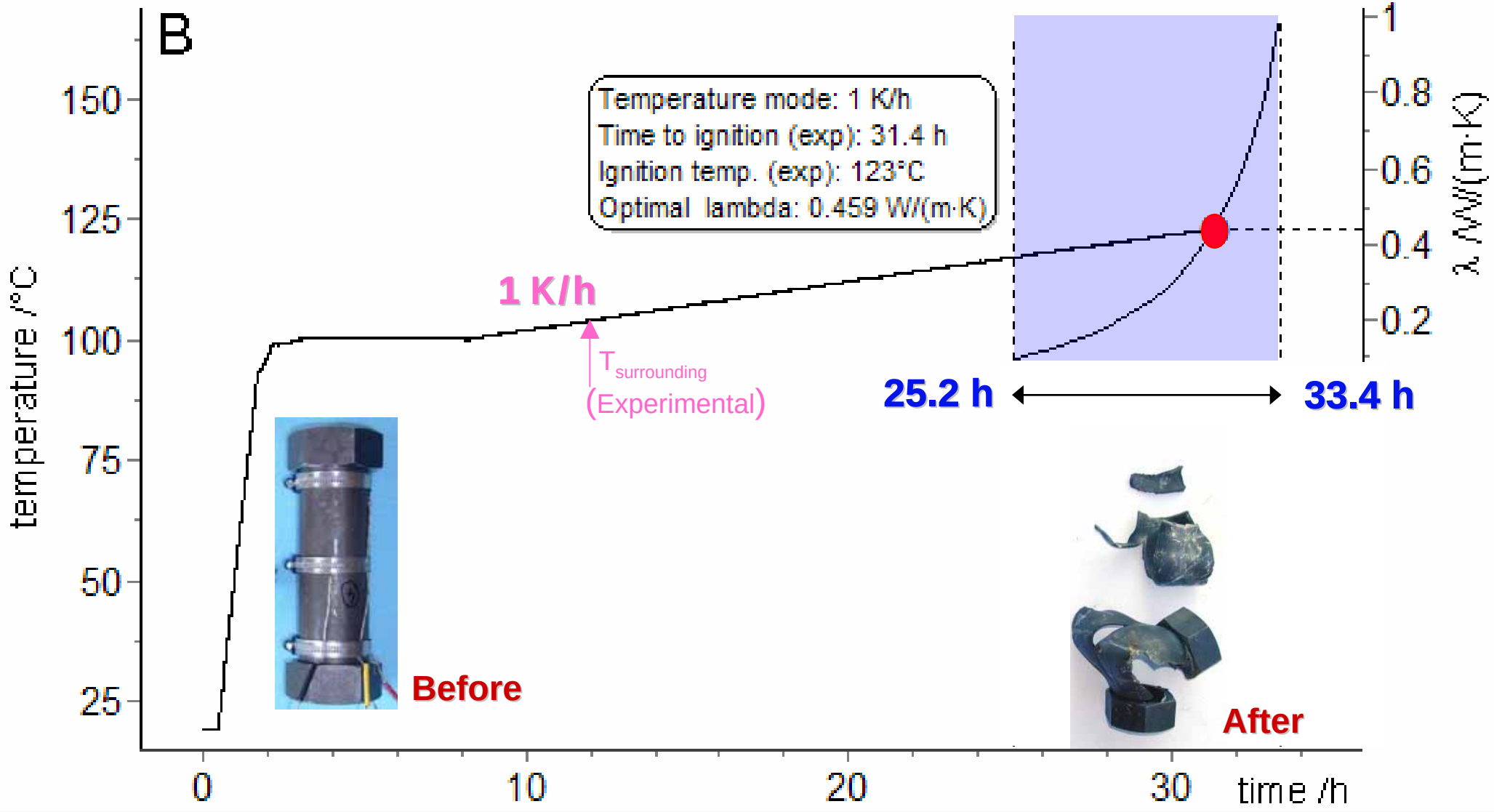
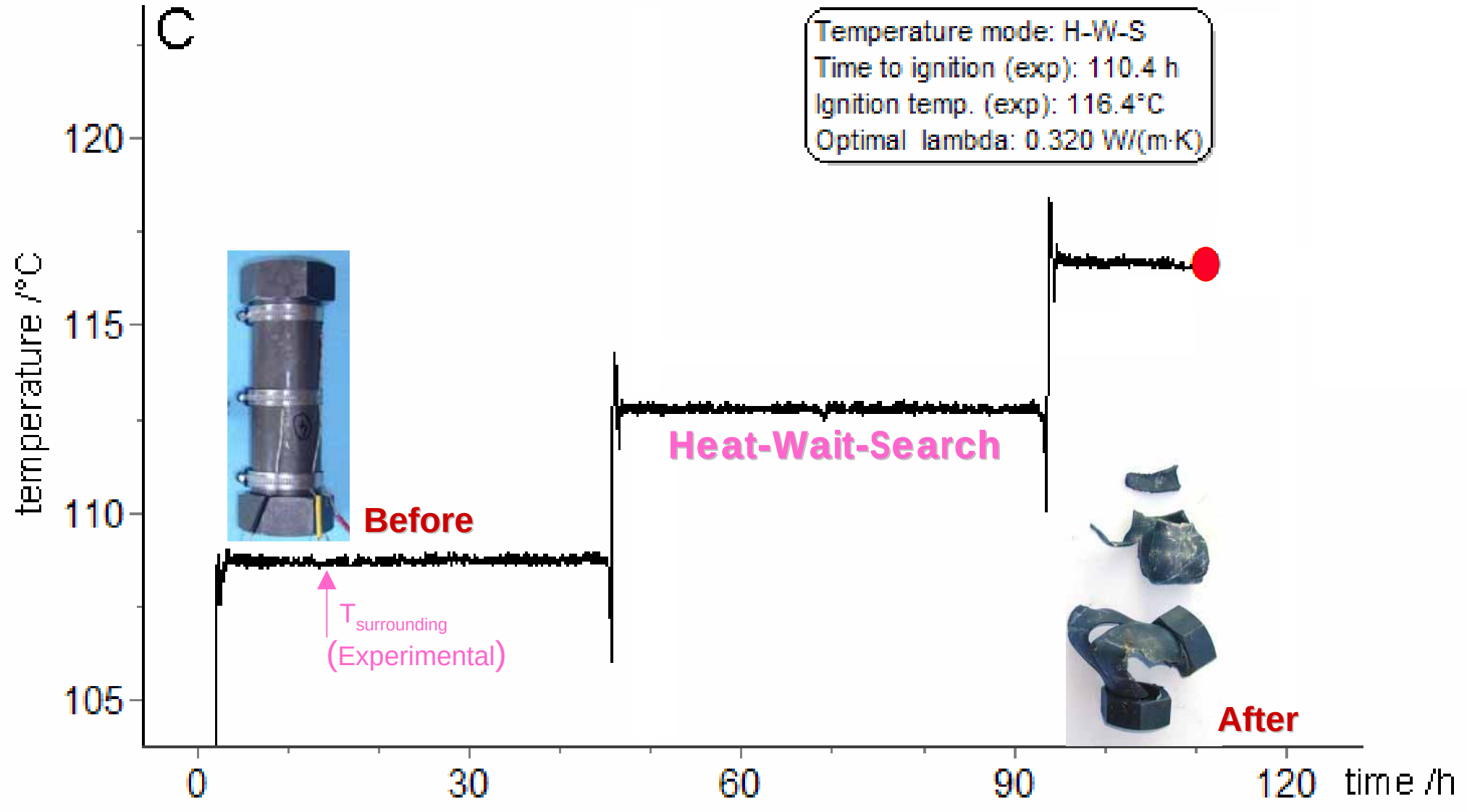
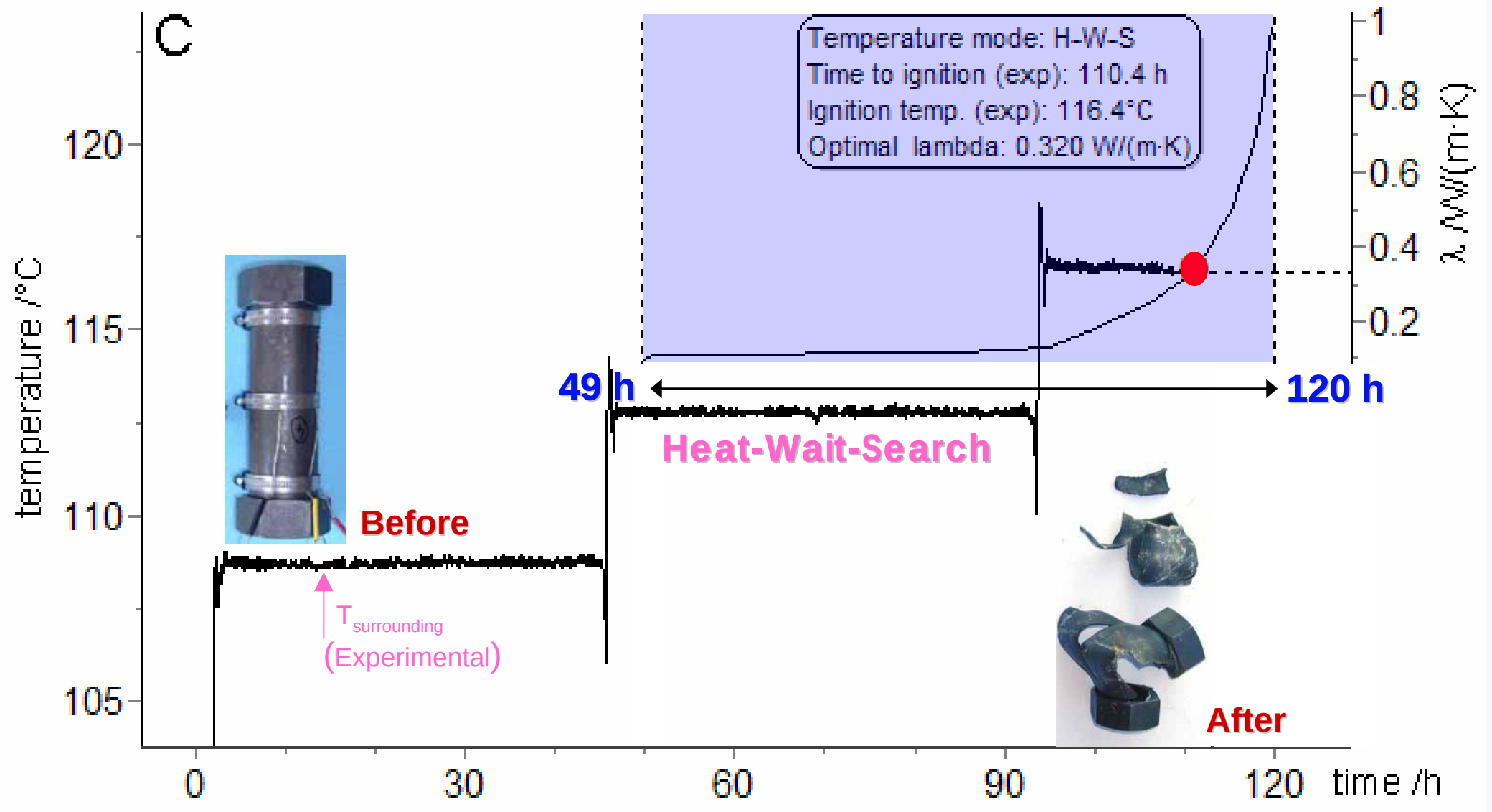


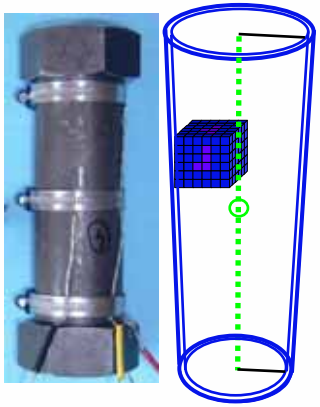
Cook-off experiment



Simulation of time to ignition for 0.1 < λ < 1 W(m· K)



Simulation of ignition under Heat-Wait-Search temperature mode applying λ = 0.32 W/m/K



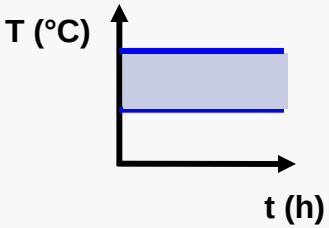
Temperature mode: H-W-S

Time to ignition (exp): 110.4 h

Ignition temp. (exp): 116.4°C

Optimal λ: 0.320 W/m/K

The concept of Self-Accelerating Decomposition Temperature (SADT)



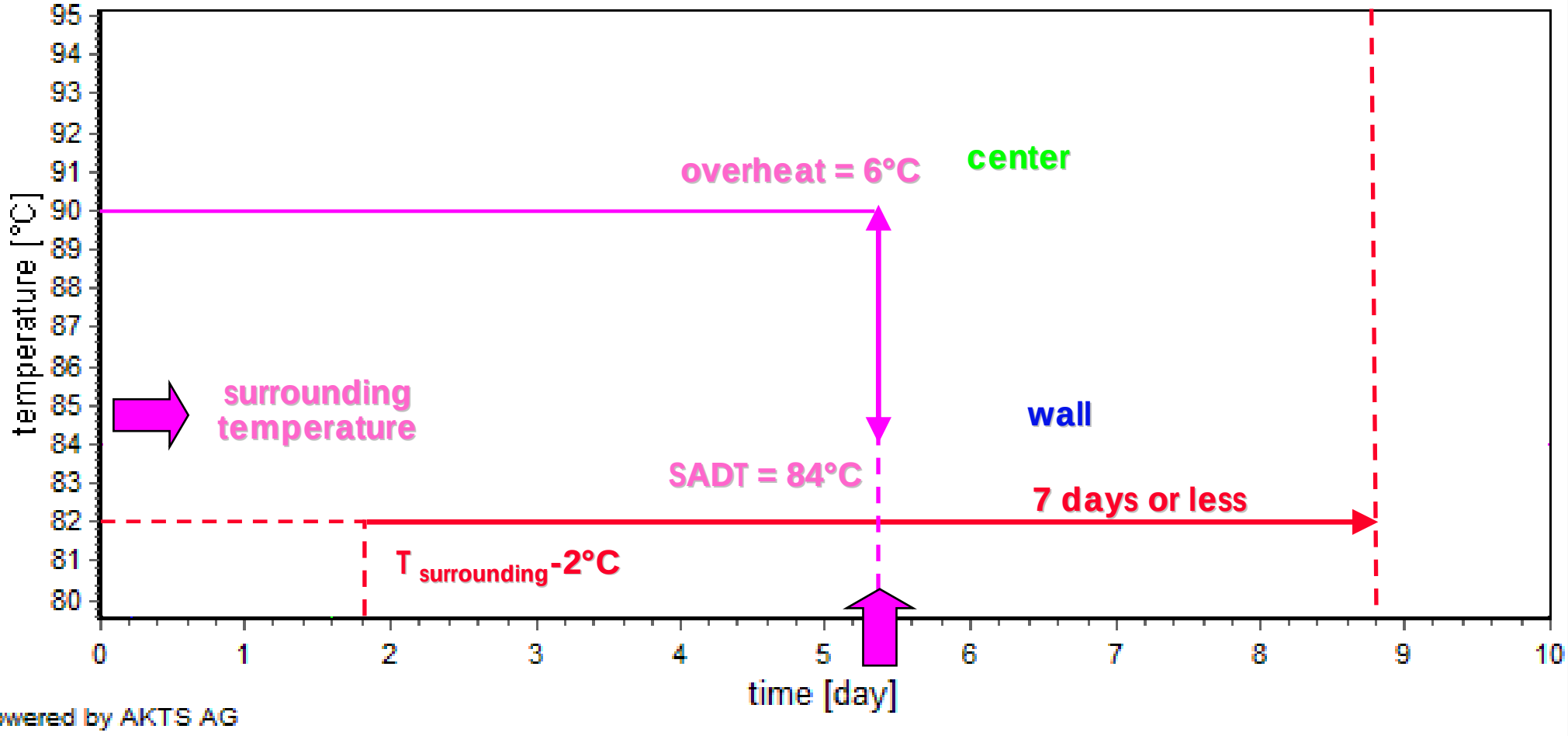
UN-Regulations…

SADT is defined as "the lowest environment temperature at which overheat in the middle of the specific commercial packing exceeds 6°C after a laps of period of seven days (168 hours) or less". This period is measured from the time when the packaging center temperature reaches 2°C below the surrounding temperature.

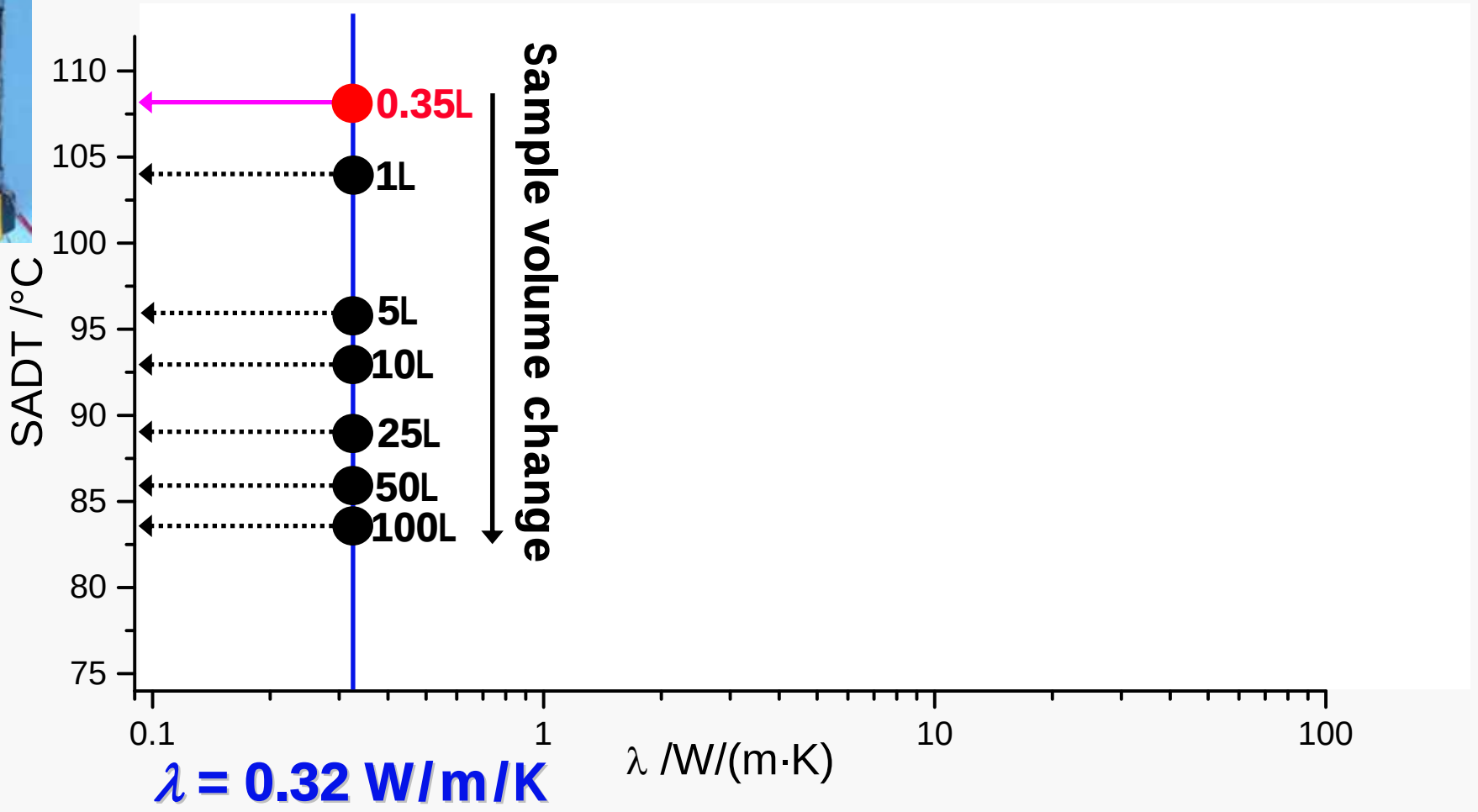
Determination of Self-Accelerating Decomposition Temperature (SADT)

SADT is 84°C.

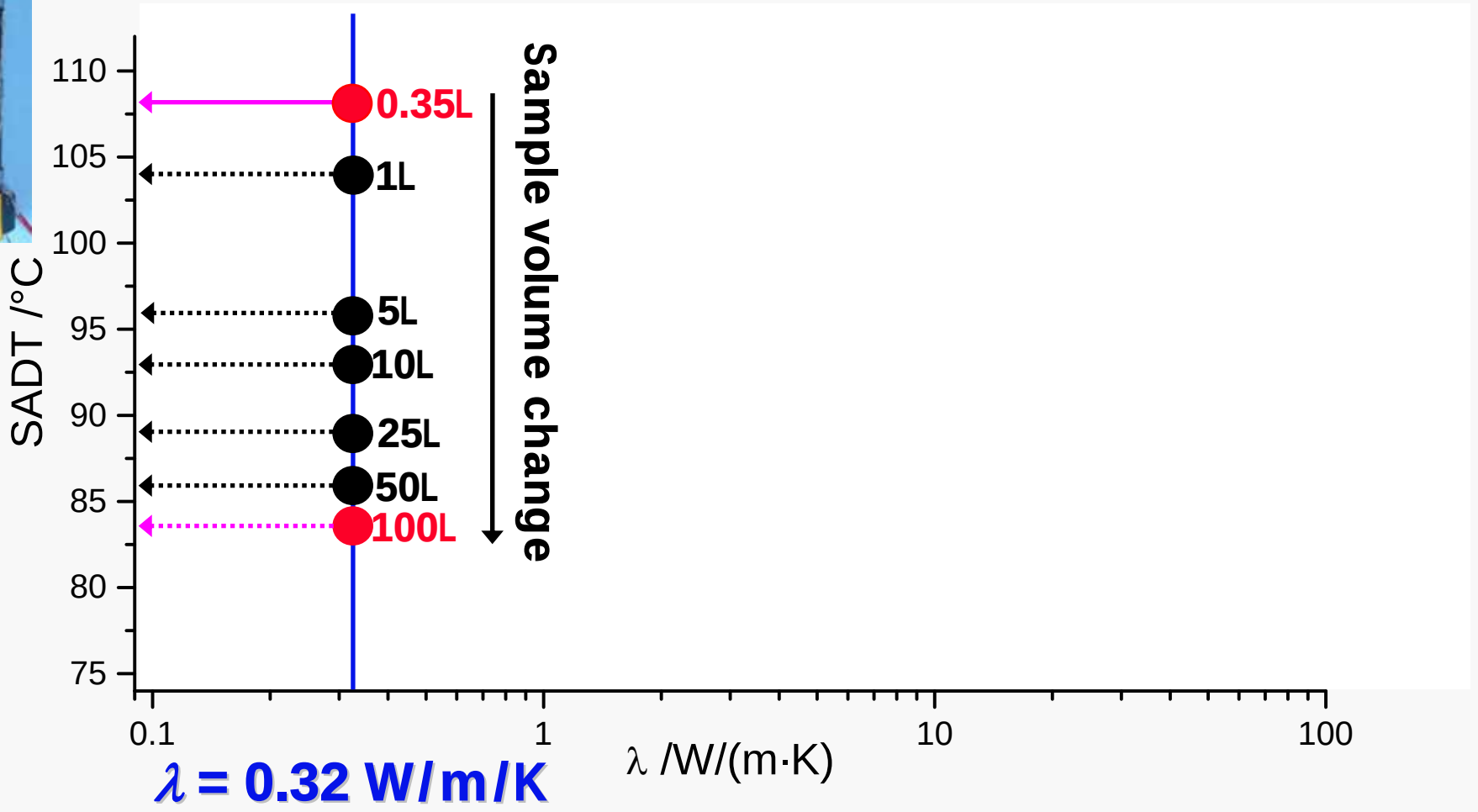
This temperature is the lowest environment temperature at which overheat in the middle of the specific packaging exceeds 6 °C (ΔT6) after a lapse of the period of seven days (168 hours) or less. This period is measured from the time when the packaging centre temperature reaches 2 °C below the surrounding temperature. This overheat of 6°C occurs after about 5 days.



SADT as a function of the thermal conductivity λ and sample volume expressed in L. The circles represent the simulation of SADT when applying the λ value taken from the H-W-S-mode simulation



SADT for various the sample volume expressed in L.
The circles represent the simulation of SADT when applying the λ value taken from the H-W-S-mode simulation



‘Safety through calculations not by accidents’

Independent of the mass of the sample investigated in any thermoanalytical experiment, the correct description of the time to thermal ignition of a decomposition reaction requires the knowledge of two important parameters

(i) the kinetics of the investigated reaction and
(ii) the heat balance of the system.

Depending on the mass of the sample both these parameters differently contribute to the reaction progress.

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