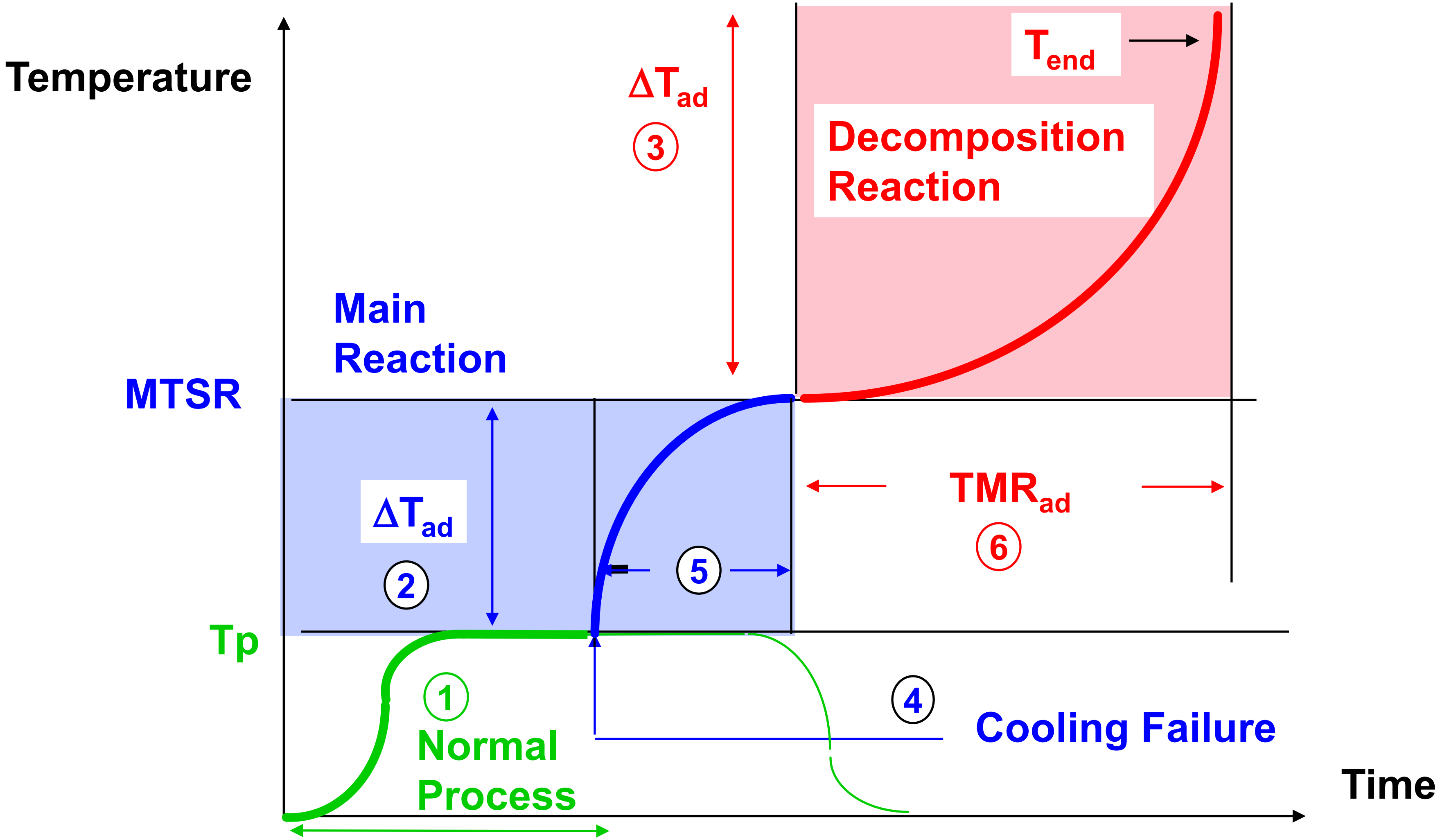
# Heat Confinement

Module 4

ENG 431: Safety Chemical Processes

Annik Nanchen

# Cooling Failure Scenario

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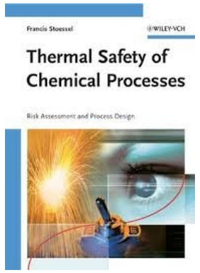
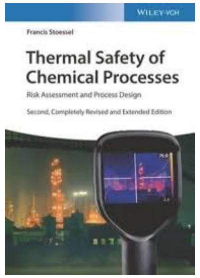
# Heat Accumulation

- Introduction
- Mechanism of heat transfer
  - Stirred systems: forced convection
  - Solid systems, viscous liquids: conduction
  - Low viscosity liquids: natural convection
- Analysis procedure
- Practical examples

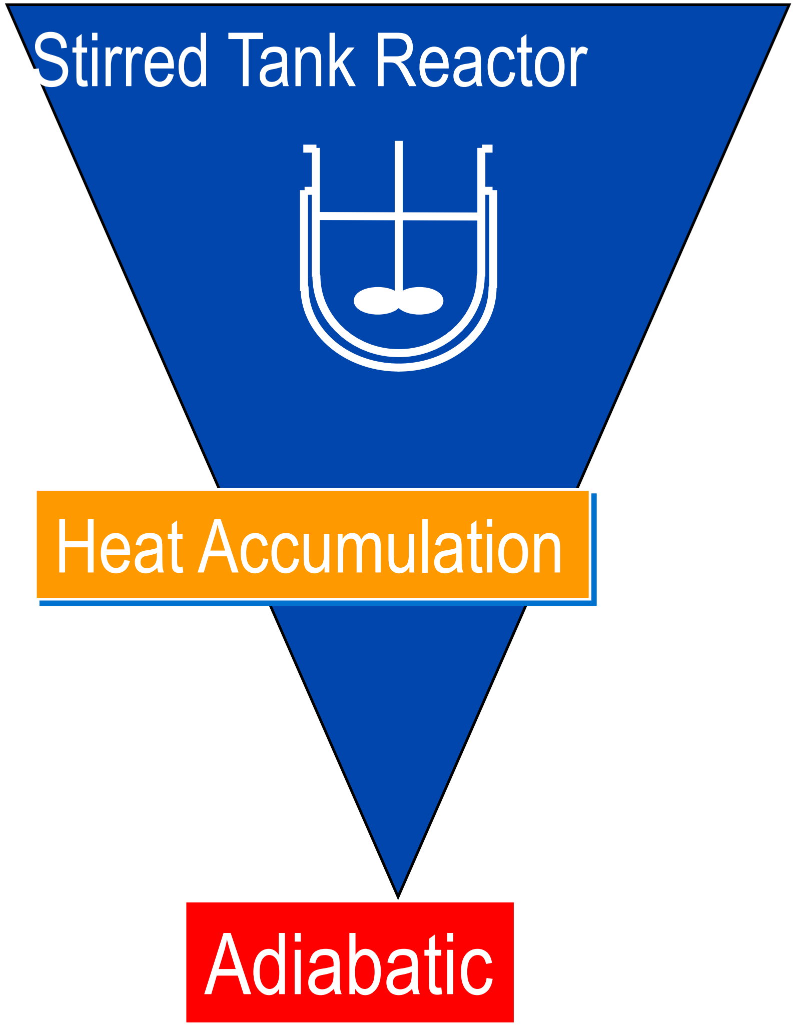



Chapter 13




Chapter 12

# How realistic are adiabatic conditions?



# Heat accumulation

## Heat accumulation situations: effect of mass

- Decomposition of a reaction mass. $\Delta T_{ad}$ 200°C, c'p: 1.7 kJ/kg.K, Ea: 100 kJ/mol
- Reaction mass is in different containers (different sizes)

| Heat release rate (W/kg) | Temperature at beginning of storage (°C) | Adiabatic | Mass | | | |
|---|---|---|---|---|---|---|
| | | | 0.5 kg | 50 kg | 5000 kg | |
| 10 | 129 | 200 | | | | ΔT [°C] |
| | | 0.6 | | | | Released after [h] |
| 1 | 100 | 200 | | | | ΔT [°C] |
| | | 5.4 | | | | Released after [h] |
| 0.1 | 75 | 200 | | | | ΔT [°C] |
| | | 47 | | | | Released after [h] |
| 0.01 | 53 | 200 | | | | ΔT [°C] |
| | | 417 | | | | Released after [h] |

# Heat accumulation

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|---|---|---|---|---|---|---|
| | | | 0.5 kg | 50 kg | 5000 kg | |
| 10 | 129 | 200°C | 191°C | 200°C | 200°C | ΔT [°C] |
| | | 0.6 h | 0.6 h | 0.6 h | 0.6 h | Released after [h] |
| 1 | 100 | | | | | ΔT [°C] |
| | | | | | | Released after [h] |
| 0.1 | 75 | | | | | ΔT [°C] |
| | | | | | | Released after [h] |
| 0.01 | 53 | | | | | ΔT [°C] |
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| | | 0.6 h | 0.6 h | 0.6 h | 0.6 h | Released after [h] |
| 1 | 100 | 200°C | 5.8°C | 200°C | 200°C | $\Delta$T [°C] |
| | | 5.5 h | 6h | 5.5 h | 5.5 h | Released after [h] |
| 0.1 | 75 | | | | | $\Delta$T [°C] |
| | | | | | | Released after [h] |
| 0.01 | 53 | | | | | $\Delta$T [°C] |
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| | | 0.6 h | 0.6 h | 0.6 h | 0.6 h | Released after [h] |
| 1 | 100 | 200°C | 5.8°C | 200°C | 200°C | ΔT [°C] |
| | | 5.5 h | 6h | 5.5 h | 5.5 h | Released after [h] |
| 0.1 | 75 | 200°C | 0.5°C | 13°C | 200°C | ΔT [°C] |
| | | 48 h | 20h | 48 h | 48 h | Released after [h] |
| 0.01 | 53 | | | | | ΔT [°C] |
| | | | | | | Released after [h] |

# Heat accumulation

## Heat accumulation situations: effect of mass

- Decomposition of a reaction mass. ∆Tad 200°C
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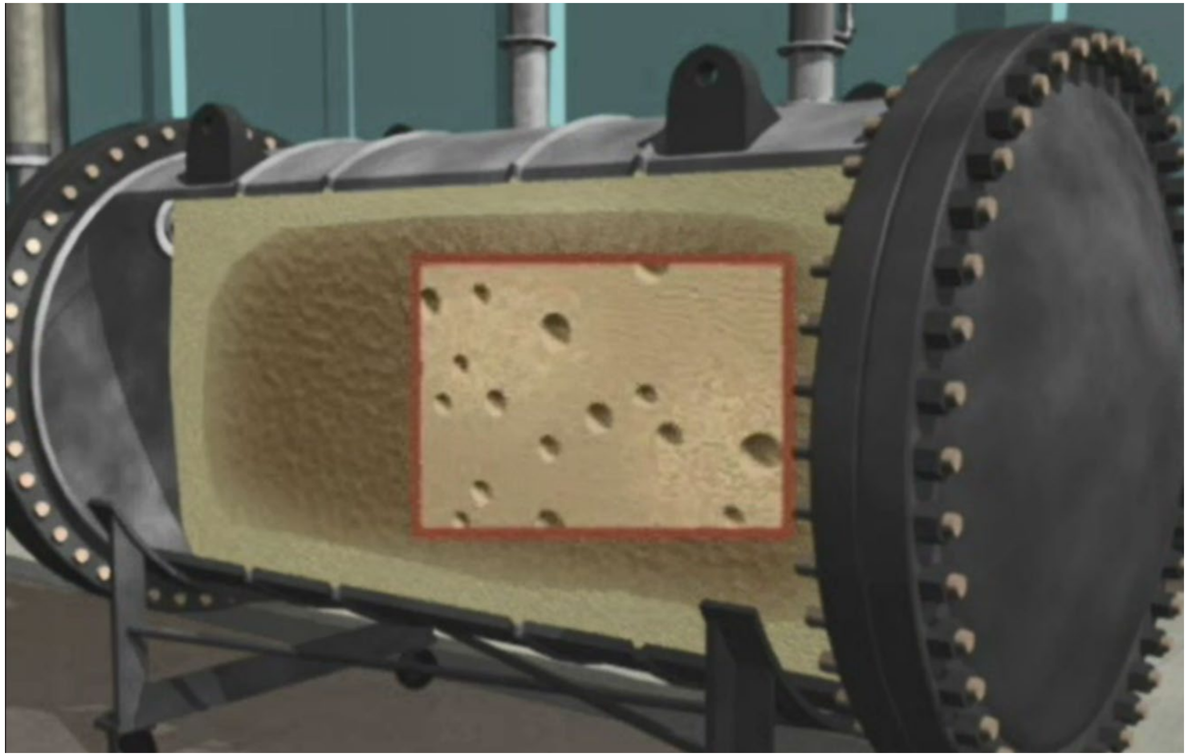
| Heat release rate (W/kg) | Temperature at beginning of storage (°C) | Adiabatic | Mass | | | |
|---|---|---|---|---|---|---|
| | | | 0.5 kg | 50 kg | 5000 kg | |
| 10 | 129 | 200°C | 191°C | 200°C | 200°C | ∆T [°C] |
| | | 0.6 h | 0.6 h | 0.6 h | 0.6 h | Released after [h] |
| 1 | 100 | 200°C | 5.8°C | 200°C | 200°C | ∆T [°C] |
| | | 5.5 h | 6h | 5.5 h | 5.5 h | Released after [h] |
| 0.1 | 75 | 200°C | 0.5°C | 13°C | 200°C | ∆T [°C] |
| | | 48 h | 20h | 48 h | 48 h | Released after [h] |
| 0.01 | 53 | 200°C | | 0.7°C | 165°C | ∆T [°C] |
| | | 420 h | | 154h | 420 h | Released after [h] |

# Heat Accumulation in Industrial Context

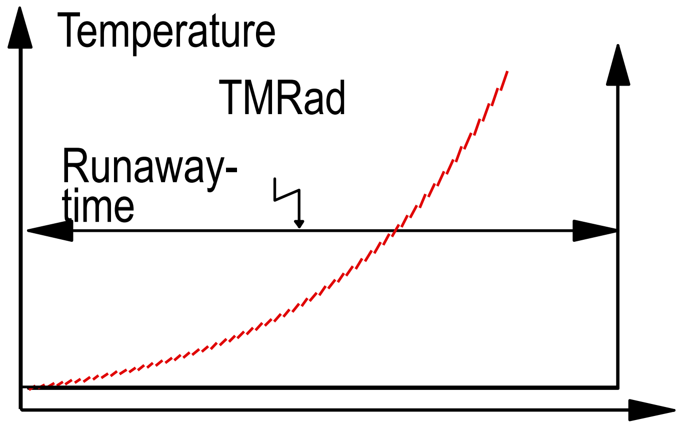
- Hot discharge
- Heating chambers
- Storage
- Transport
- Inadvertent shut down
- Heated pipes



- https://www.csb.gov/videos/reactive-hazards/

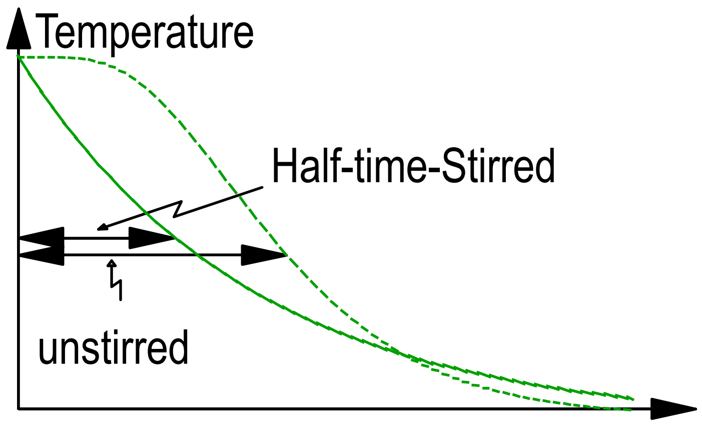
# Heat balance using time scales

Heat production




adiabatic runaway

Heat removal




Cooling curve

**Thermal Explosion if:** Heat production > Heat removal

Adiabatic Runaway-time < Cooling time

# Heat Accumulation

- Introduction
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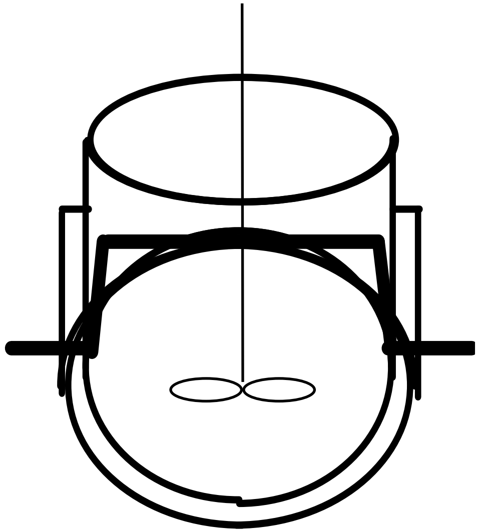
# Agitated System

- Semenov
- Newtonian cooling

$$q_{ex} = U \cdot A \cdot (T - T_C)$$



$U$ : *Overal heat transfer coefficient* $[W\ m^{-2}\ K^{-1}]$

$A$ : *Heat exchange area* $[m^2]$

$T$ : *Temperature reacting medium* $[°C, K]$

$T_C$ : *Temperature cooling medium* $[°C, K]$

# Heat balance

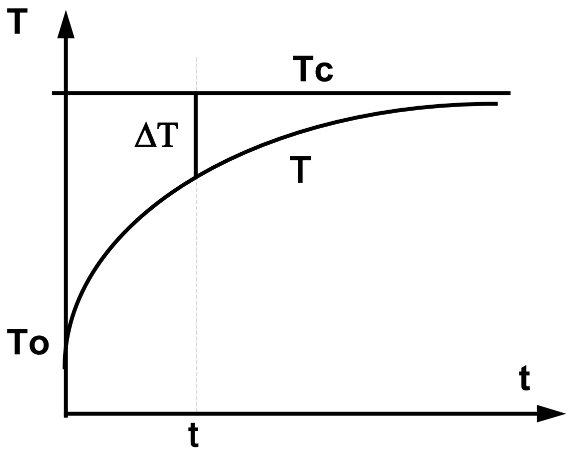
$$M \cdot c'_p \cdot \frac{dT}{dt} = -U \cdot A \cdot \left(T - T_C\right)$$

$$-M \cdot c'_p \cdot \frac{d\left(\Delta T\right)}{dt} = U \cdot A \cdot \Delta T$$

$$-\frac{M \cdot c'_p}{U \cdot A} \cdot \frac{d\left(\Delta T\right)}{\Delta T} = dt$$

$$\frac{M \cdot c'_p}{U \cdot A} = \tau_C$$

$$-\frac{d\left(\Delta T\right)}{\Delta T} = \frac{t}{\tau_C}$$




$$\left(\frac{\Delta T}{\Delta T_0}\right) = \exp\left(-\frac{t}{\tau_C}\right)$$

# Heat Balance

Solves both equation if $\Delta T_{crit} = T_{crit} - T_0 = \frac{RT_{crit}^2}{E} \approx \frac{RT_0^2}{E}$

$$Q_{rx}.\rho \cdot V \cdot k_0 \cdot \exp\left[\frac{-E}{R}\left(\frac{1}{T_{crit}} - \frac{1}{T_0}\right)\right] = U \cdot A \cdot \Delta T_{crit} \quad \text{since} \quad q_{crit} = q_0 \cdot \exp\left[\frac{-E}{R}\left(\frac{1}{T_{crit}} - \frac{1}{T_0}\right)\right]$$

$$\frac{-E}{R}\left(\frac{1}{T_{crit}} - \frac{1}{T_0}\right) \approx \frac{-E}{RT_{crit}^2}(T_{crit} - T_0) = 1 \quad \text{since} \quad \Delta T_{crit} = \frac{RT_0^2}{E}$$

$$k_0 \cdot e \cdot \Delta T_{ad} = \frac{U \cdot A}{\rho \cdot V \cdot c'_p} \cdot \frac{RT_0^2}{E}$$

$$\frac{1}{k_0 \cdot \Delta T_{ad}} \cdot \frac{RT_0^2}{E} = TMR_{ad}$$

Thermal half-life $t_{1/2} = \ln(2) \cdot \tau$

Thermal time constant $\tau = \frac{\rho \cdot V \cdot c'_p}{U \cdot A}$

$$TMR_{ad} = \frac{e}{\ln(2)} \cdot t_{1/2} = 3.92 \cdot t_{1/2}$$

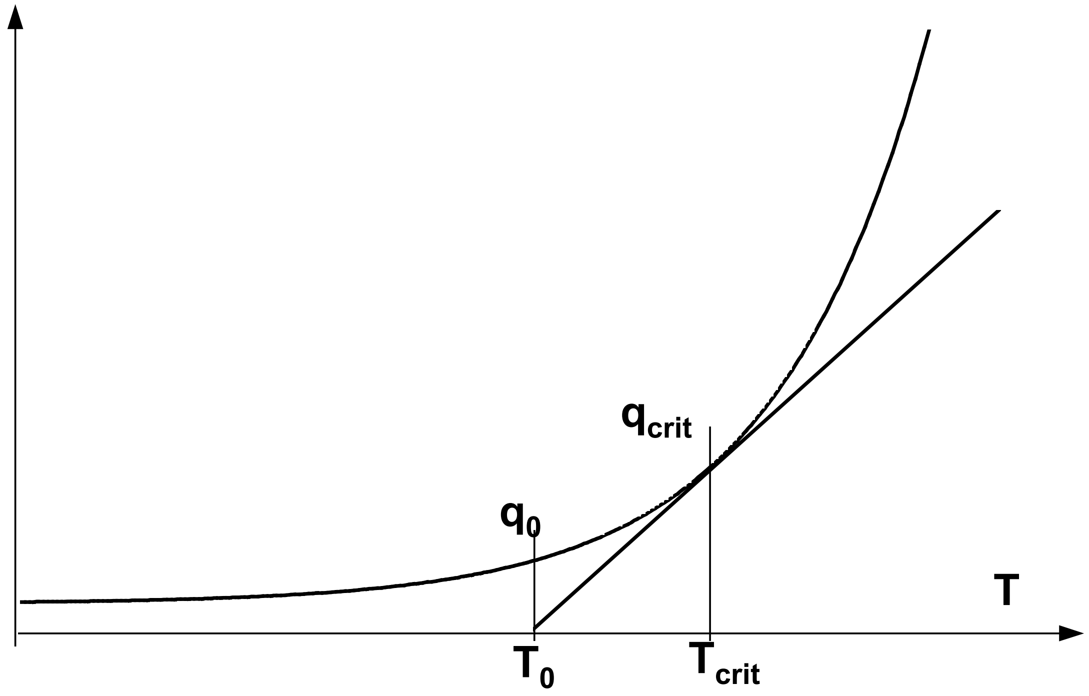
# Agitated System

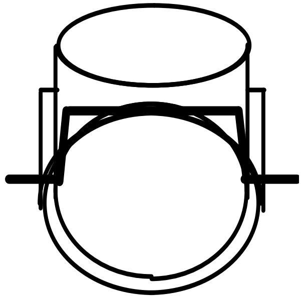
- Semenov

$$TMR_{ad} > 3.92 \cdot t_{1/2}$$

$$\tau = \frac{\rho \cdot V \cdot c'_p}{U \cdot A}$$ Thermal time constant

$$t_{1/2} = \ln(2) \cdot \tau$$ Thermal half-life



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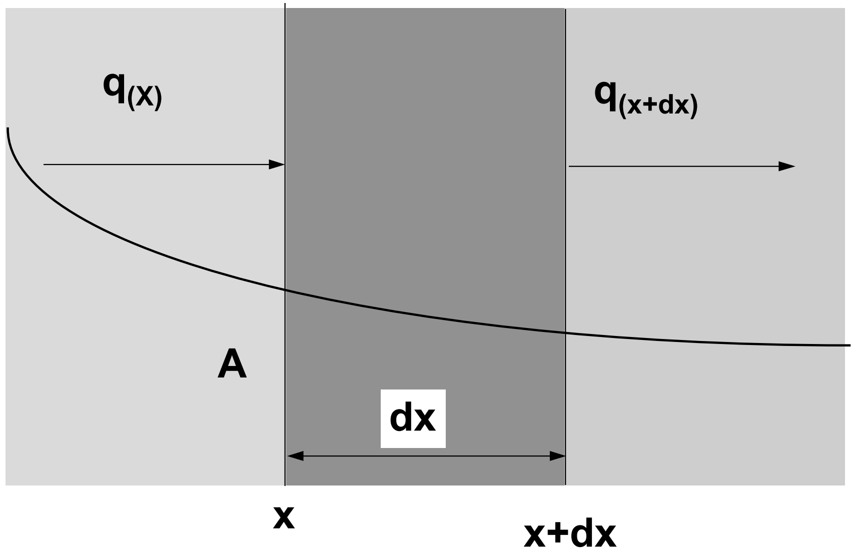
# Heat Conduction in a Solid



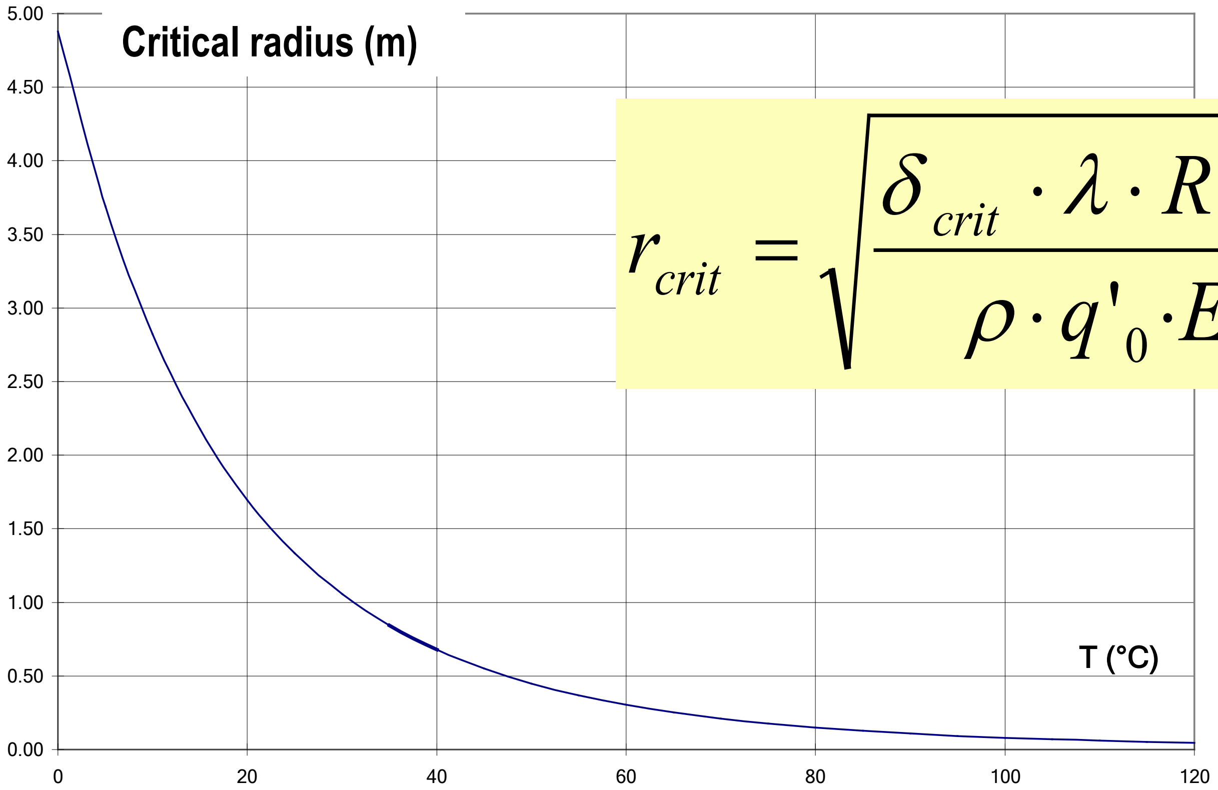

$$\vec{q} = -\lambda \vec{\nabla} T$$

Thermal conductivity: $\lambda$ [W/(K·m)]

$$\frac{\partial^2 T}{\partial x^2} = \frac{\rho \cdot c_p'}{\lambda} \frac{\partial T}{\partial t} = \frac{1}{a} \frac{\partial T}{\partial t}$$

Thermal diffusivity: a [$m^2$/s] $$a = \frac{\lambda}{\rho \cdot c_p'} = \frac{\text{heat conducted}}{\text{heat stored}}$$

# Critical Radius




$$r_{crit} = \sqrt{\frac{\delta_{crit} \cdot \lambda \cdot R T_0^{\ 2}}{\rho \cdot q'_0 \cdot E}}$$

# Form Factor Frank-Kamenetskii criterion

- Slab $\delta_{crit}$ = 0.88 $r_{crit}$: half of thickness of the slab
- Infinite Cylinder $\delta_{crit}$ = 2.0 $r_{crit}$: radius of the cylinder
- Sphere $\delta_{crit}$ = 3.32 $r_{crit}$: radius of the sphere

- Cylinder h = 3 r $\delta_{crit}$ = 2.37 $r_{crit}$: radius of the cylinder
- Cube $\delta_{crit}$ = 2.5 $r_{crit}$: half of side length

# Conduction in solid and transfer at wall

## Thomas Model

$$\frac{\partial^2 T}{\partial x^2} = \frac{1}{a}\frac{\partial T}{\partial t}$$

$$z = \frac{x}{r_0} \quad \text{and} \quad \theta = \frac{\mathrm{E}\left(\mathrm{T}-\mathrm{T}_0\right)}{RT_0^{\;2}}$$

Wall

$$\lambda \frac{dT}{dx} + h\cdot\left(T_s - T_0\right) = 0 \quad \text{à } x = r_0$$

$$\frac{d\theta}{dz} + Bi\cdot\theta_S = 0 \quad \text{at} \quad z = 1$$

Center

$$\frac{dT}{dx} = 0 \quad \text{à} \quad x = 0$$

$$Bi = \frac{h\cdot r_0}{\lambda}$$

Biot number

Variable exchange

# Conduction in solid and transfer at wall

Zero order reaction

$$\nabla_z^{\,2}\theta = \frac{d^2\theta}{dz^2} + \frac{k}{z}\frac{d\theta}{dz} = \frac{d\theta}{d\tau} - \delta \exp\theta$$

$$\tau = \frac{at}{r_0^{\,2}} \qquad a = \frac{\lambda}{\rho \cdot Cp'}$$

Reaction characteristics

$$\delta = \frac{\rho_0 \cdot q'_0}{\lambda} \cdot \frac{E}{RT_0^{\,2}} \cdot r_0^{\,2}$$

Heat transfer

$$\delta_{crit} = \frac{1+k}{e \cdot \left(\frac{1}{\beta_\infty} - \frac{1}{Bi}\right)}$$

$\beta_\infty$ is called the effective Biot number

k: shape coefficient

| | | |
|---|---|---|
| Slab: | $k = 0$ | $\beta_\infty = 2.39$ |
| Cylinder: | $k = 1$ | $\beta_\infty = 2.72$ |
| Sphere: | $k = 2$ | $\beta_\infty = 3.01$ |

$$Bi = \frac{h \cdot r_0}{\lambda}$$

$\delta_{crit}$ from Thomas model ≠ $\delta_{crit}$ from Frank-Kamenetskii model

# Conduction in solid and transfer at wall

**Reaction characteristics**

$$\delta = \frac{\rho_0 \cdot q'_0}{\lambda} \cdot \frac{E}{RT_0^{\,2}} \cdot r_0^{\,2}$$

↔

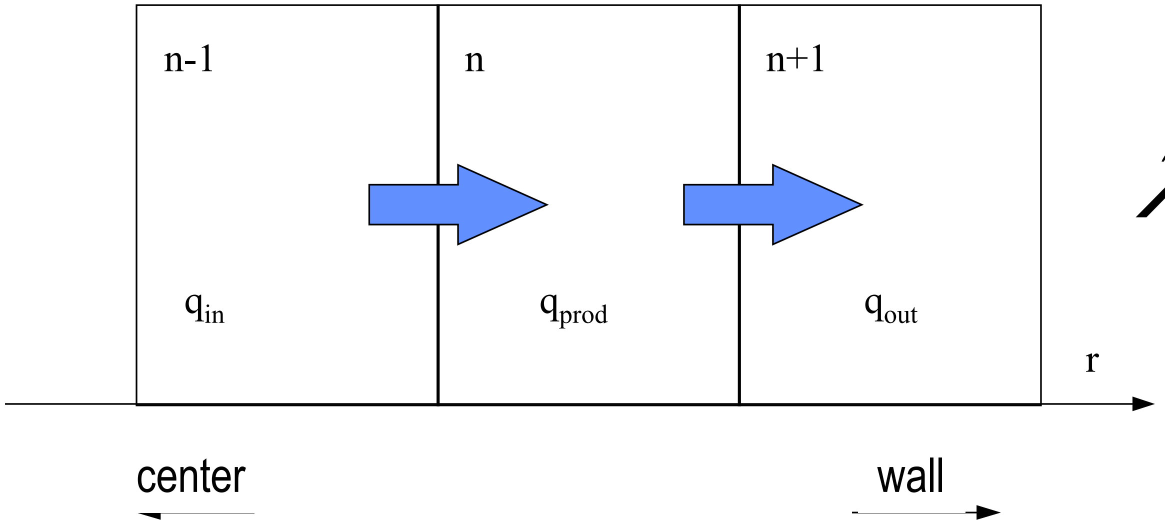
**Heat transfer**

$$\delta_{crit} = \frac{1+k}{e \cdot \left( \frac{1}{\beta_\infty} - \frac{1}{Bi} \right)}$$

- $\delta > \delta_{crit}$ → Temperature situation is unstable → runaway
- $\delta < \delta_{crit}$ → Temperature situation is stable

- Can search iteratively for the highest T

# Finite elements




$$\lambda \frac{\partial^2 T}{\partial x^2} = q_{rx}$$

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# Natural Convection

$$Nu = C^{te} \cdot Ra^{m}$$

with: $Nu = \dfrac{hL}{\lambda}$

and: $Ra = \dfrac{g \cdot \beta \cdot L^3 \cdot \rho^2 \cdot Cp' \cdot \Delta T}{\mu \cdot \lambda} = Gr \cdot \Pr$

Turbulent flow : $Ra > 10^9$ — $Nu = 0{,}13\ Ra^{1/3}$

Intermediate flow : $10^4 < Ra < 10^9$ — $Nu = 0{,}59\ Ra^{1/4}$

Laminar flow : $Ra < 10^4$ — $Nu = 1{,}36\ Ra^{1/6}$

Turbulent flow: likely to have natural convection.

Otherwise, safe not rely on natural convection

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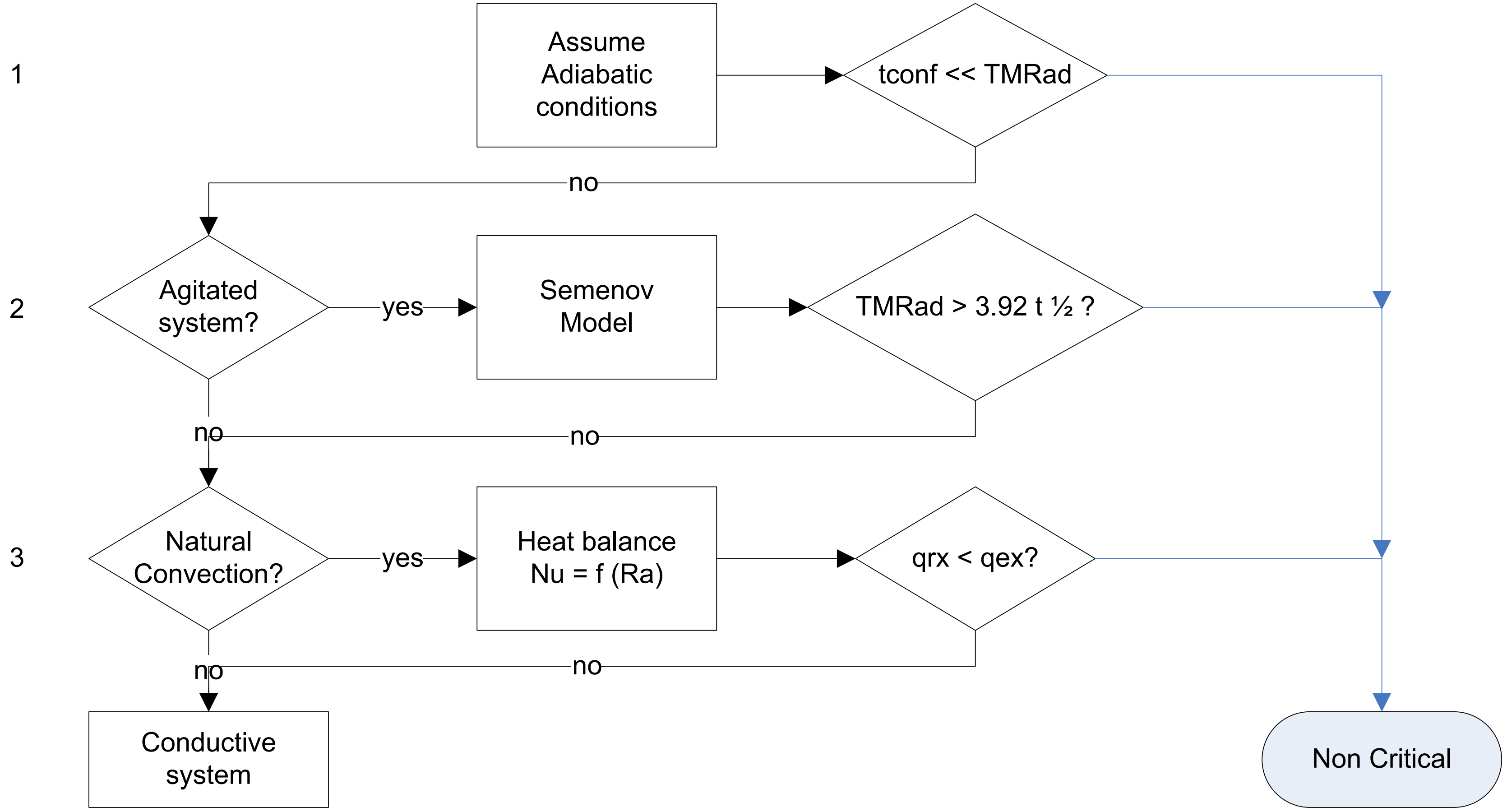
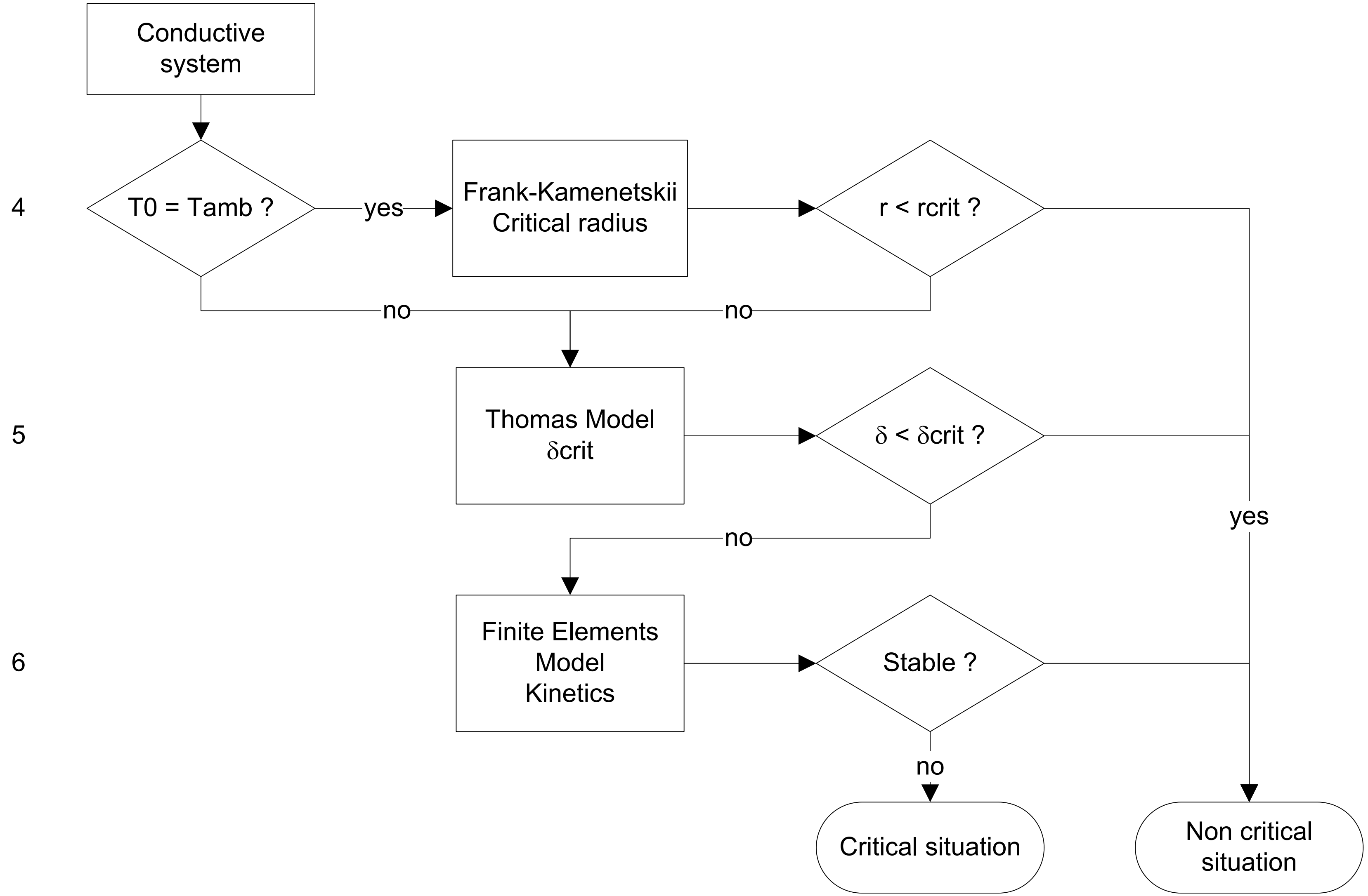
# Decision tree (Part 1)



# Decision tree (Part 2)



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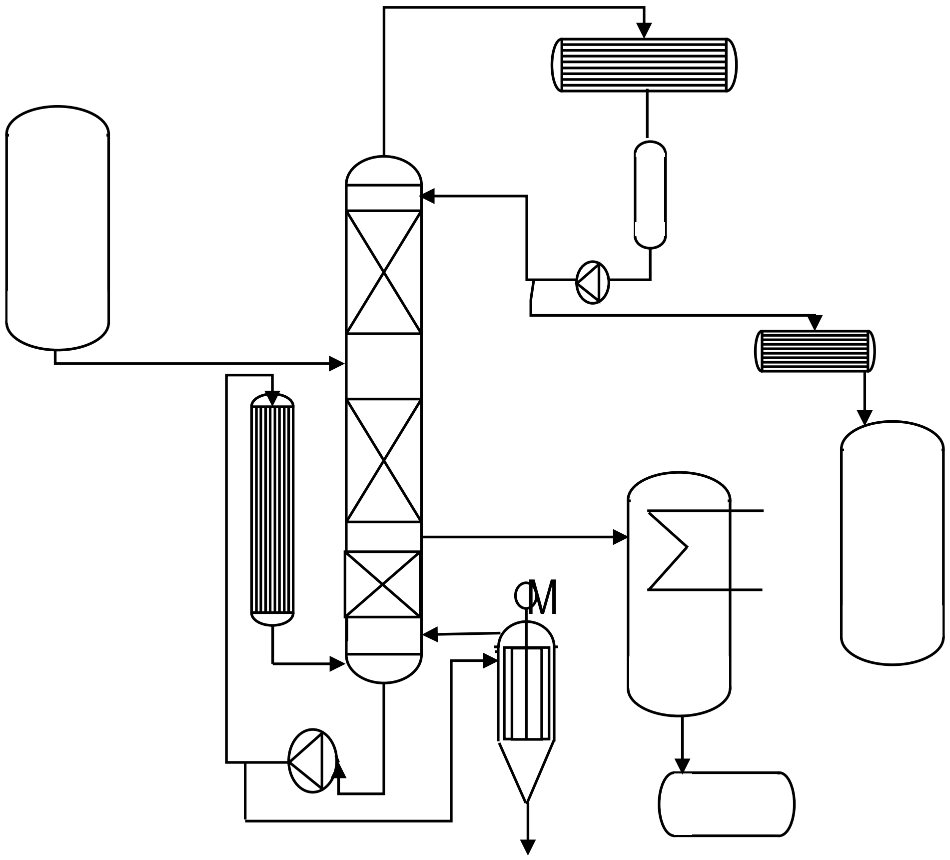
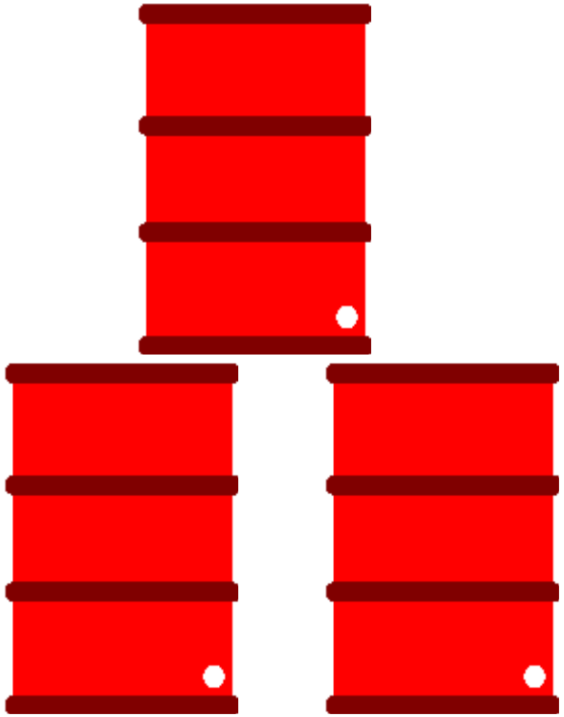
# Where may Heat Accumulation Occur ?




*Equipment:*

- Distillation residue
- Isolated equipment
- Continous processes at shut down

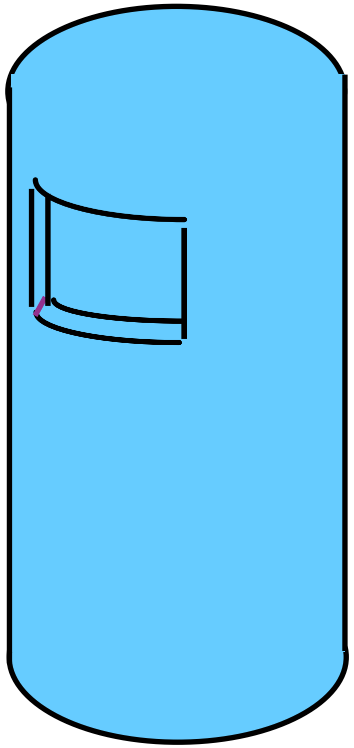
# Where may Heat Accumulation Occur ?



- Storage
- Hot discharge
- Discharge after thermal stress (Drying, Milling, Blending, Formulation)

**Monitor Temperature at Center !**

# Where may Heat Accumulation Occur ?

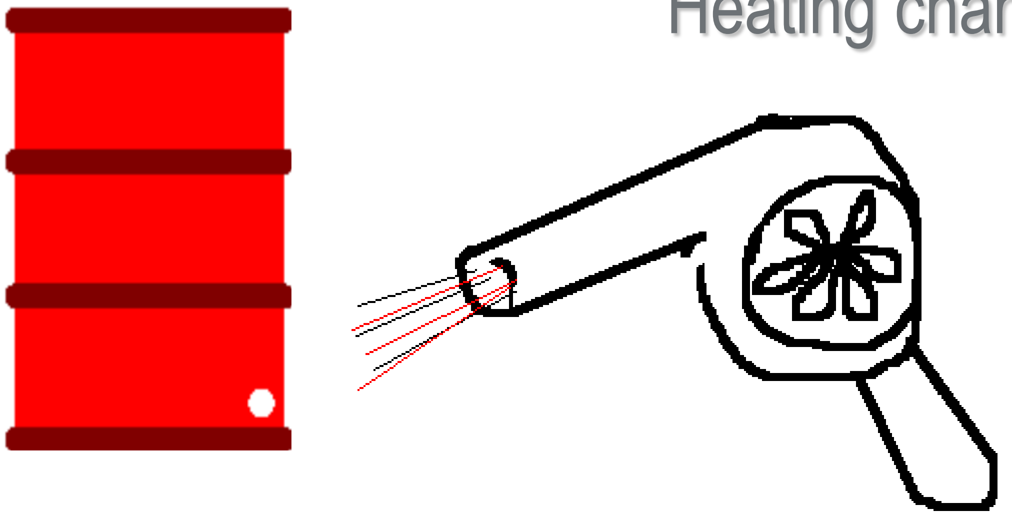


- Tanks with reactive contents
- Insulated storage tanks
- Changes in thermal insulation

Monitor Temperatur at center !

# Where may Heat Accumulation Occur ?

Melting in hot air
Heating chamber



Monitor Temperature at Center of bulk !

# Where may Heat Accumulation Occur ?





Transport


TCVU 791 031 4

VAN HOOL
TCVU 791 031 4

# Example of an exercise

- Intermediate storage of a solid in $1 m^3$ container (IBC) at either 10°C or 30°C
- Stability of the product: Left limit of decomposition peak in DSC is at 125°C and decomposition energy is 500 J/g
- Bulk density is 500 $kg/m^3$; specific heat capacity is 1.3 kJ/(kg·K) thermal conductivity of the solid is 0.25 W/(m·K)

- Is storage possible for 1 day, 1 week, 1 month, 1 year?

- How does the assessment change if the storage situation is as shown on the picture