Heat Confinement

Module 4
ENG 431: Safety Chemical Processes

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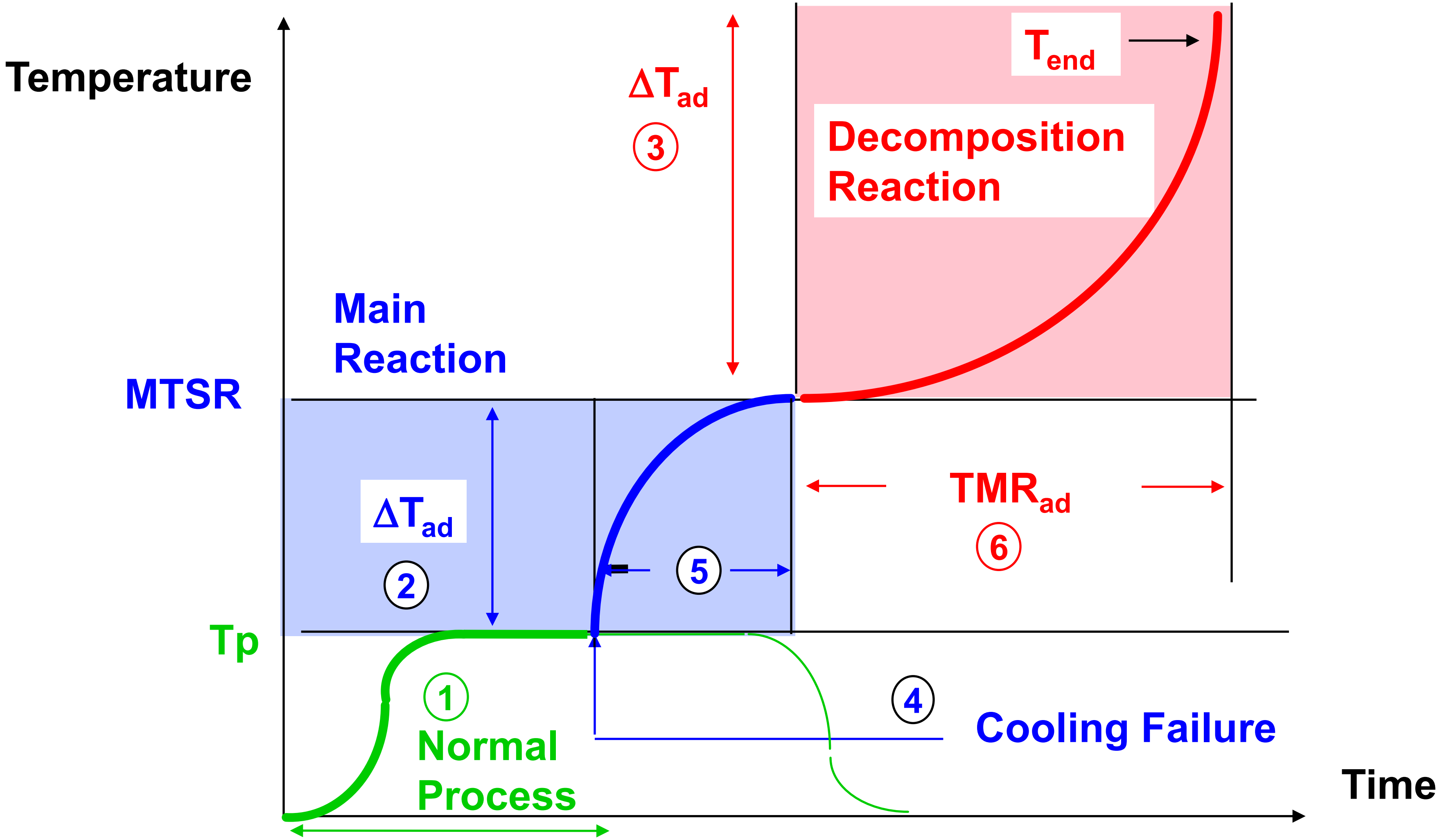
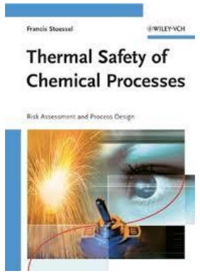
Cooling Failure Scenario

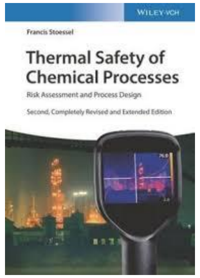


Heat Accumulation

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

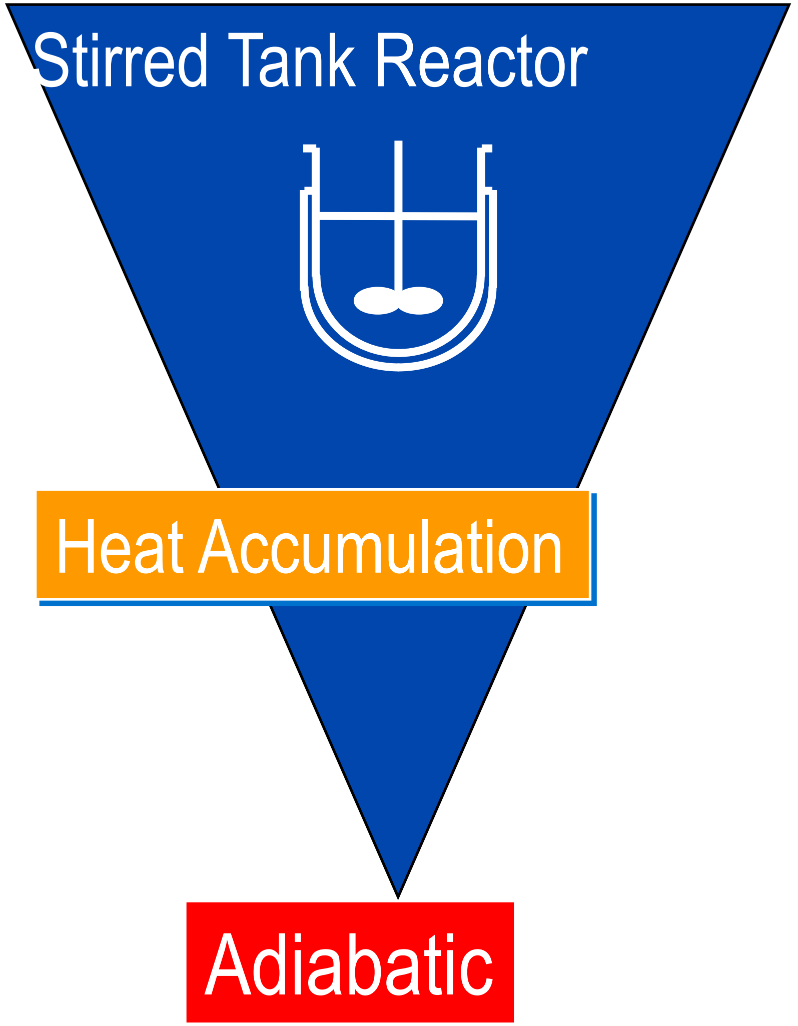


Chapter 13



Chapter 12

How realistic are adiabatic conditions?



Heat accumulation

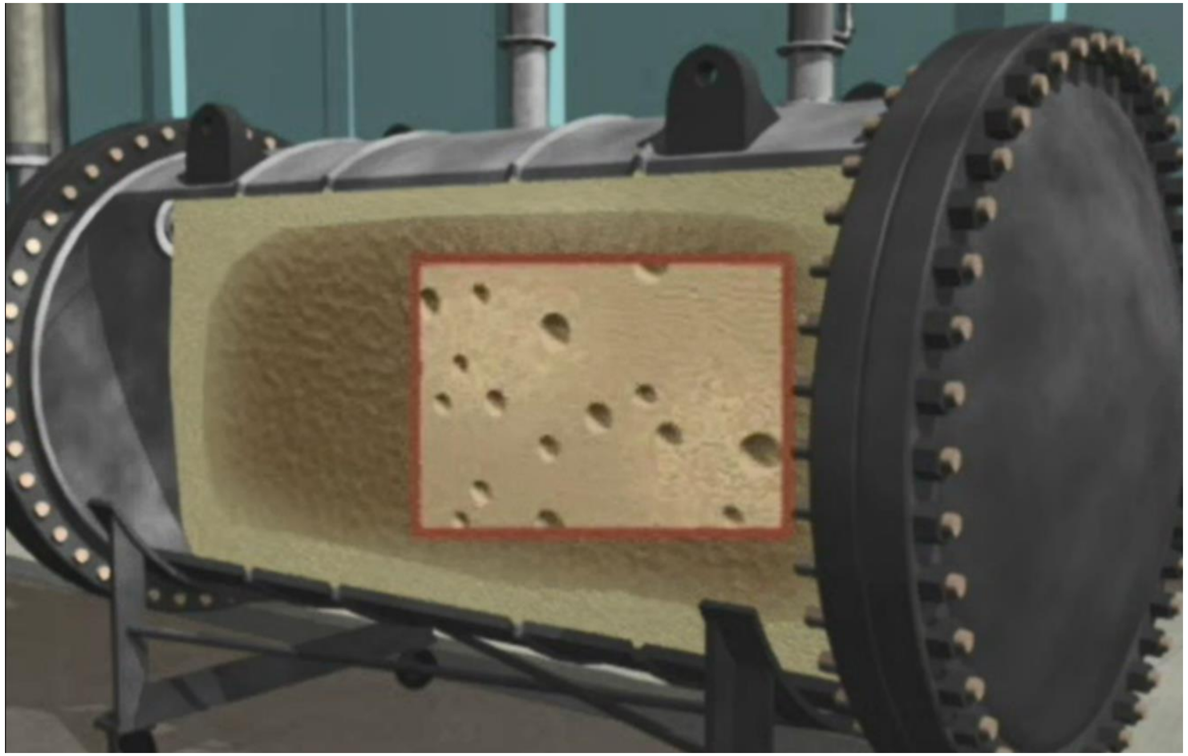
Heat accumulation situations: effect of mass

- Decomposition of a reaction mass. ΔTad 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 in Industrial Context

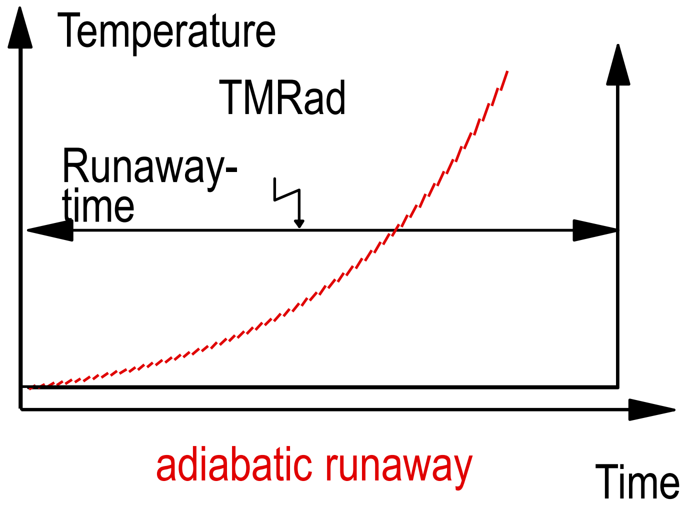
- Hot discharge
- Heating chambers
- Storage
- Transport
- Inadvertent shut down
- Heated pipes



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

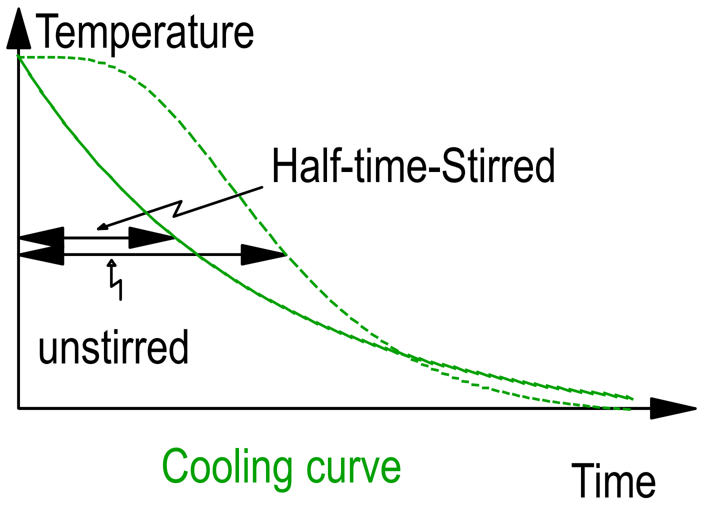
Heat balance using time scales

Heat production



adiabatic runaway

Heat removal



Cooling curve

Thermal Explosion if: Heat production > Heat removal

Adiabatic Runaway-time < Cooling time

Heat Accumulation

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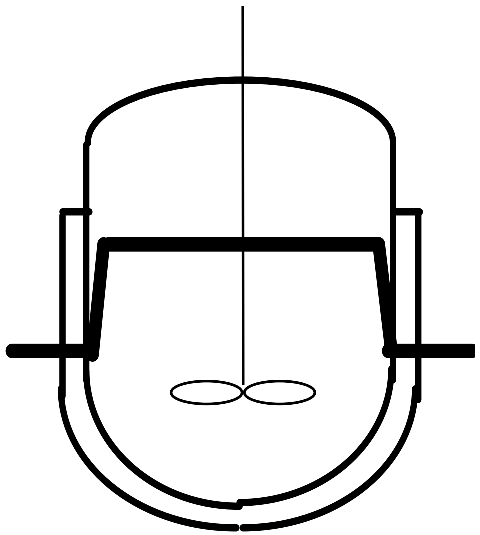
Agitated System

- Semenov
- Newtonian cooling

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



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

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

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

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

Heat balance

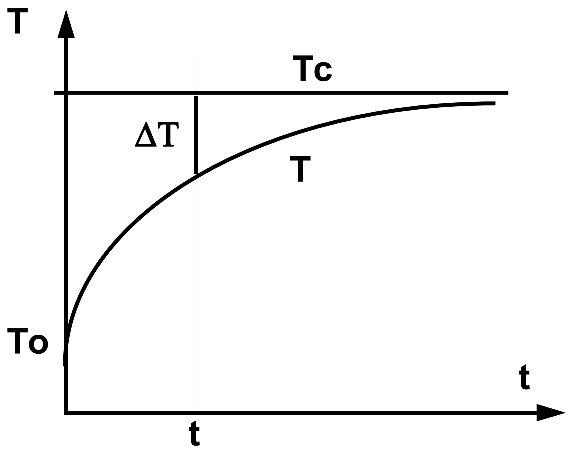
$$M \cdot c_p' \cdot \frac{dT}{dt} = -U \cdot A \cdot \left(T - T_C\right)$$

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

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

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

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



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

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

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

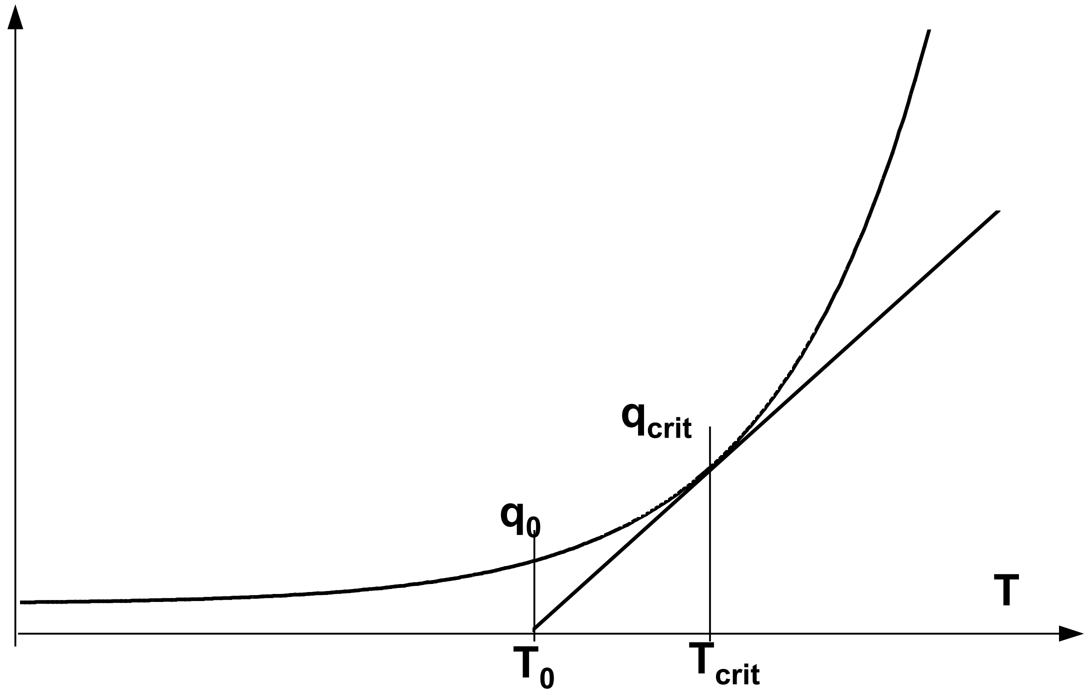
Agitated System

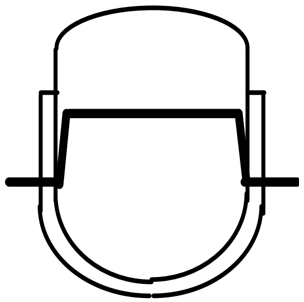
- Semenov

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

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

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





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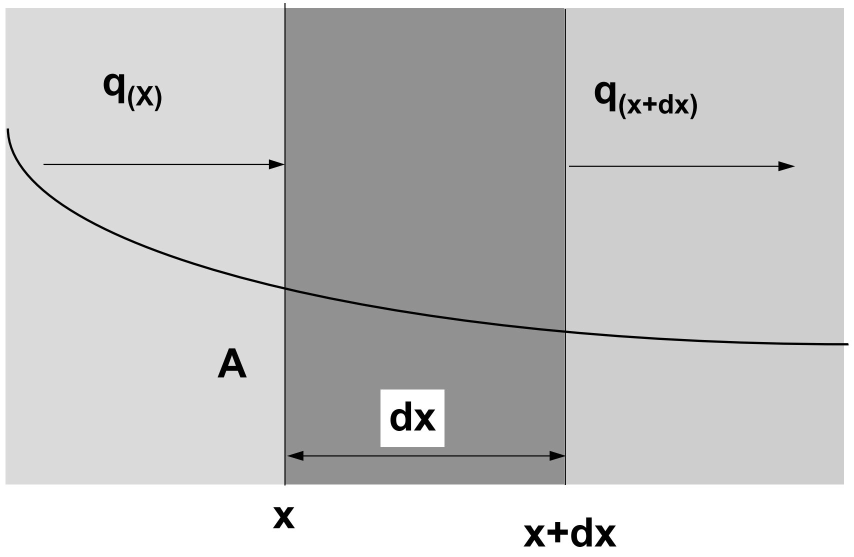
Heat Conduction in a Solid



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

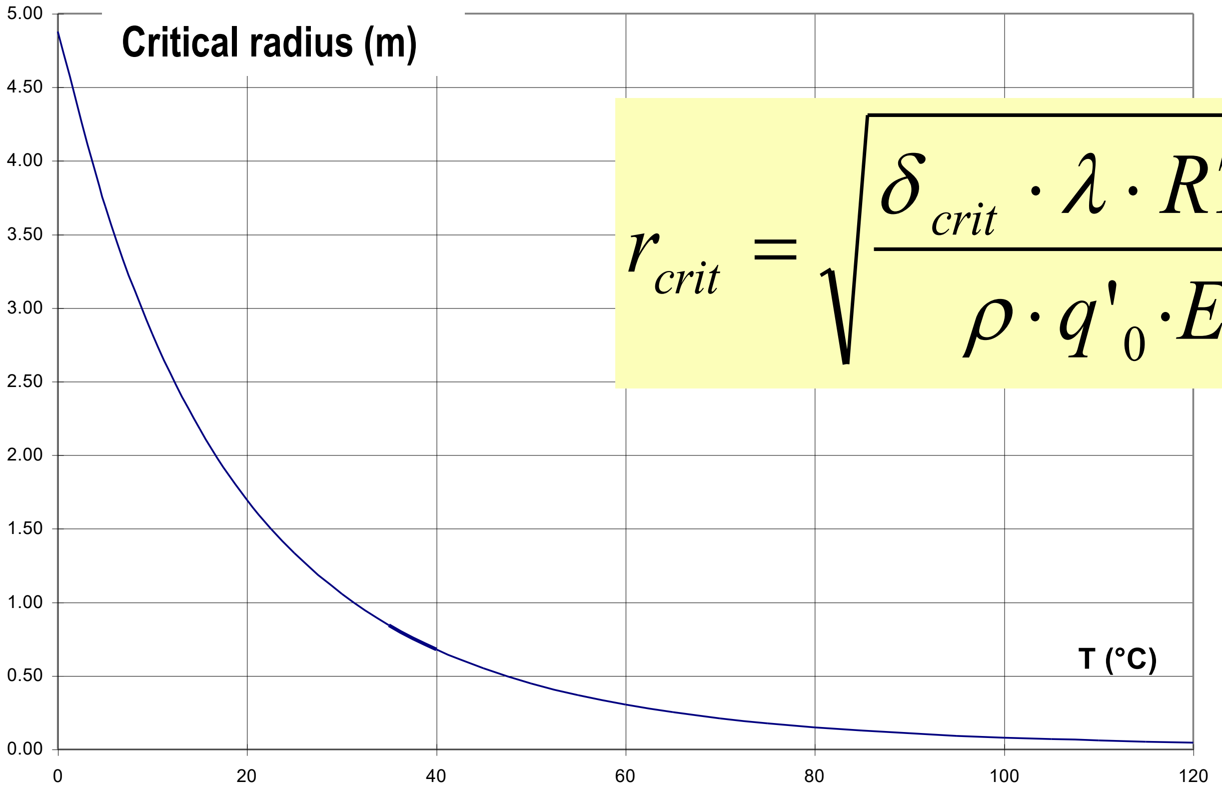
Thermal conductivity: λ [W/(K·m)]

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

Thermal diffusivity: a [m^2/s]

$$a = \frac{\lambda}{\rho \cdot c'_p} = \frac{\text{heat conducted}}{\text{heat stored}}$$

Critical Radius



$$r_{crit} = \sqrt{\frac{\delta_{crit} \cdot \lambda \cdot RT_0^{\;2}}{\rho \cdot q'_0 \cdot E}}$$

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

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

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

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

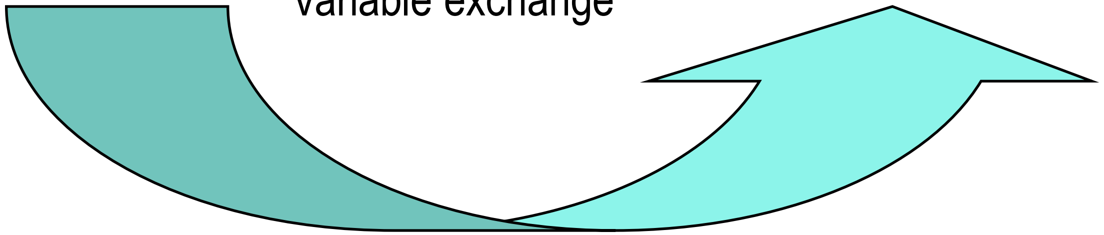
$$\frac{d\theta}{dz} + Bi \cdot \theta_S = 0 \quad \text{at} \quad z = 1$$

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

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

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

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

β_∞ is called the effective Biot number

k: shape coefficient

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

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

δ_{crit} from Thomas model ≠ δ_{crit} from Frank-Kamenetskii model

Conduction in solid and transfer at wall

Reaction characteristics

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

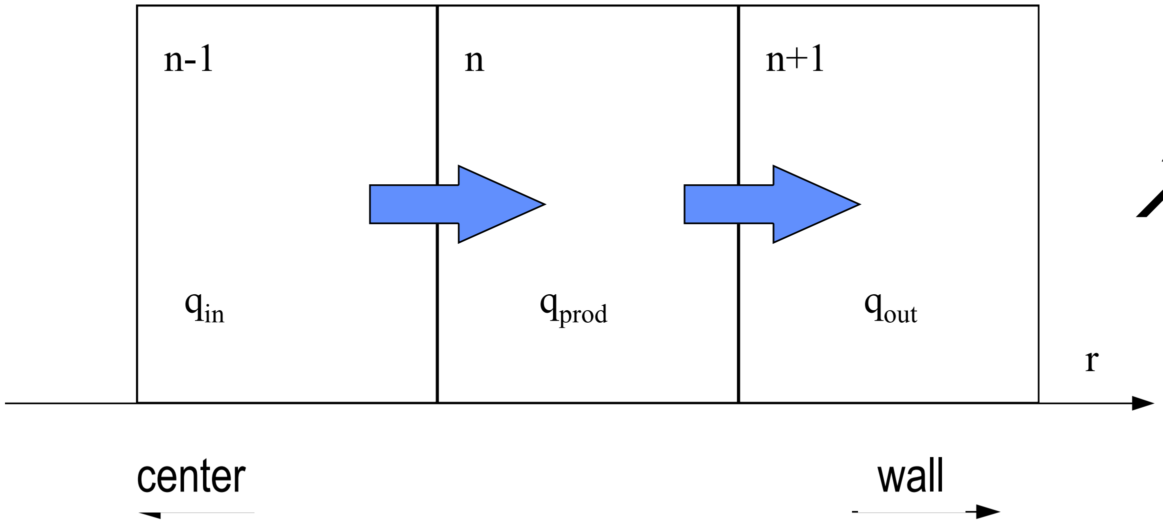
Heat transfer

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

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

- Can search iterativelly 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: $$Nu = \frac{hL}{\lambda}$$

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

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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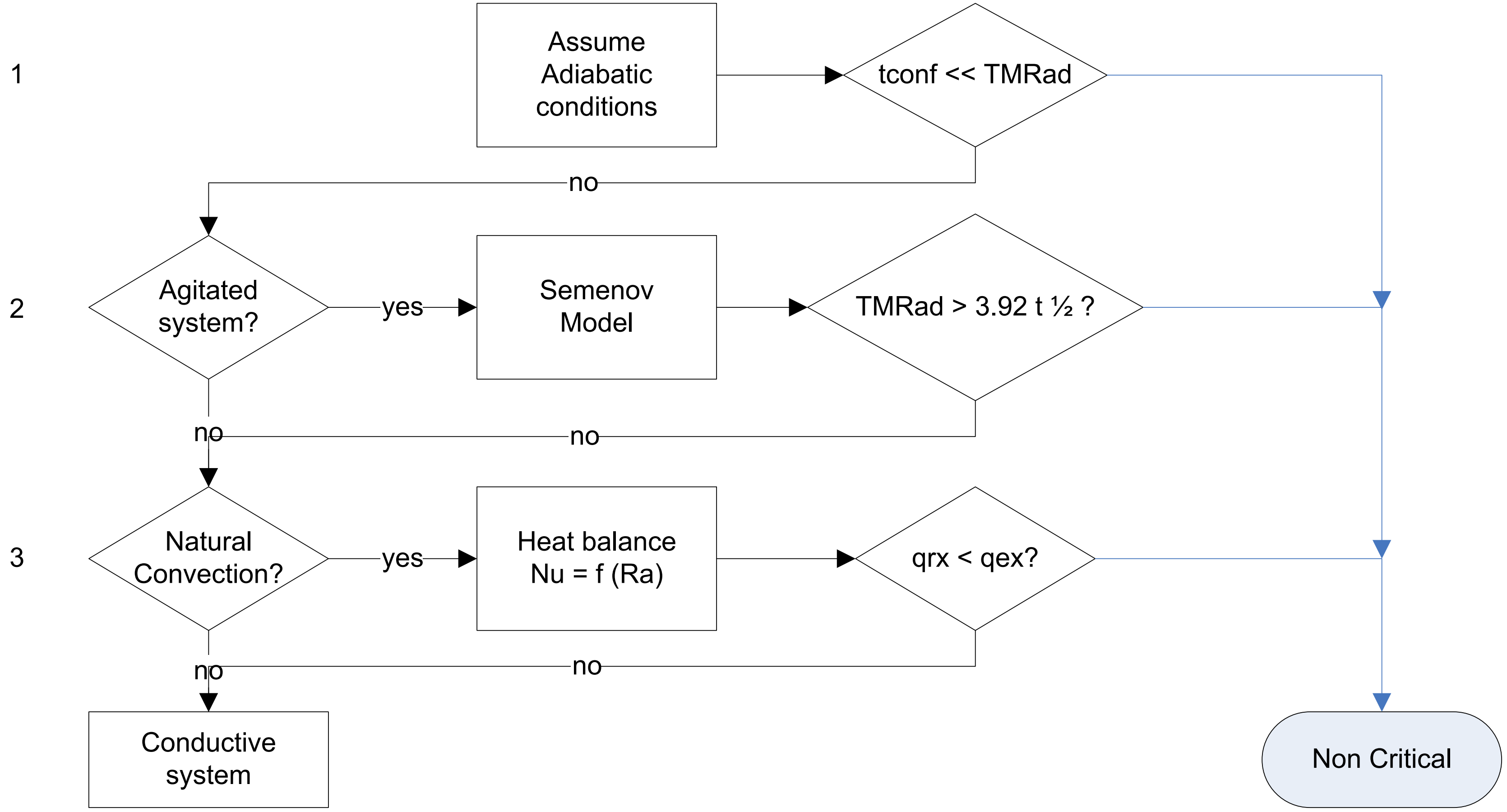
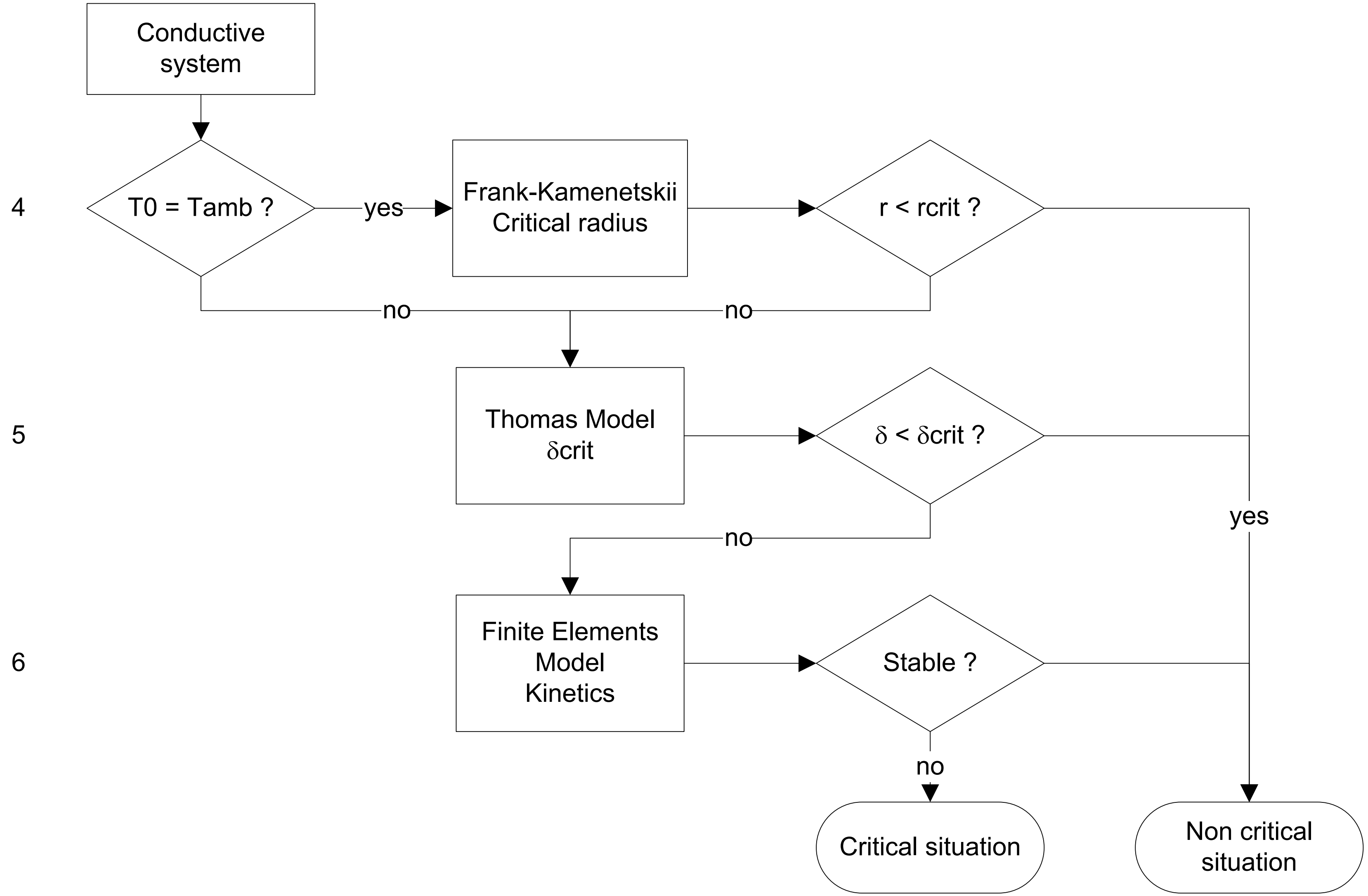
Decision tree (Part 1)



Decision tree (Part 2)



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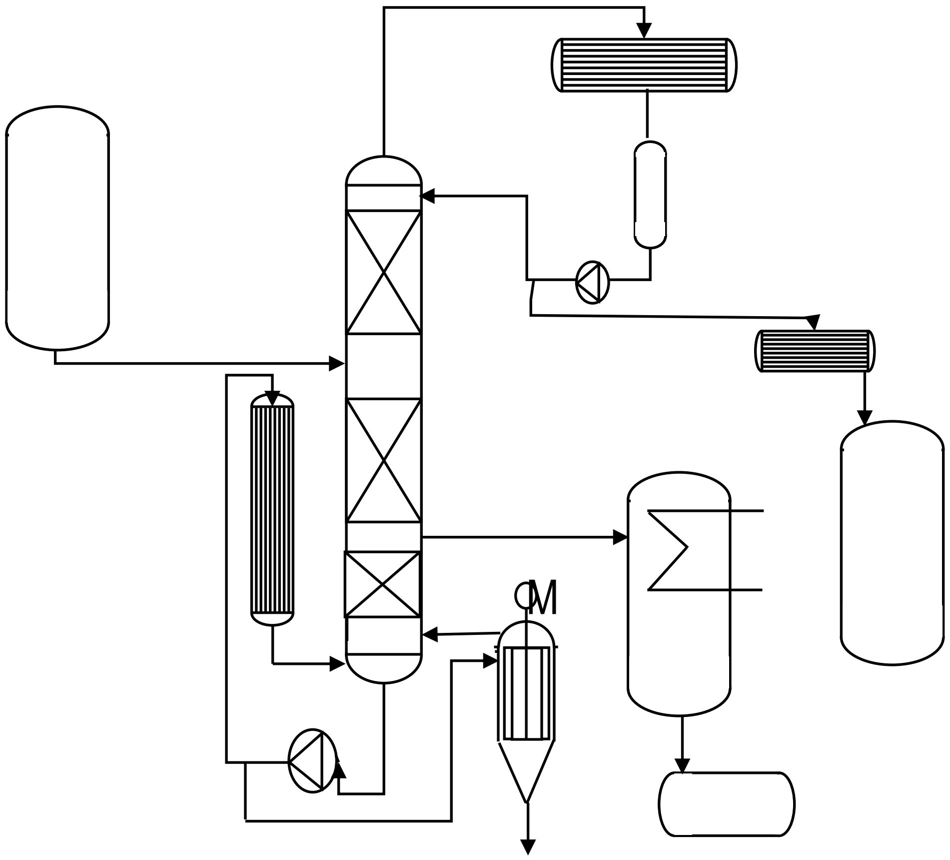
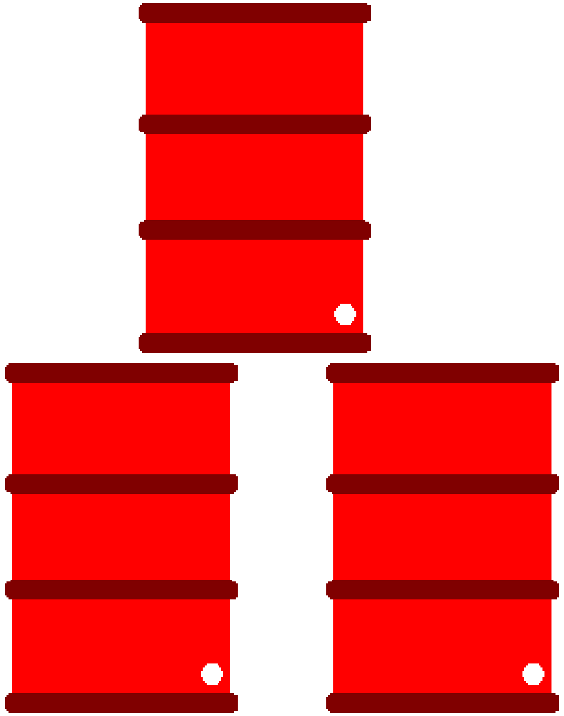
Where may Heat Accumulation Occur ?



Equipment:

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

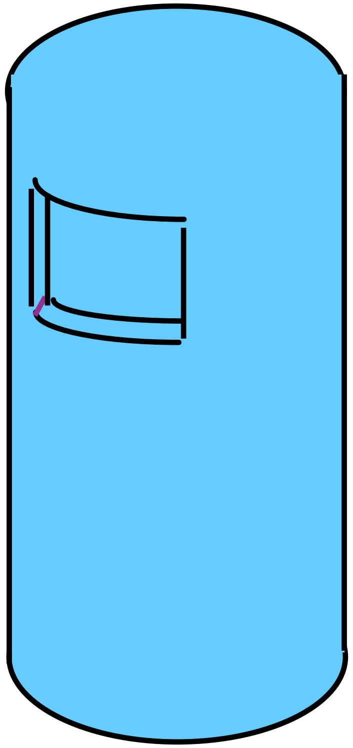
Where may Heat Accumulation Occur ?



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

Monitor Temperature at Center !

Where may Heat Accumulation Occur ?

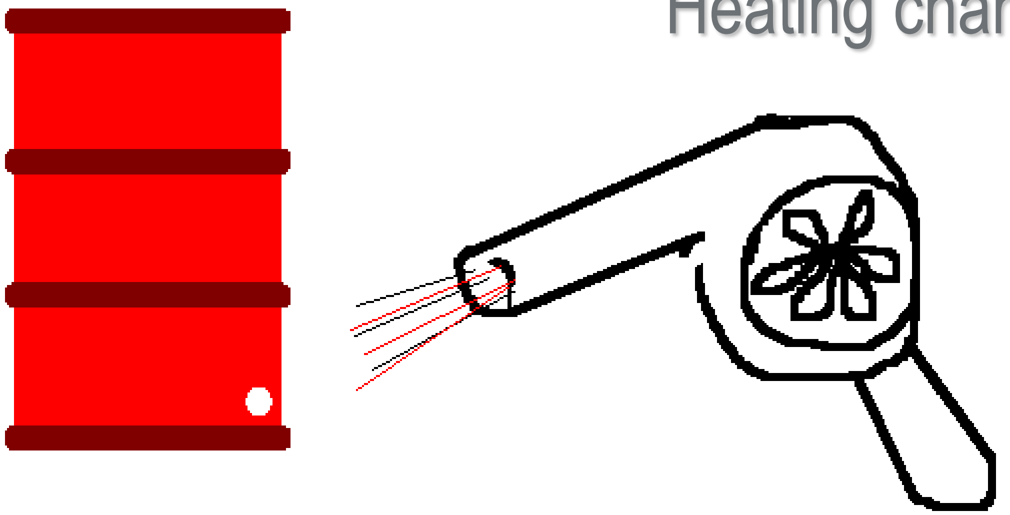


- Tanks with reactive contents
- Insulated storage tanks
- Changes in thermal insulation

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

Example of an exercise

- Intermediate storage of a solid in $1m^3$ 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