Criticality classes and risk reduction

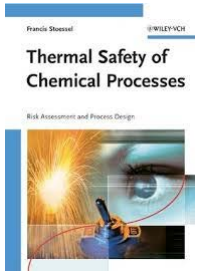
Module 6

ENG 431: Safety Chemical Processes

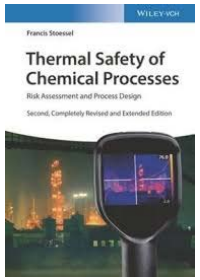
Annik Nanchen

Criticality classes and risk reduction

- Criticality classes
- Assessment of severity
- Assessment of controlability
- Examples: protection against runaway

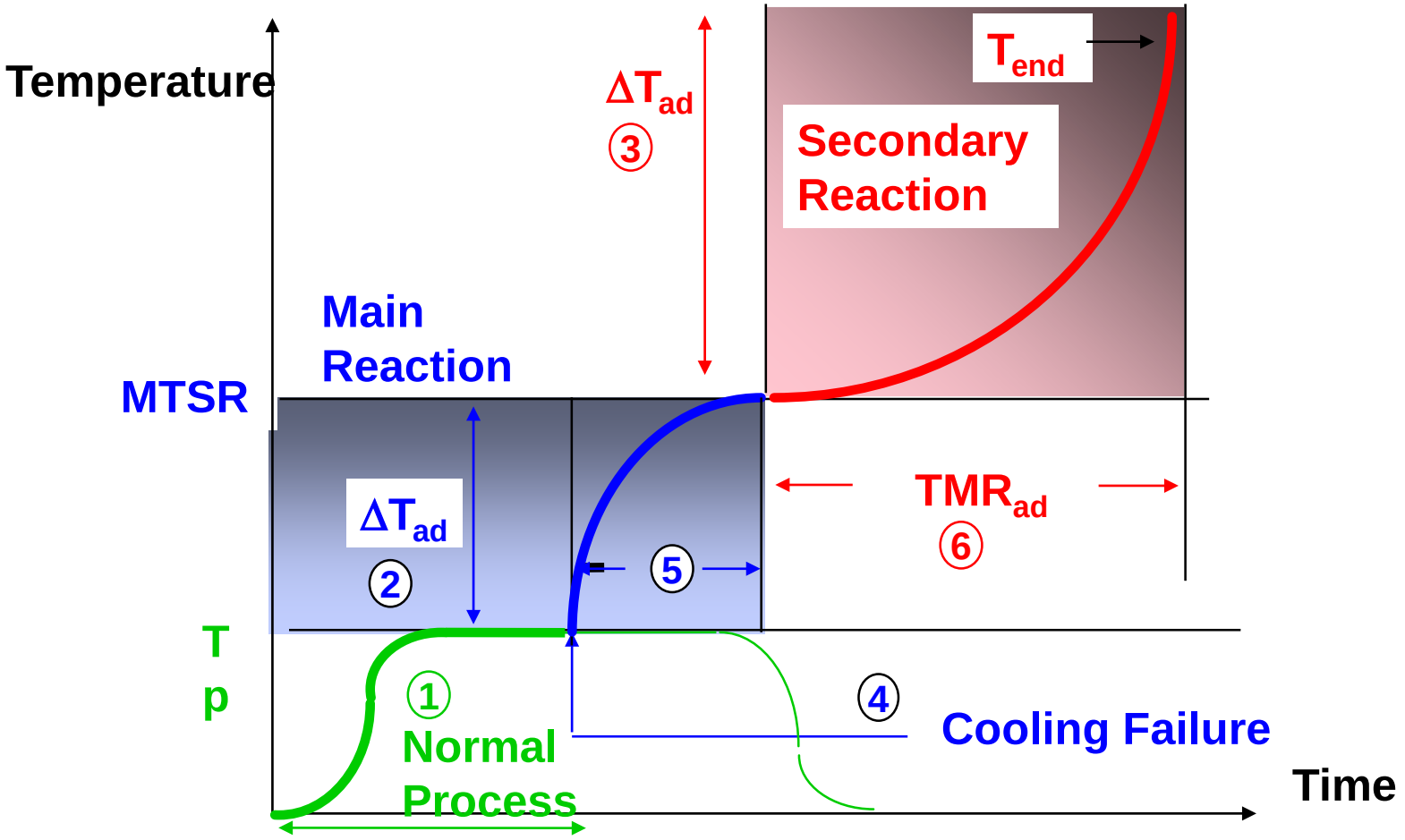


Chapter 10



Chapter 15

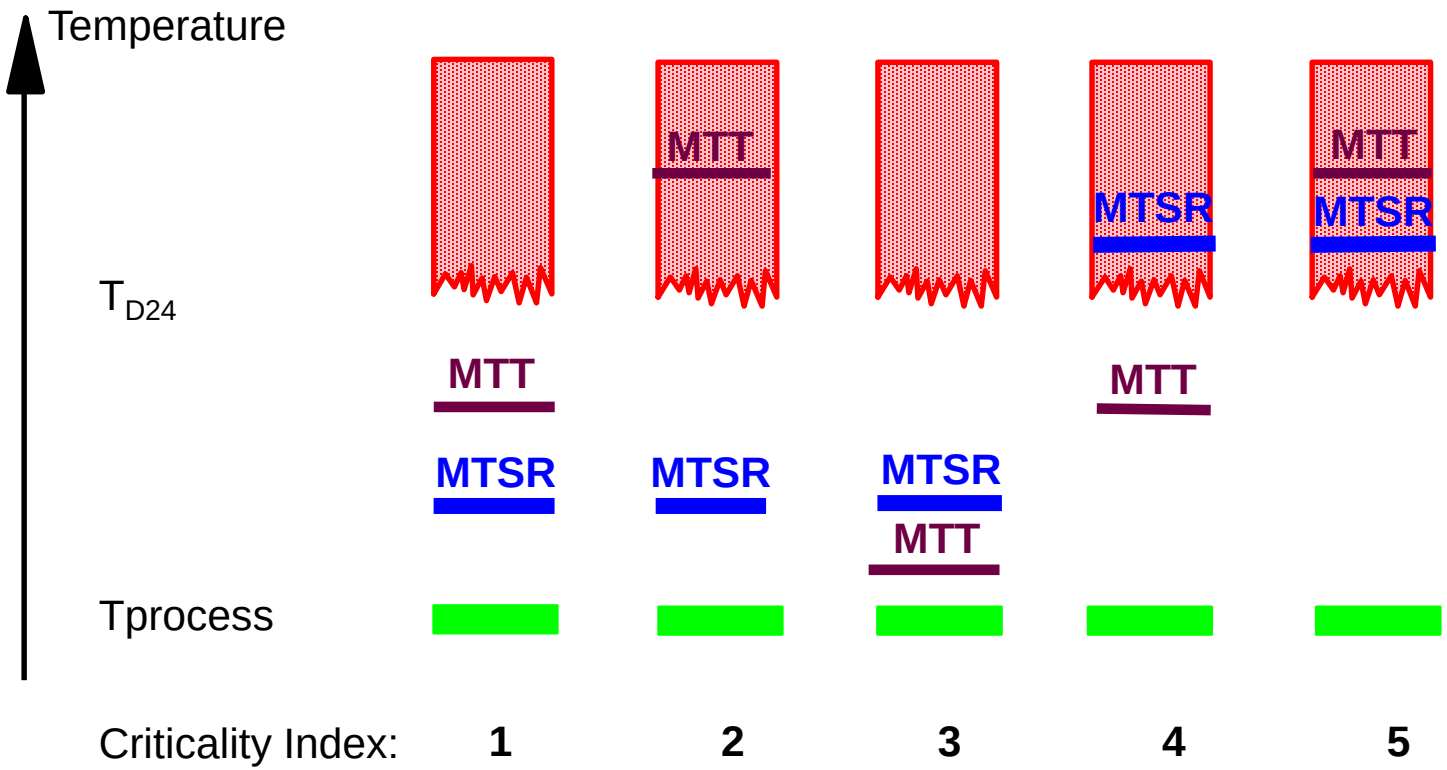
Cooling Failure Scenario



Characteristic Temperatures

- Tp : Process Temperature
  Defined by the mode of operation
- MTSR: Maximum Temperature of Synthesis Reaction
  Defined by the accumulation of reactants and Tp
- T_{D24}: Temperature at which the Decomposition becomes critical TMR_{ad} = 24 hrs
  Defined by the thermal stability of reaction mass
- MTT: Maximum Temperature for Technical Reasons
  Defined by the equipment

Classification of Scenarios



Principles

- Define the criticality class
  - For criticality class 3 and above (possible to do it also for class 1 and 2):

- Determine the energy potential
  - Criticality class 3: only desired reaction
  - Criticality class 4: desired and secondary reactions
  - Criticality class 5: desired and secondary reactions

- Assess the consequences of the resulting scenario
  - Severity using the energy to be released
  - Define appropriate risk reducing measures
  - Probability of loss of control

Criticality classes and risk reduction

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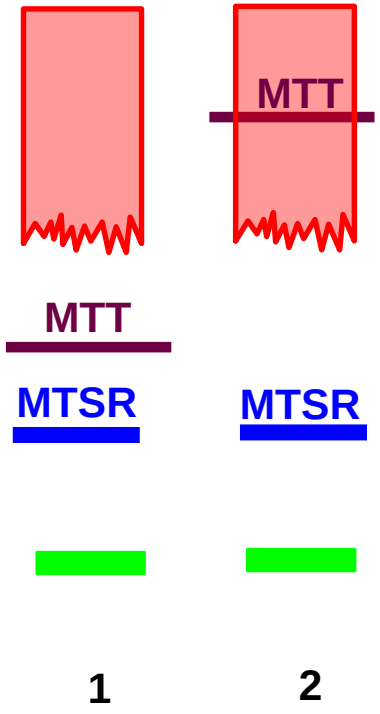
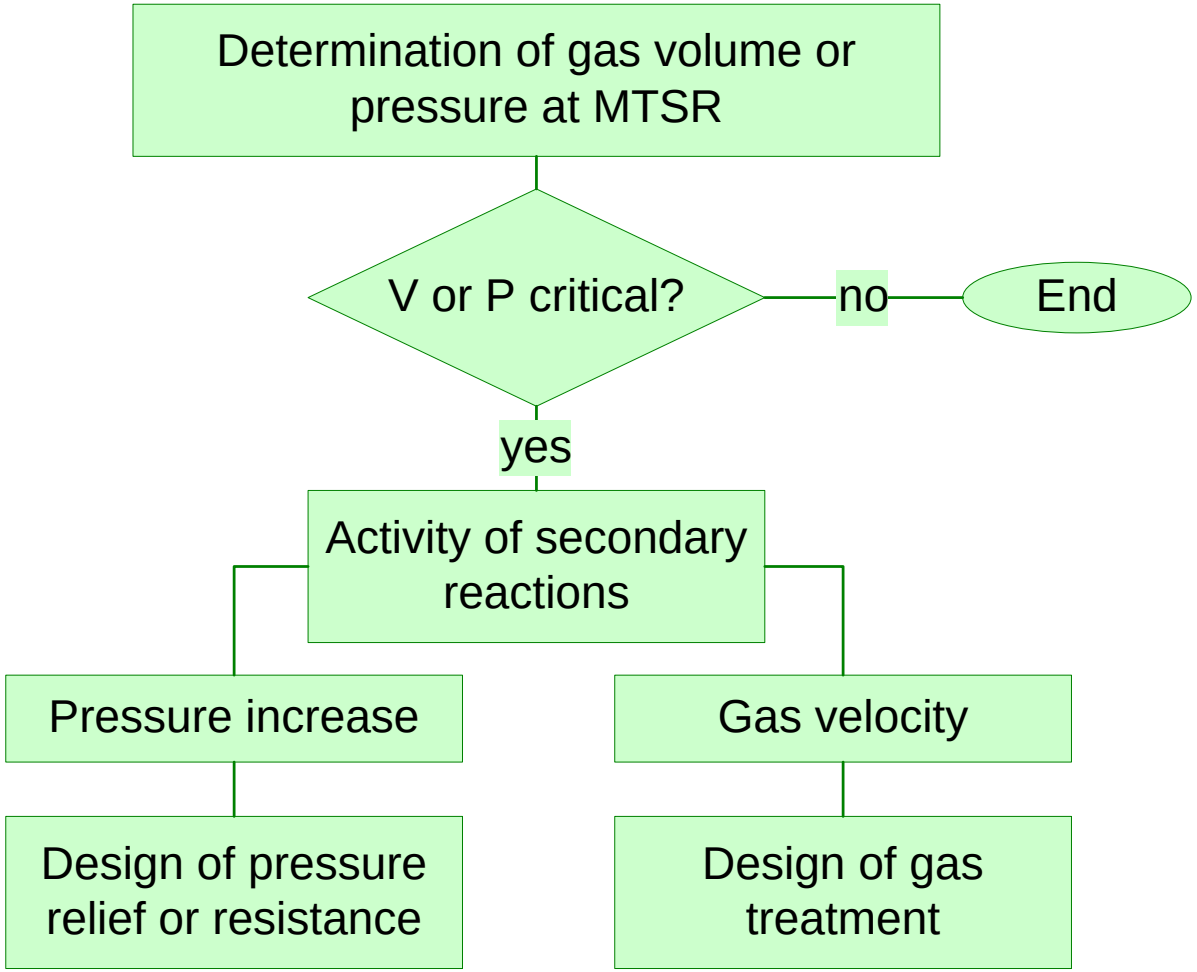
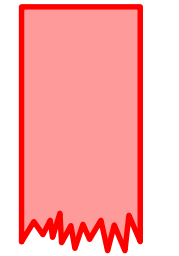
Criticality classes 1 & 2





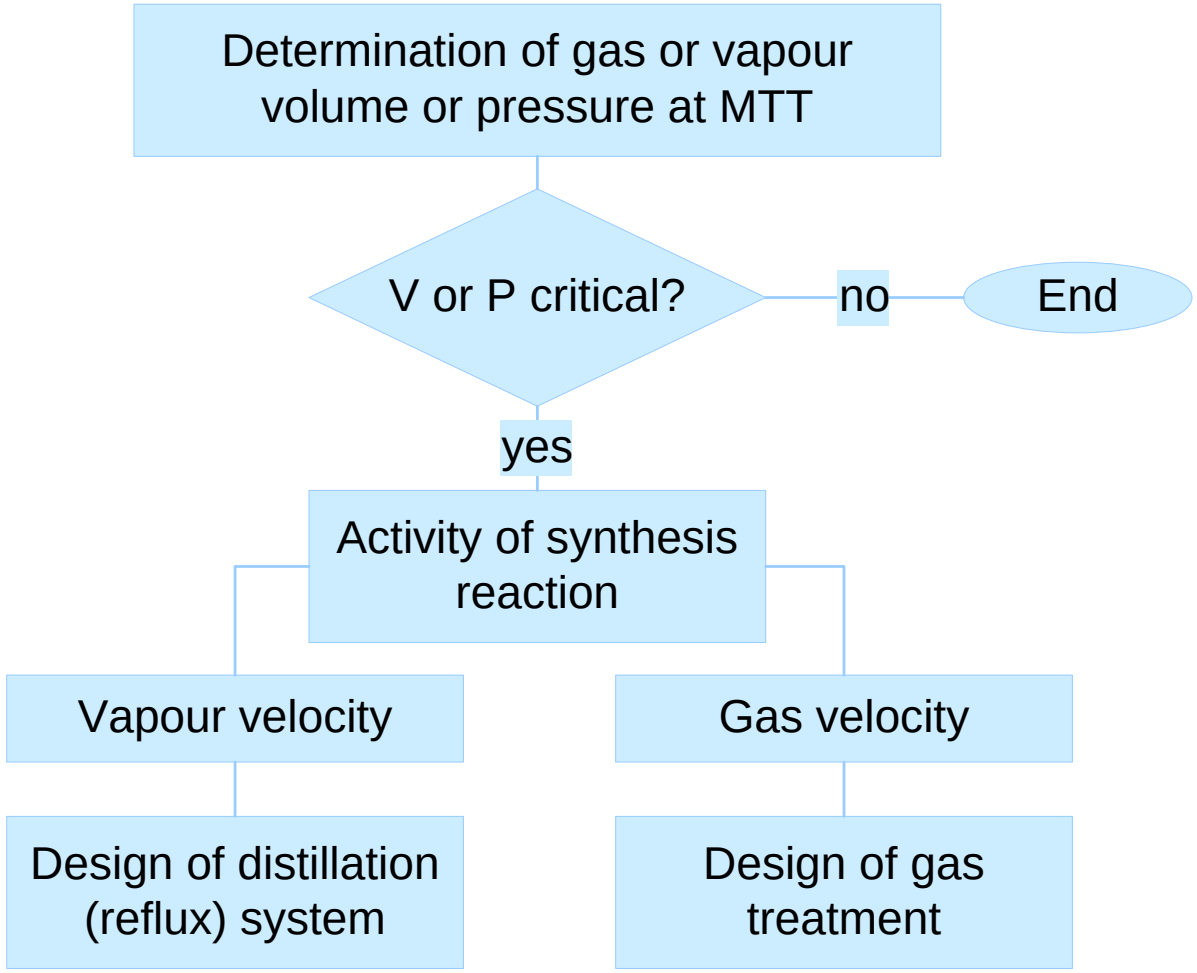
Criticality class 3



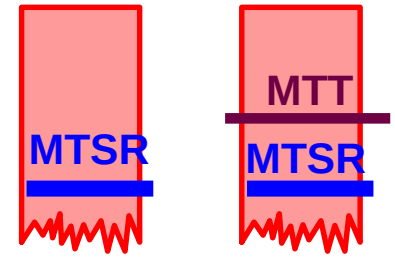
MTSR

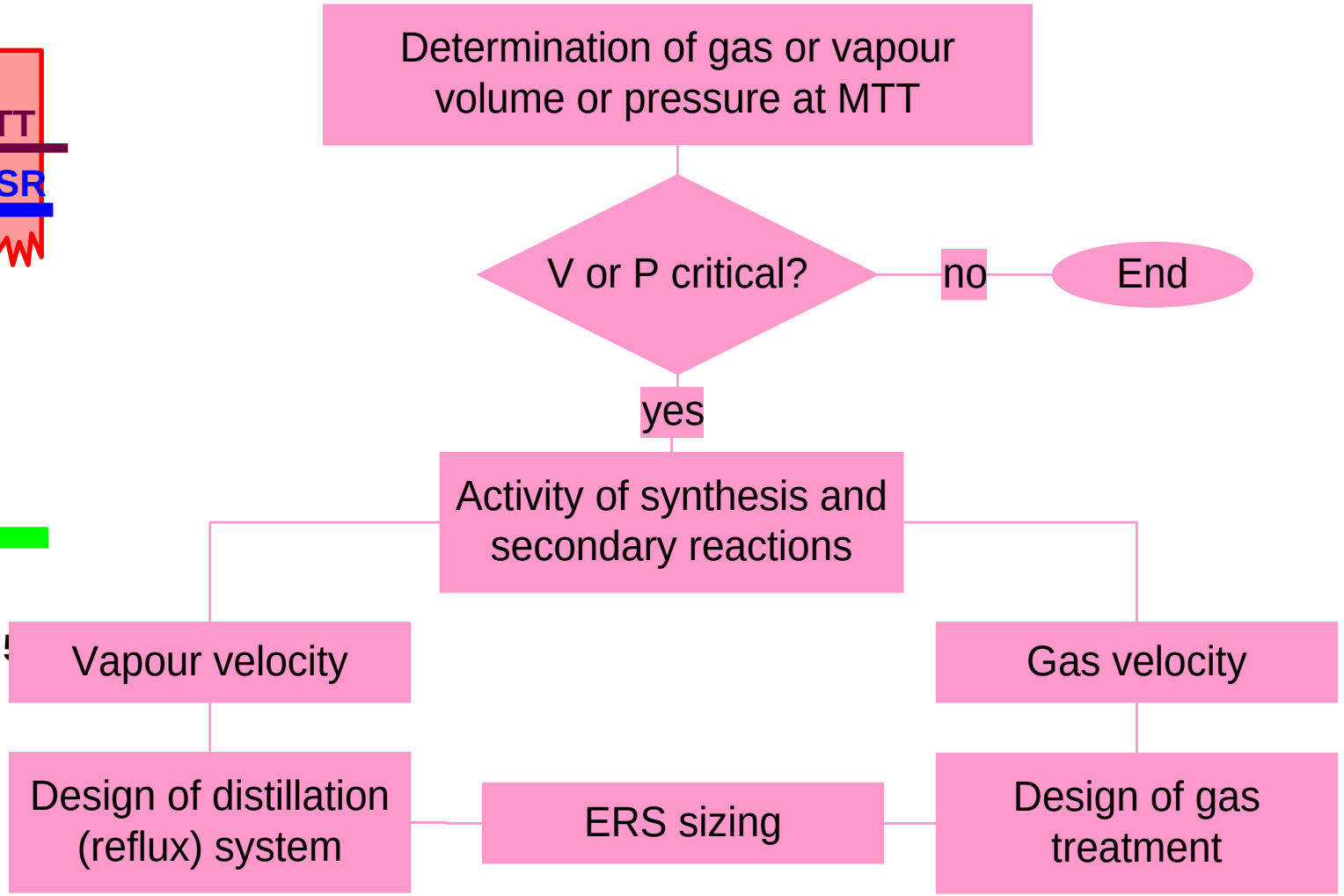
MTT

3



Criticality classes 4 & 5





Closed system: Pressure

- Gas pressure

$$P = P_0 + \frac{V_g}{V_{r,g}} \cdot (P_{mes})$$

Measurement e.g.
- Setaram C80
- Miniautoclave
- Radex
- RC

Void volume in equipment

P: Pressure bar

P_0: Initial pressure (pad gas in the installation) bar

V_g: Volume released in the installation m^3

$V_{r,g}$: Void volume in the installation m^3

P_{mes}: Measured pressure bar

- Vapour pressure

$$\ln\left(\frac{P}{P_0}\right) = \frac{-\Delta H_v}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right)$$

P : Pressure bar

T : Temperature K

P_0 : Reference pressure bar

T_0 : Reference temperature K

ΔH_v : latent heat of evaporation J mol^{-1}

$$\log(P) = A - \frac{B}{C+T}$$

P : Pressure bar

T : Temperature K

A,B,C; Antoine Parameter

Open system: volume

- Gas volume

Measurement e.g.
- Setaram C80
- Miniautoclave
- Radex
- RC

$$V_g = M_r \cdot V_g' \cdot X \cdot \frac{T_{(K)}}{T_{mes(K)}}$$

V_g : *Gas volume* m^3

m_r : *Reaction mass kg*

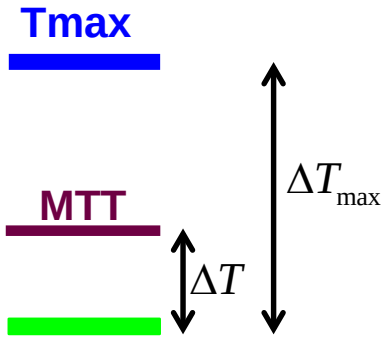
V_g' : *specific gas volume* $m^3\ kg^{-1}$

X : *Conversion*

T : *Temperature*

T_{mes} : *Temperature at measurement*

- Vapour volume



$$V_v = \frac{M_v}{\rho_v}$$

$$M_v = \frac{\left(T_{\max} - MTT\right) \cdot c_p' \cdot M_r}{\Delta H_v'}$$

$$\rho_v = \frac{P \cdot M_w}{R \cdot \left(MTT\right)}$$

V_V:Vapour volume m^3

m_V:Mass of vapour kg

ρ_V:Vapour density kg m^{-3}

T_{max}:Maximum achievable temperature K

T_{boil}:Boiling pointK

c_p':specific heat capacity J kg^{-1} K^{-1}

m_r:reaction mass kg

ΔH_v:Latent enthalpy of evaporation J mol^{-1}

P: Pressure Pa

M_w: Mole weight kg mol^{-1}

R: Gas constant:3.14 J mol^{-1} K^{-1}

Consequences based on volume

- Flammability
  - Largest explosible cloud
  - Dilution to LEL (lower explosive limit)
  - Calculation as half-sphere

$$V_{ex} = \frac{V}{LEL} \Rightarrow r = \sqrt[3]{\frac{3 \cdot V_{ex}}{2\pi}}$$

- Toxicity
  - Volume of toxic cloud
  - Dilution to toxicity limit
  - Calculation as half-sphere
    - AEGL: Acute Exposure Guideline Level
    - Or IDLH: Immediatly Dangerous to Life and Health

$$V_{tox} = \frac{M}{\rho \cdot AEGL} \Rightarrow r = \sqrt[3]{\frac{3 \cdot V_{tox}}{2\pi}}$$

❖ Caution ! Calculation as a half-sphere has nothing to do with atmospheric dispersion calculations.

Proposed Severity Criteria

Severity	ΔT_{ad}	P	Area concerned
Catastrophic	>400 K	> P_{test}	> Site
Critical	200 – 400 K	P_{max} – P_{test}	Site
Medium	50 – 200 K	P_{set} - P_{max}	Plant
Negligible	< 50 K	< P_{set}	Equipment

Criticality classes and risk reduction

- Criticality classes
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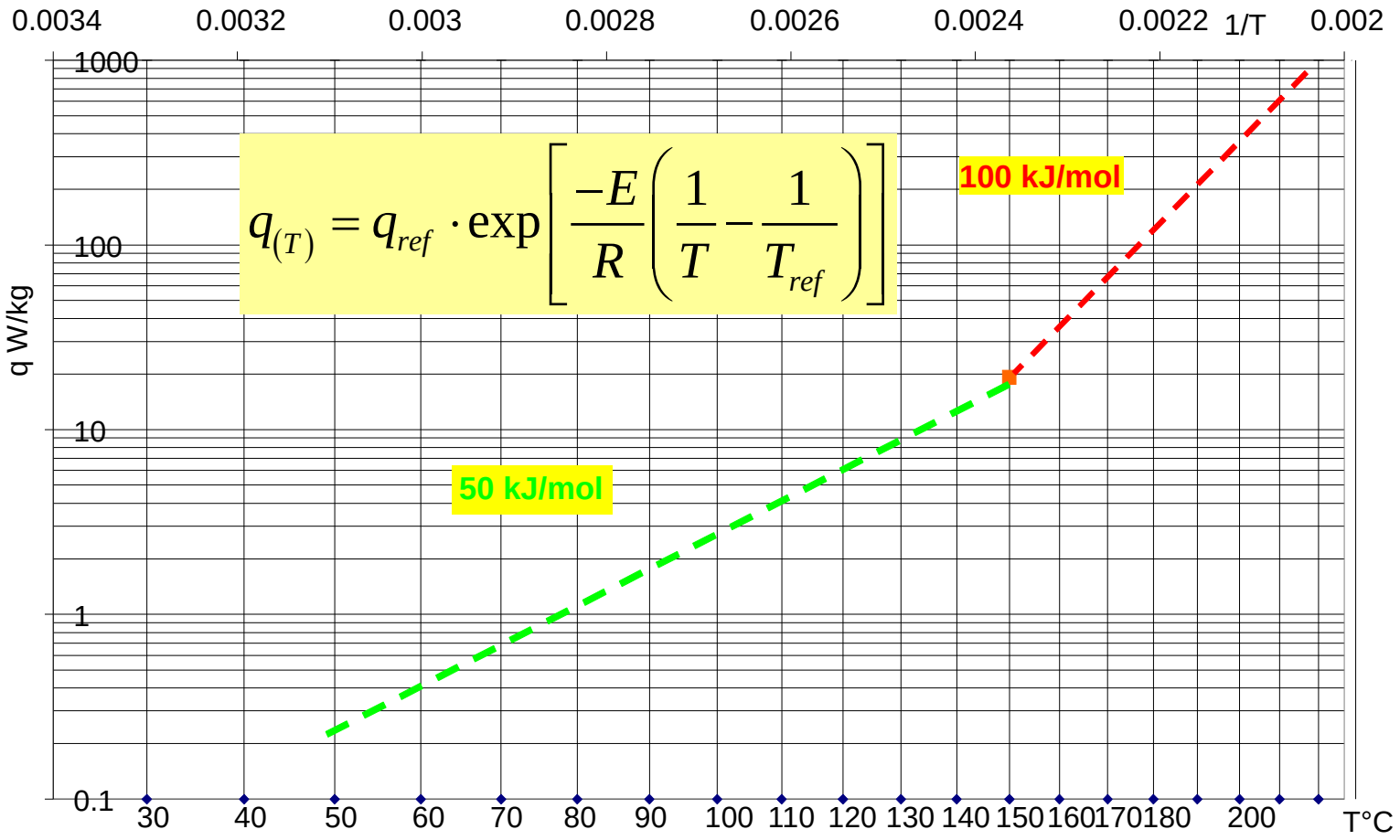
Controllability: Thermal activity

- Assessment of behaviour of reaction at MTT
  - Thermal power
    - Runaway: TMR_{ad} from MTT or MTSR
    - Power compared to cooling capacity
    - Evaporation: vapour velocity
  - Gas release rate
    - Pressure increase rate
    - Gas velocity

➢ The higher the activity, the higher the probability of loss of control

Arrhenius Diagramme

- One point extrapolation



Controllability: gas release

- Volume flow rate at MTT
  - Assumption: flow rate proportional to heat release rate (same reaction produces gas and heat)

- Gas velocity

$$\dot{v}_g = V_g' \cdot M_r \cdot \frac{q'_{(MTT)}}{Q'}$$

$\dot{v}_g$: *volumeflow rate* m^3 / s
V_g' : *gas volume* m^3 / kg
M_r : *reaction mass* kg
$q'_{(MTT)}$: *thermal power* W / kg
Q' : *heat of reaction* J / kg

- Data from
  - Experiments: Calvet or reaction calorimetry

$$u_g = \frac{\dot{v}_g}{S}$$

u_g : gas velocity m/s
$\dot{v}_g$: volume flow rate m^3/s
S : tube section m^2

In a closed system: allways ensure that gas release remains uncritical

Controllability: Evaporation

- Mass flow rate at MTT

$$\dot{m}_v = \frac{q'_{(MTT)} \cdot M_r}{\Delta H_v}$$

- Density

$$\rho_v = \frac{P \cdot M_w}{R \cdot MTT}$$

- Volume flow rate

$$\dot{v}_v = \frac{\dot{m}_v}{\rho_v}$$

- Vapour velocity

$$u_v = \frac{\dot{v}_v}{S}$$

$\dot{m}_v$: *mass flow rate* $[kg_v / s]$

$q'_{(MTT)}$: *thermal power at MTT* $\left[W / kg_{M_r}\right]$

M_r : *reaction mass* $[kg]$

ΔH_v : *latent heat of evaporation* $[J / kg_v]$

ρ_v : *density* $\left[kg / m^3\right]$

P : *pressure* $[Pa]$

R : *gas constant* = 8.314 J/(mol · K)

MTT $[K]$

u_v : *gas velocity* m / s

$\dot{v}_v$: *volume flow rate* m^3 / s

S : *pipe section* m^2

In case of simulatneous gas and vapour release add velocities u_v and u_g

Probability of Reactor Loss of Control

Probability	Controllability	TMR_{ad} (h) from MTT	q' (W/kg) Stirred	q' (W/kg) Unstirred	u (m/s)
Frequent	Unlikely	<1	> 100	> 10	> 20
Probable	Difficult	1 – 8	50 – 100	5 – 10	10 – 20
Occasional	Marginal	8 – 24	10 – 50	1 – 5	5 – 10
Low	Feasible	24 – 50	5 – 10	0.5 – 1	2 – 5
Remote	Easy	50 – 100	1 – 5	0.1 – 0.5	1 – 2
Almost impossible	Un-problematic	> 100	< 1	< 0.1	< 1

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Choice of Measures

"Avoid the problem rather than solve it"

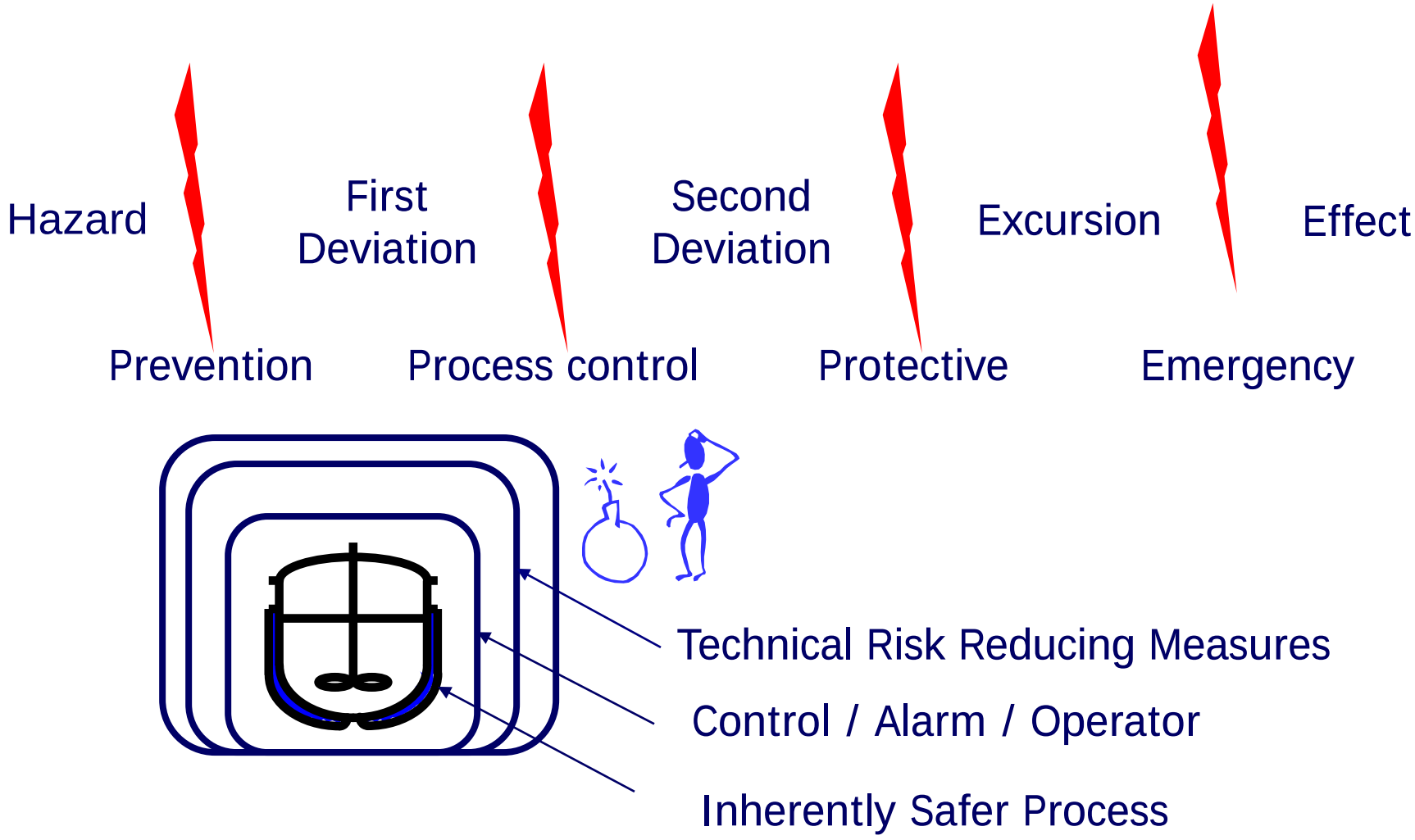
Trevor Kletz

Avoid the runaway rather than mitigate its consequences

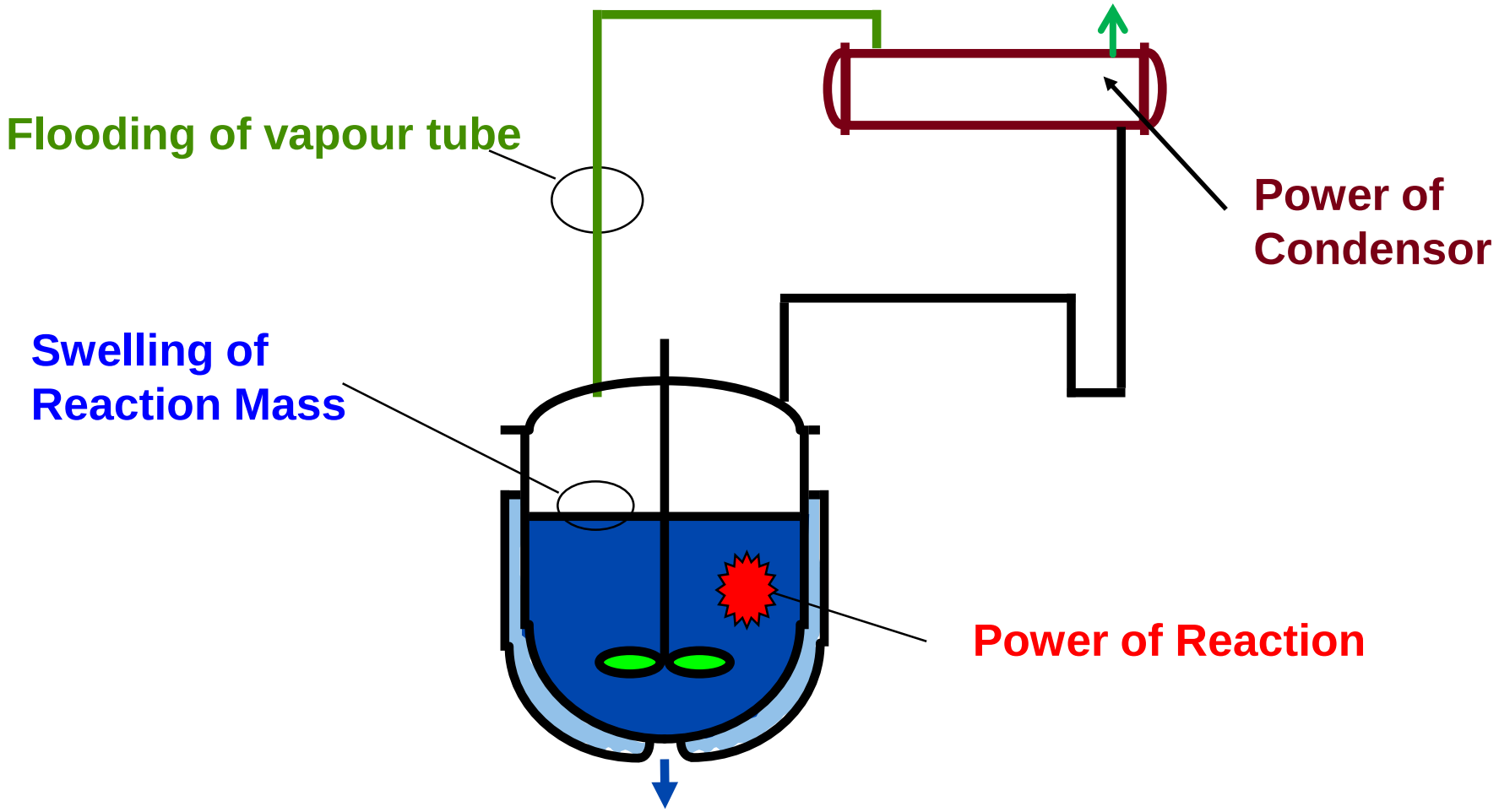
Measures: Strategies for choice

- Risk reduction by design
  - Reduction of the severity
  - Semi-batch / Batch
  - Continuous / Batch
- Risk reduction by control
  - Technical measures
  - Avoid runaway
  - Fail safe process
- Emergency measures
  - Mitigate the consequences of runaway
  - Containment
  - Pressure relief

Protection Layers for Batch Reactors after IEC 61511



Cooling by Evaporation: using the boiling barrier
Limiting Factors



Amount of Vapour

- All the energy used for boiling (reaction mass is at the boiling temperature)

$$m_{vap} = \frac{Q'_R \cdot m_R}{\Delta H'_V}$$

m_{vap} :	Mass of evaporated solvent	[kg Solvent]
Q'r :	Heat of reaction	[kJ/kg Reaction mass]
$\Delta H'_v$:	Heat of vaporisation	[kJ/kg Solvent]
m_R:	Mass of reaction mixture	[kg Reaction mass]

- As a function of the "distance" from Boiling Point

$$m'_{vap} = \left(1 - \frac{(T_b - T_o)}{\Delta T_{ad}}\right) \cdot \frac{Q'_r}{\Delta H'_v}$$

m'_{vap} :	Mass of evaporated solvent	[kg Solvent/kg reaction mass]
T_b :	Boiling Temperature	[°C]
T_0:	Starting temperature	[°C]
ΔT_{ad} :	Heat of vaporisation	[kJ/kg Solvent]
$\Delta H'_v$:	Heat of vaporisation	[kJ/kg Solvent]
Q'_R:	Reaction energy	[kJ/kg Reaction mass]

Vapour flow, velocity

- Mass flow rate of vapour $$\dot{m}_V = \frac{q'_R \cdot m_R}{\Delta H'_V}$$

$\dot{m}_V$	Rate of evaporation	[kg Solvent /s]
q'_R :	Heat release rate of reaction	[W/kg]
$\Delta H'_v$:	Heat of vaporisation	[J/kg Solvent]

- Vapour specific weight $$\rho_G = \frac{P \cdot M_W}{R \cdot T}$$

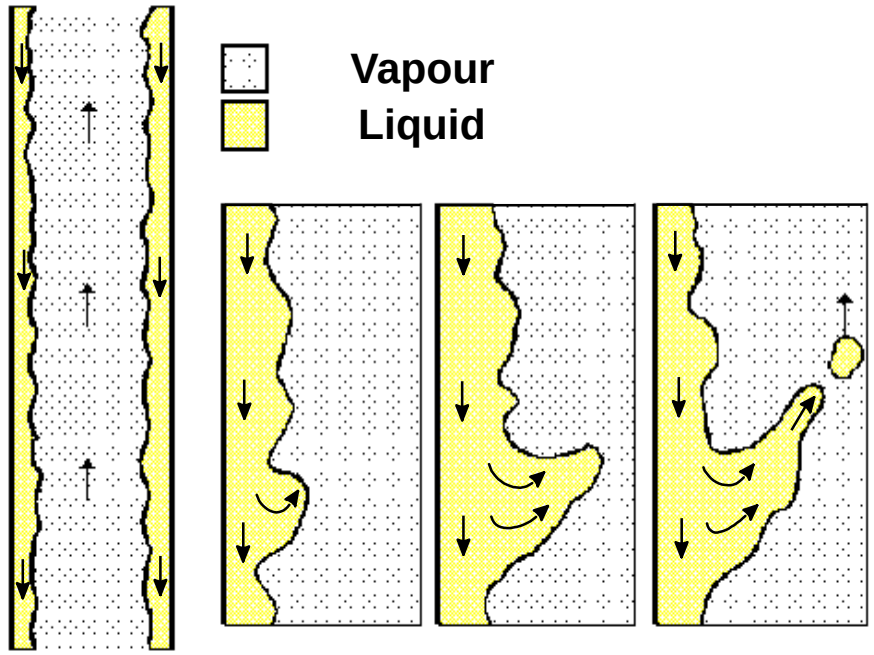
ρ_G:	Vapour specific weight	[kg/m^3]
P:	Pressure	[Pa (abs)]
M_W:	Molar weight	[kg/mol]
R:	ideal gas constant 8.314	[m^3.Pa/(mol.K)]
T:	Temperature	[K]

- Vapour velocity $$u_V = \frac{\dot{m}_v}{\rho_G \cdot S}$$

S:	Section of the pipe/reactor	[m^2]
u_v:	Vapour velocity	[m/s]

Flooding

- Flooding of the vapour tube:
  - Consequence: increased pressure drop
  - Boiling barrier does not work: pressure increases



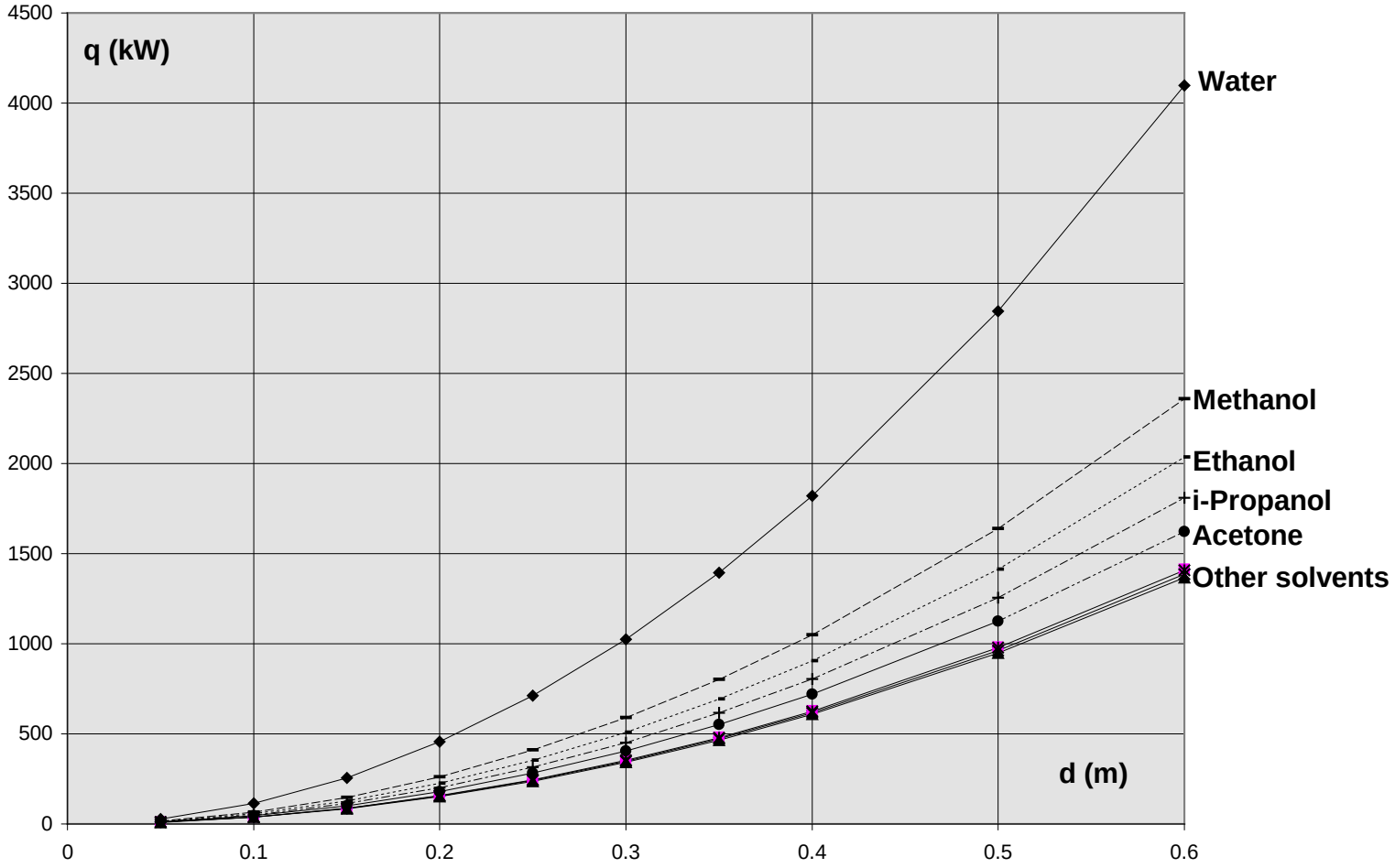
Flooding of Vapour Tube

$$q_{\max}\left[W\right] = \left(4520 \cdot \Delta H'_V + 3.37 \cdot 10^6\right) \cdot s$$

$$u_{G\max} = \frac{4520 \cdot \Delta H'_V + 3.37 \cdot 10^6}{1000 \cdot \Delta H'_V \cdot \rho_G}$$

u_{Gmax} :	Limit velocity at interface, $m.s^{-1}$
$\Delta H'v$:	Heat of vaporisation, kJ / kg
ρ_G :	specific Weight of **vapour**, $kg.m^{-3}$
s :	Section of tube, m^2
4520:	Constant: Mass flux, kg solvent / (m^2.s)
$3.37.10^6$	Constant: Heat flux, J / (m^2.s)

Flooding of Vapor Tube



Solvents	$u_{G\ max}$ Atmospheric boiling conditions
Water	10.3
Methanol	6.6
Ethanol	5.4
Isopropanol	4.7
Acetone	5.2
Toluene	4.8
THF	5

Swelling of Reaction Mass

$$\alpha = K \cdot \left(\frac{\rho_G}{\rho_L - \rho_G} \right)^{0.17} \cdot D_H^{*\,-0.1} \cdot u_G^{*\,a}$$

$$\alpha = \frac{H_B - H_0}{H_B}$$

$$D_H^{\,*} = \frac{D_H}{\sqrt{\frac{\sigma}{g \cdot (\rho_L - \rho_G)}}}$$

$$u_G^{\,*} = \frac{u_G}{\sqrt{g \cdot \sqrt{\frac{\sigma}{g \cdot (\rho_L - \rho_G)}}}}$$

$$\begin{cases} u_G^{\,*} < 2 \Rightarrow K = 0.68 \quad a = 0.62 \\ u_G^{\,*} \geq 2 \Rightarrow K = 0.88 \quad a = 0.40 \end{cases}$$

H_B : Liquid level during boiling

H_0 : Liquid level without boiling

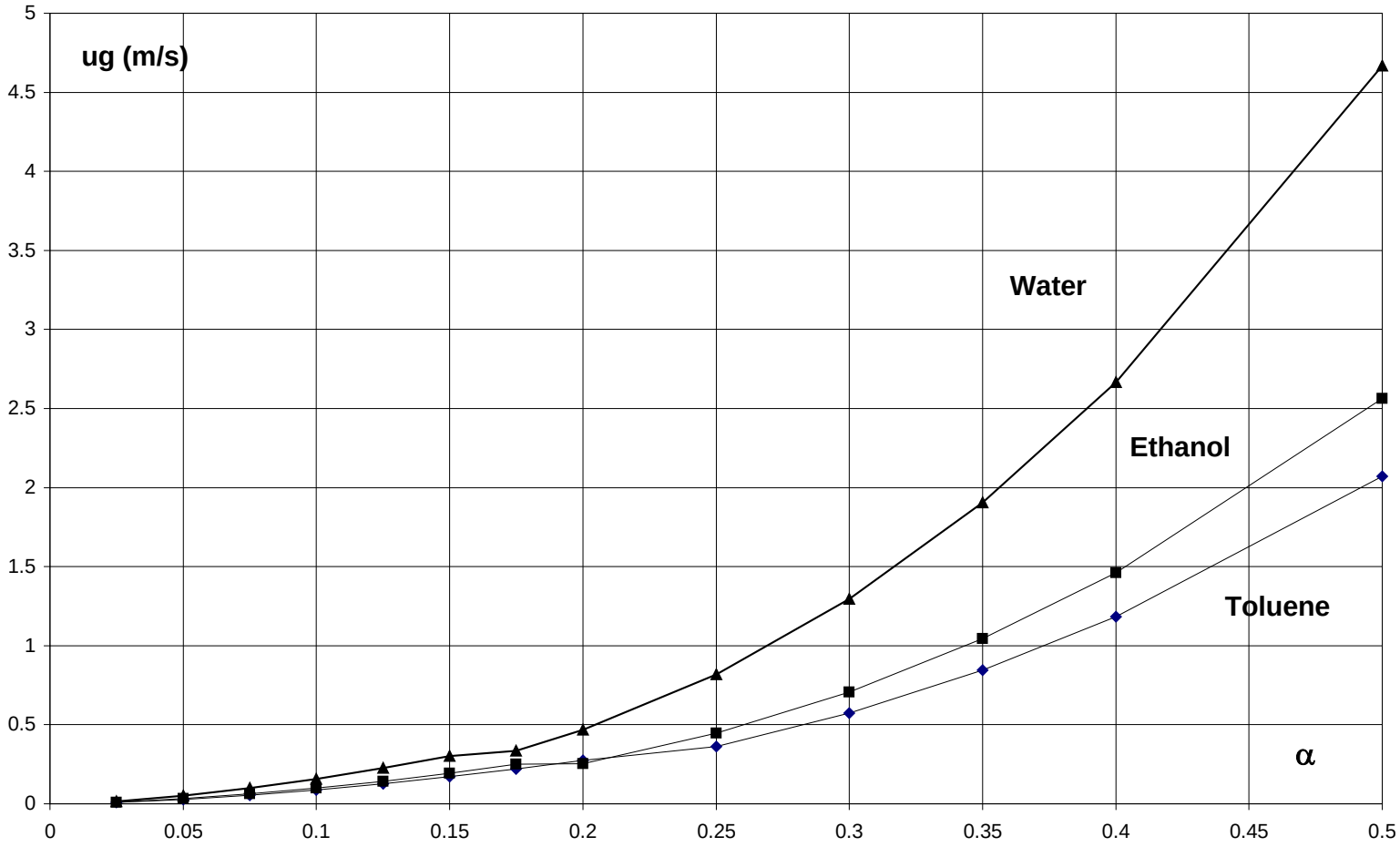
ρ_G : specific weight of vapour, $kg.m^{-3}$

ρ_L : specific weight of liquid, $kg.m^{-3}$

σ : interfacial tension $kg.s^{-2}$

D_H : Hydraulic diameter of reactor, m

Swelling due to evaporation



Example: Cooling by evaporation

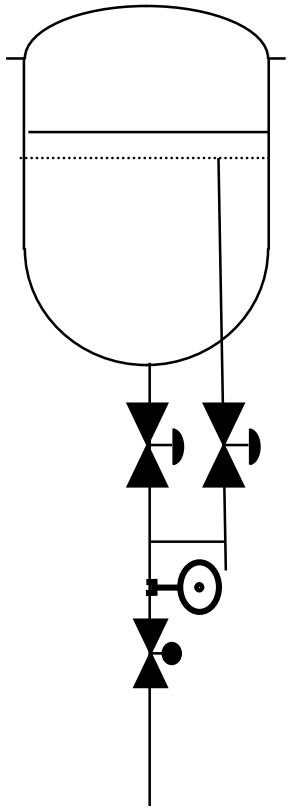
6.3 m^3 reactor filled with 6.3 m^3 of acetone

$V_{max} = 7\ m^3$

Diameter of vapour tube	200 mm	300 mm
Max. heat release rate	35 W/kg	68 W/kg
Limiting factor	Flooding	Swelling

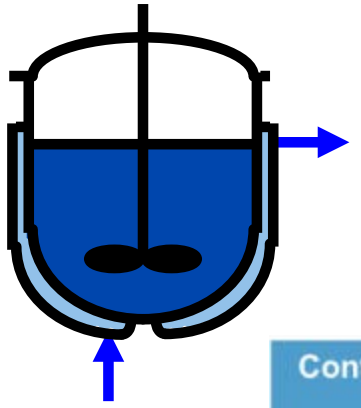
Technical Measures
Limitation of feed in SBR

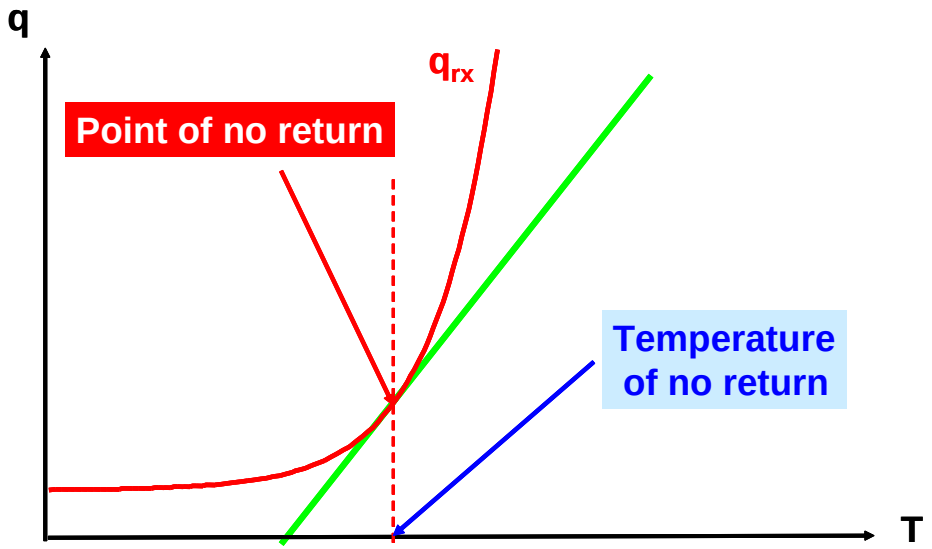
- Amount of feed
  - Portions
  - Redundant feed valves
- Feed rate
  - Orifice
  - Volumetric pump
- Interlocks
  - Temperature + / -
  - Stirrer



Emergency Cooling

- Must be independant of utilities
- Limitation in case of solidification
- Agitation is critical



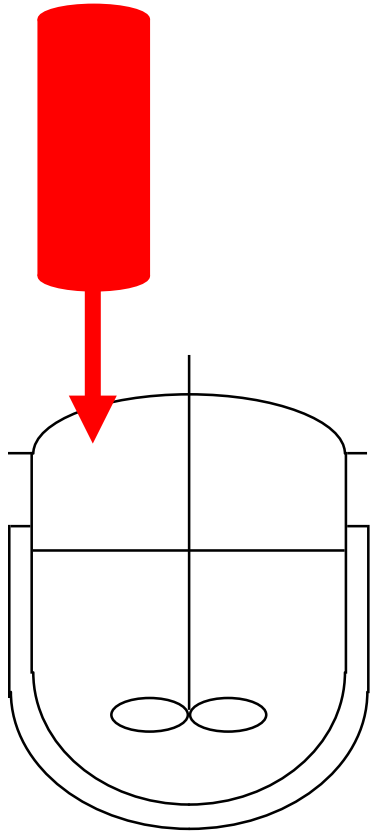


Controllability	q' (W/kg) Stirred	q' (W/kg) Unstirred
Unlikely	> 100	> 10
Difficult	50 – 100	5 – 10
Marginal	10 – 50	1 – 5
Feasible	5 – 10	0.5 – 1
Easy	1 – 5	0.1 – 0.5
Un-problematic	< 1	< 0.1

Quenching

- Amount of inhibitor
- Temperature of inhibitor
- Rate of addition
- Degree of mixing

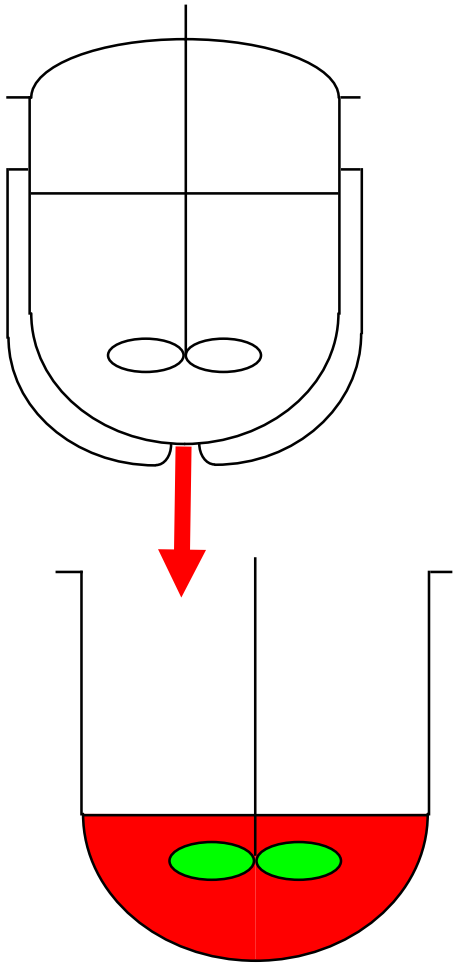
Probability	Controllability	TMRad (h) from MTT
Frequent	Unlikely	<1
Probable	Difficult	1 – 8
Occasional	Marginal	8 – 24
Low	Feasible	24 – 50
Remote	Easy	50 – 100
Almost impossible	Un-problematic	> 100



Dumping

- Dumping vessel with required volume
- Transfer line

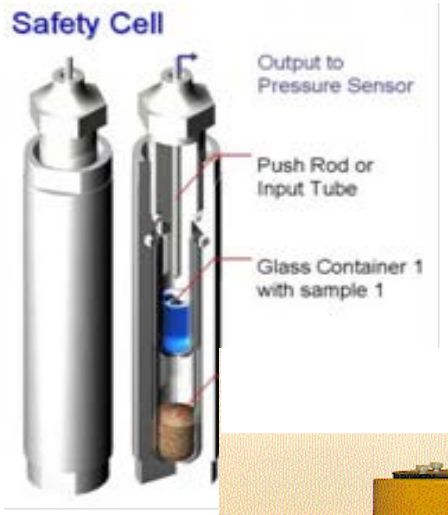
Probability	Controllability	TMRad (h) from MTT
Frequent	Unlikely	<1
Probable	Difficult	1 – 8
Occasional	Marginal	8 – 24
Low	Feasible	24 – 50
Remote	Easy	50 – 100
Almost impossible	Un-problematic	> 100

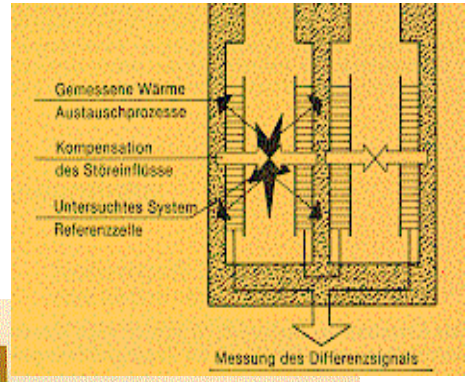


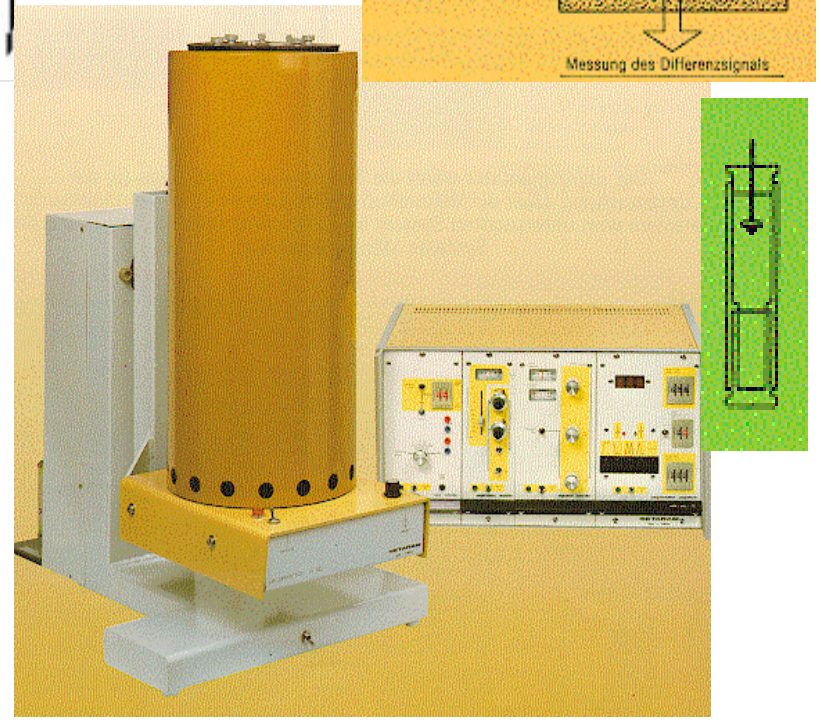
Calvet Calorimetry

Quantitative measurement

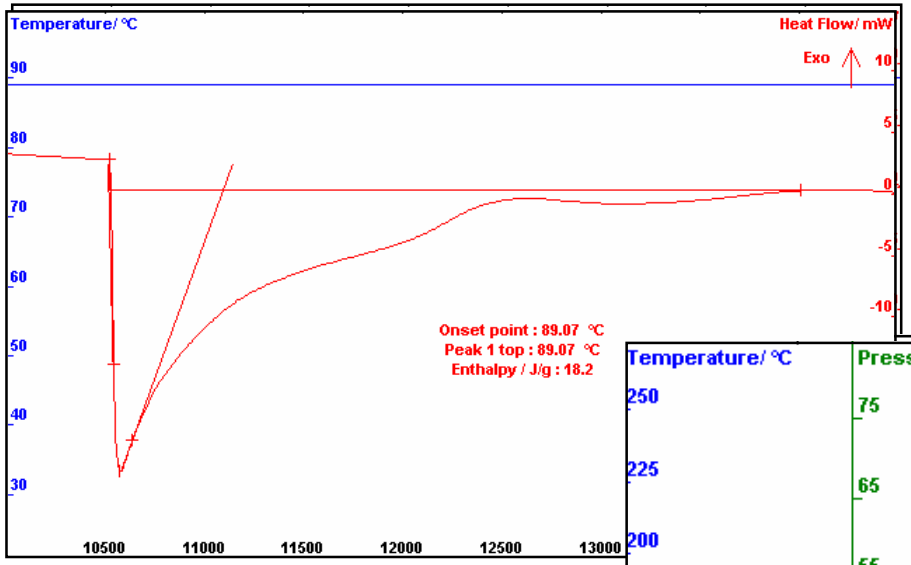
- Simulation of dumping or quench
- Measurement of pressure
- Mixing cell
  - Water ingress
  - Quenching
  - Inhibition
  - Dumping



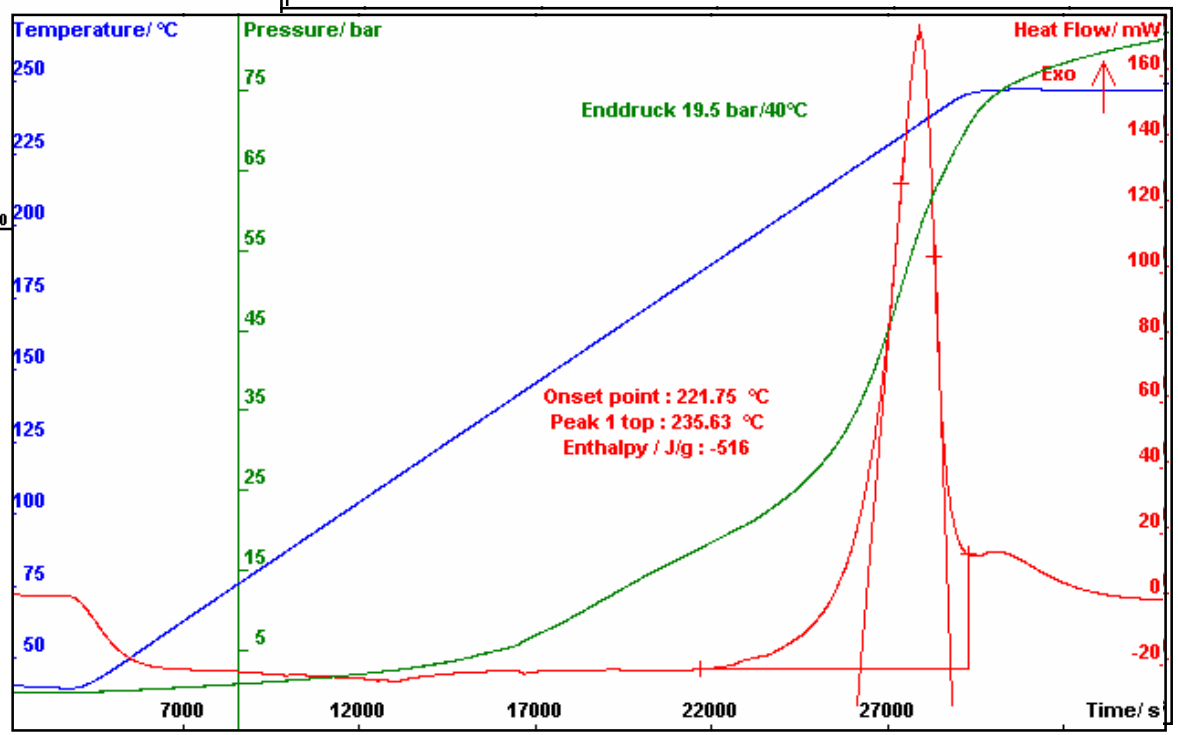




Inhibition



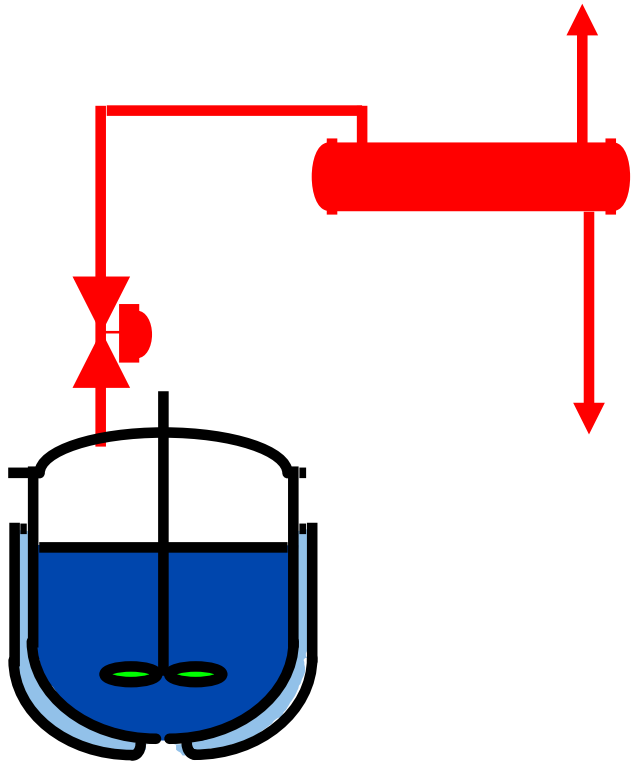
Stability after quench



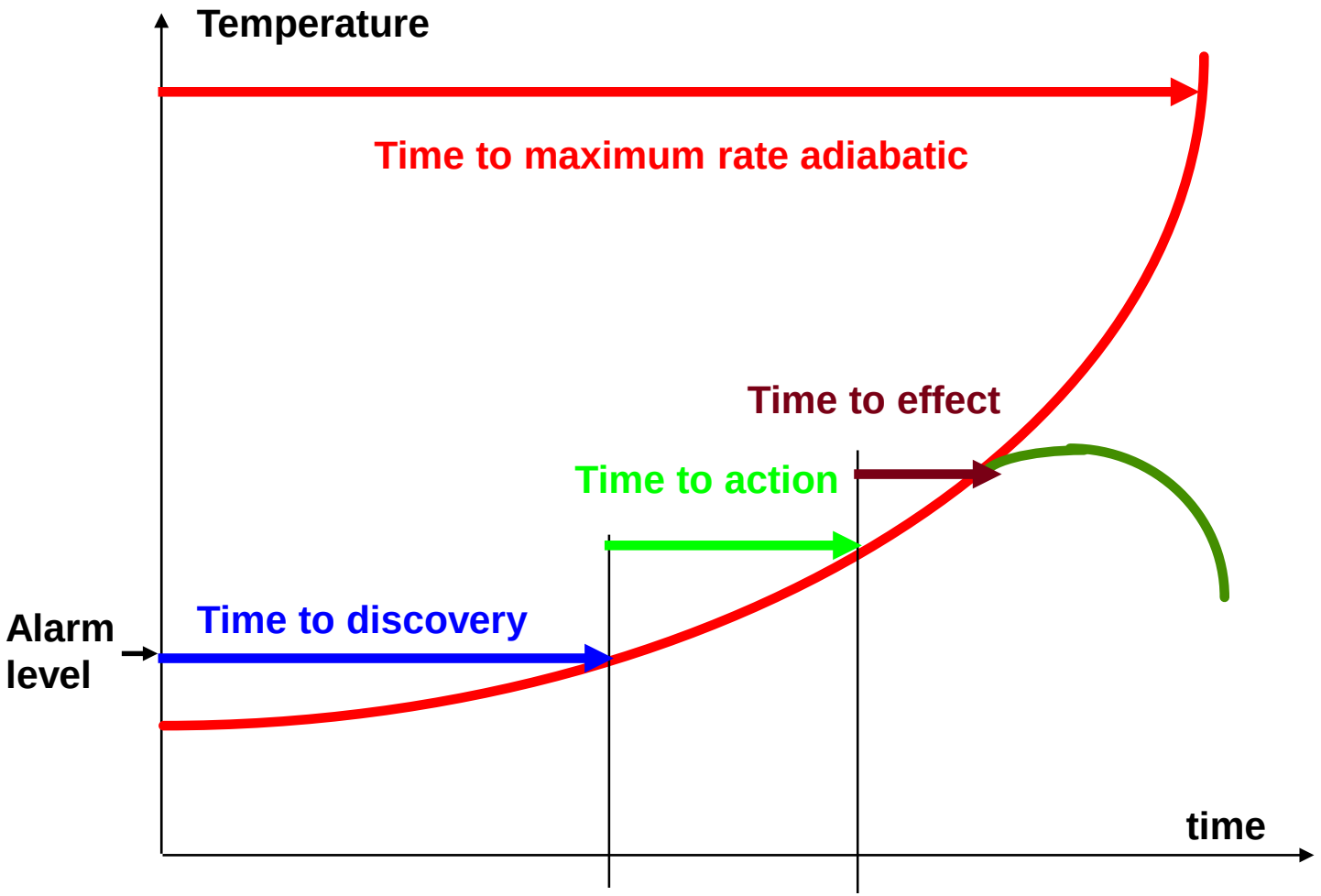
Controlled depressurisation

- Different from pressure relief
- Allows to use evaporative cooling
- Condenser or scrubber
- Independent of utilities

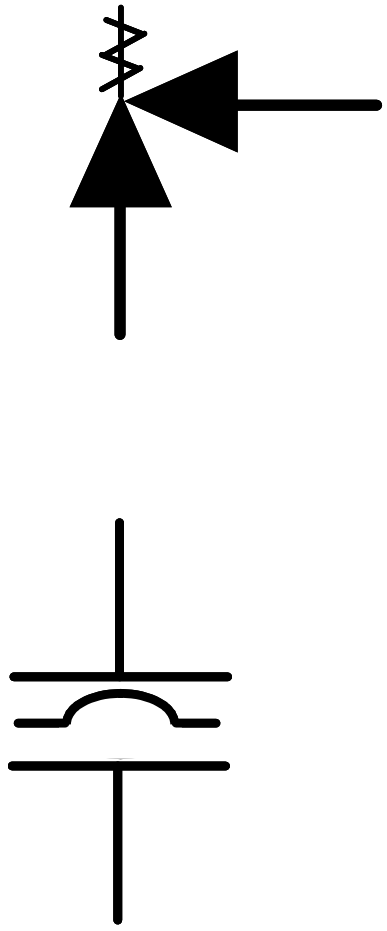
Probability	Controllability	u (m/s)
Frequent	Unlikely	> 20
Probable	Difficult	10 – 20
Occasional	Marginal	5 – 10
Low	Feasible	2 – 5
Remote	Easy	1 – 2
Almost impossible	Un-problematic	< 1



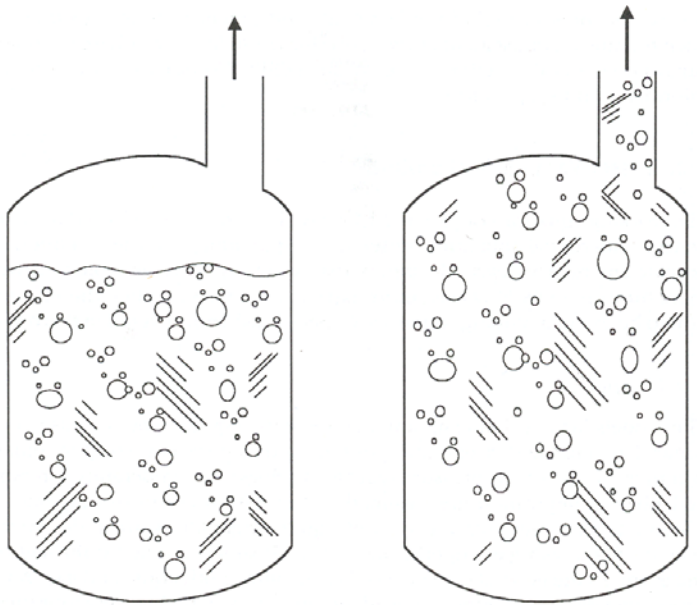
Time Factor


Temperature
Time to maximum rate adiabatic
Time to effect
Time to action
Alarm level
Time to discovery
time

Emergency Pressure Relief

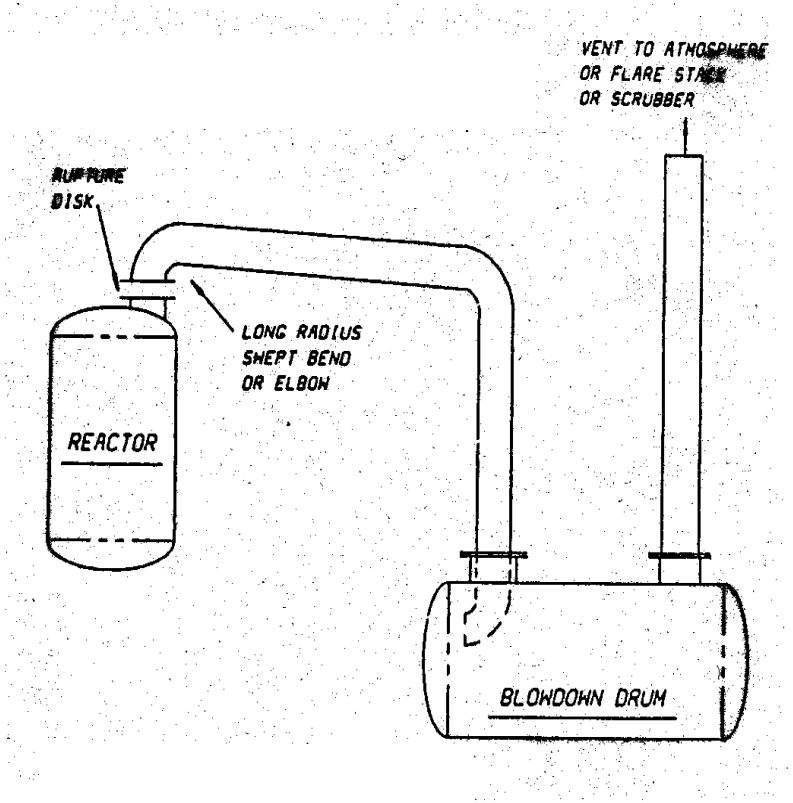


Champagne-Effect



Design for two phase flow

- Increased head loss
- Larger section required
- Evaporation due to expansion
- High velocity



➔Specific Design Method according to DIERS (Design Institute for Emergency Relief Systems)

Sizing Examples

Required diameter for a rupture disk

- Physical scenario
  - Maximum heating (150°C) with acetone
  - Heating power: 110 W/kg
  - One phase flow: 50 mm
  - Two phase flow: 150 mm
- Chemical reaction
  - Power at process temperature: 20 W/kg
  - Power at relief conditions: 310 W/kg
  - Two phase flow: 250 mm

Emergency Pressure Relief

- Emergency pressure relief shall only be used as a last line of defence

- Two phase flow is likely to occur
- Two phase flow requires larger diameters
- High velocities: mechanical design: thrust
- Effluent treatment is required
- Effluent treatment to be sized to separate liquid
- Secondary explosion likely with flammable compounds