

Introduction to the assessment of thermal process safety

Module 2

ENG 431: Safety of chemical Processes

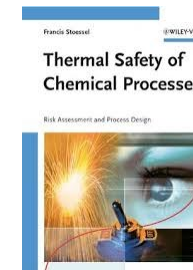
Annik Nanchen

Content Module 2

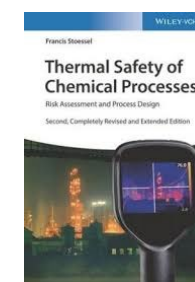
- Thermal Risks
 - Heat Balance
 - Failure Scenario
- Criticality
- Assessment Procedure
- Assessment of the energy potential
 - Energy
 - Pressure



Chapters 2 and 3



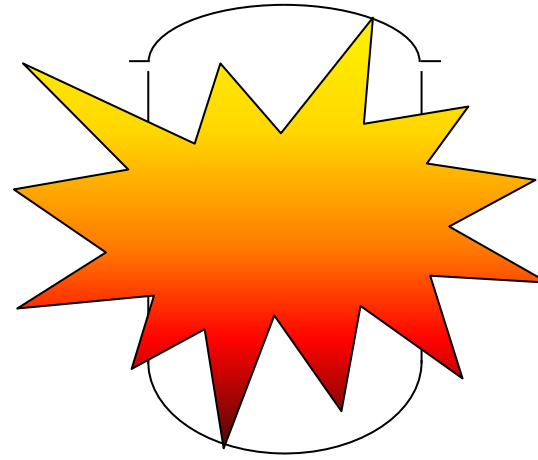
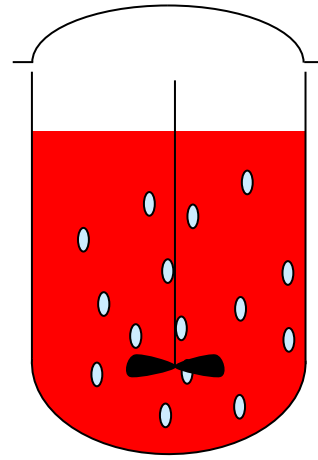
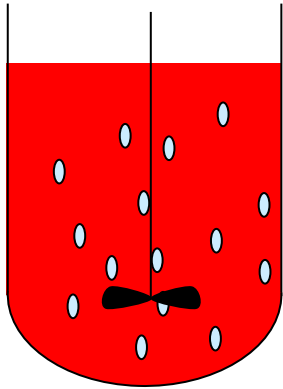
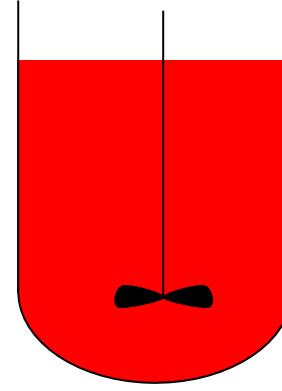
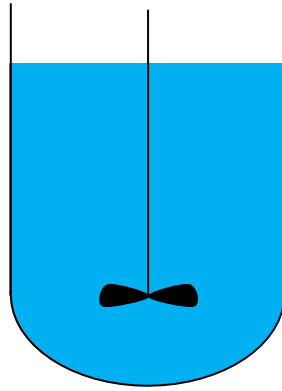
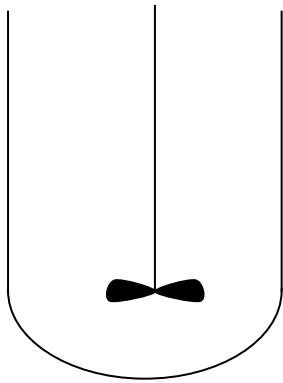
Chapter 2

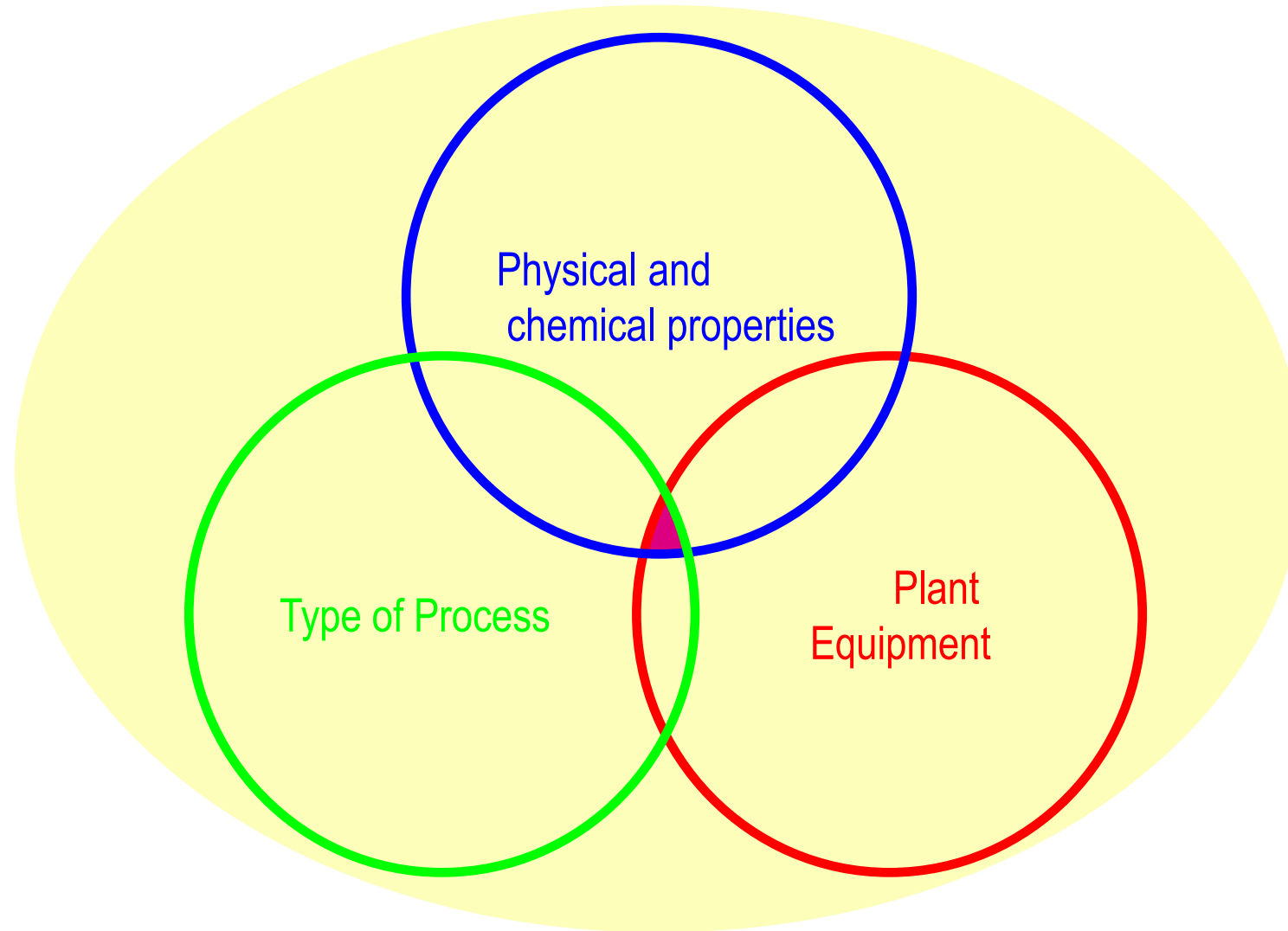


Chapters 2 and 5

Potential hazard

- Exothermic reaction
 - Heat produced must be removed
 - Otherwise Temperature increase
 - At higher temperatures, secondary reactions
 - Boiling point: vapour produced
- Secondary reactions:
 - Heat production
 - Gas production
- Hazard: thermal runaway



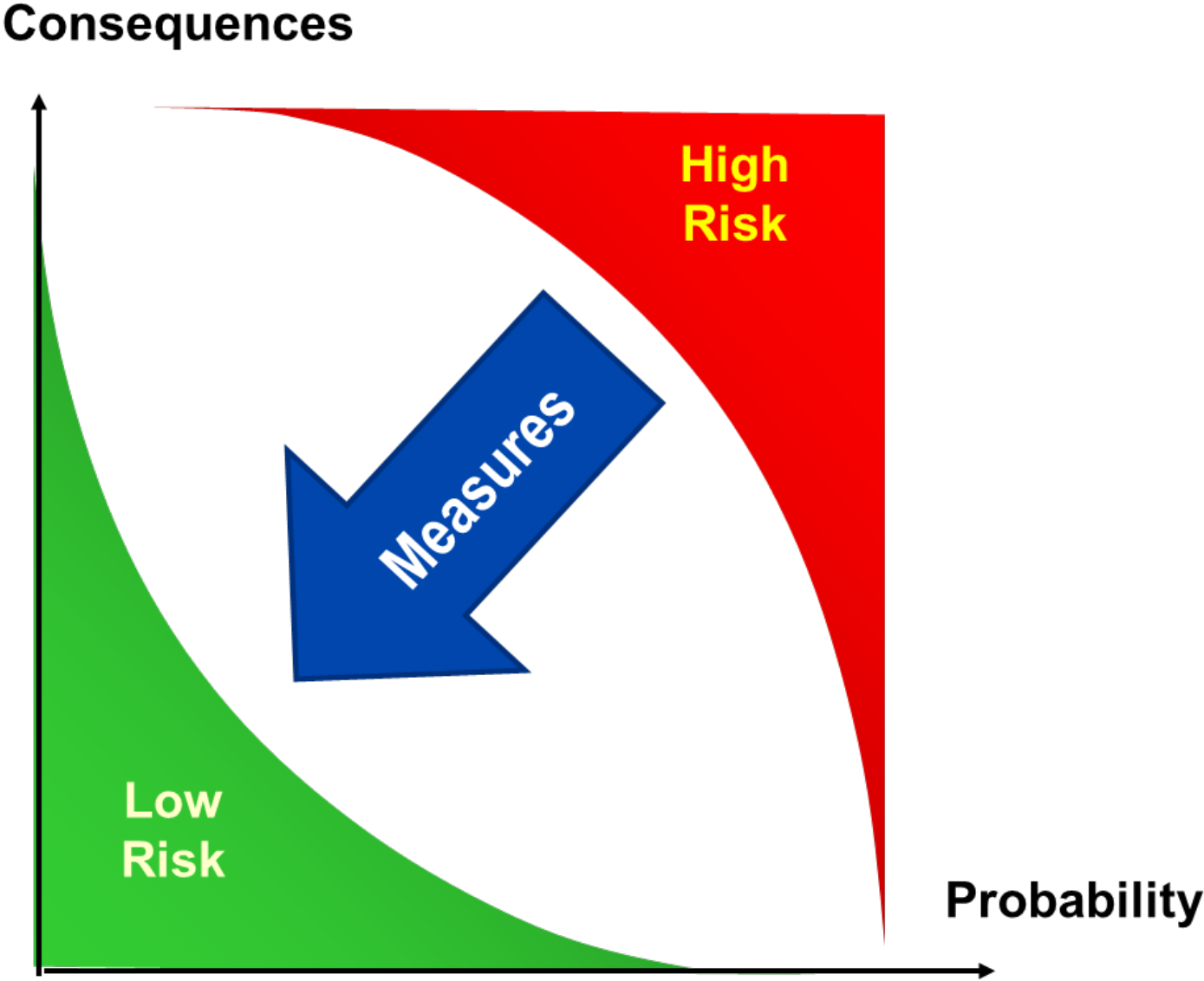


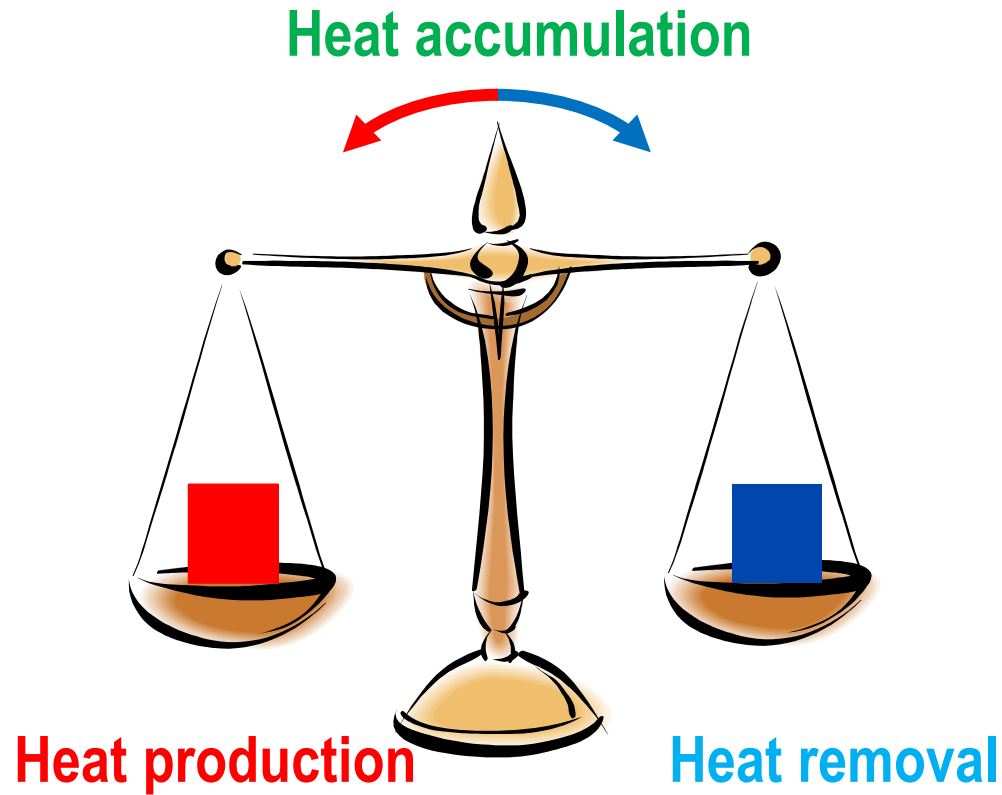
Content Module 2

- Video/ introduction to the hazard
- Thermal Risks
 - Heat Balance
 - Failure Scenario
- Criticality
- Assessment Procedure



Chapters 2 and 3





$$\frac{dT}{dt} = k(1 - X_A)^n c_{A0}^{n-1} \Delta T_{ad} - \frac{UA(T - T_c)}{\rho V c'_p}$$

T: temperature

t: time

k: rate constant

X: conversion

n: order of the reaction

c_{A0} : starting concentration of A

ΔT_{ad} : adiabatic temperature rise

U: heat transfer coefficient

A: heat exchange area

T_c : temperature cooling media

ρ : density

c'_p : specific heat capacity

V: volume

K

s

$s^{-1} \text{mol}^{1-n} \text{l}^{n-1}$

-

-

mol/l

K or °C

$\text{W}/(\text{m}^2 \cdot \text{K})$

m^2

K

kg/l

$\text{J}/(\text{kg} \cdot \text{K})$

l

$$q_{acc} = M \cdot c'_P \cdot \frac{dT}{dt} = q_{rx} - q_{ex}$$

$$q_{rx} = k_0 \cdot e^{-E/RT} \cdot C_0 (1 - X) \cdot V \cdot (-\Delta H_r)$$

1st order reaction

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

acc: accumulation

rx: reaction

ex: exchange

q: heat flow

M: mass

c'_P : specific heat capacity

T: temperature

W

kg

J/(kg·K)

K

t: time

k_0 : pre-exponential factor

E: activation energy

c: concentration

X: conversion

V: volume

ΔH_r : molar reaction enthalpy

U: heat transfer coefficient

A: heat exchange area

T_c : temperature cooling media

s

s⁻¹

J/mol

mol/l

-

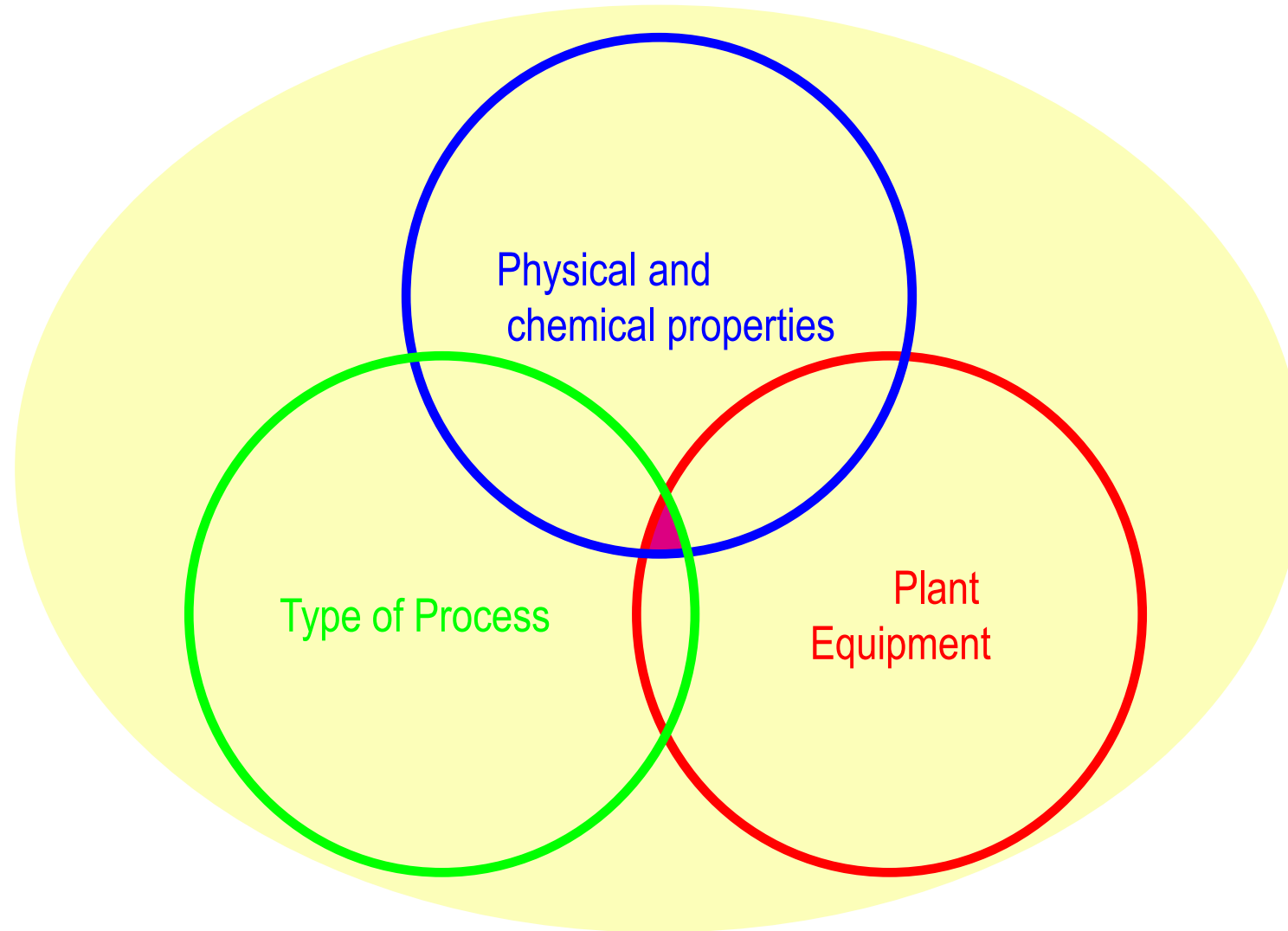
l

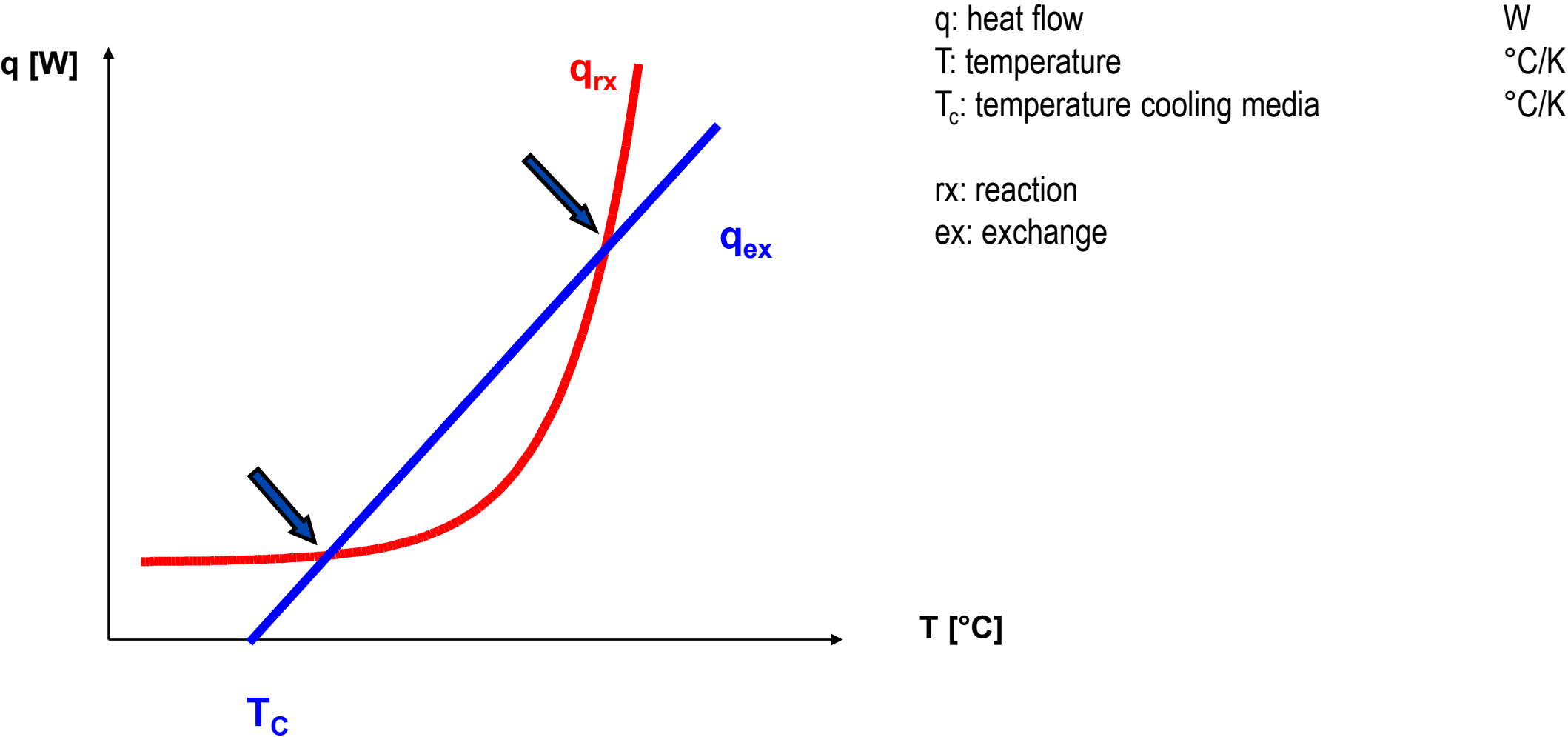
J/mol

W/(m²·K)

m²

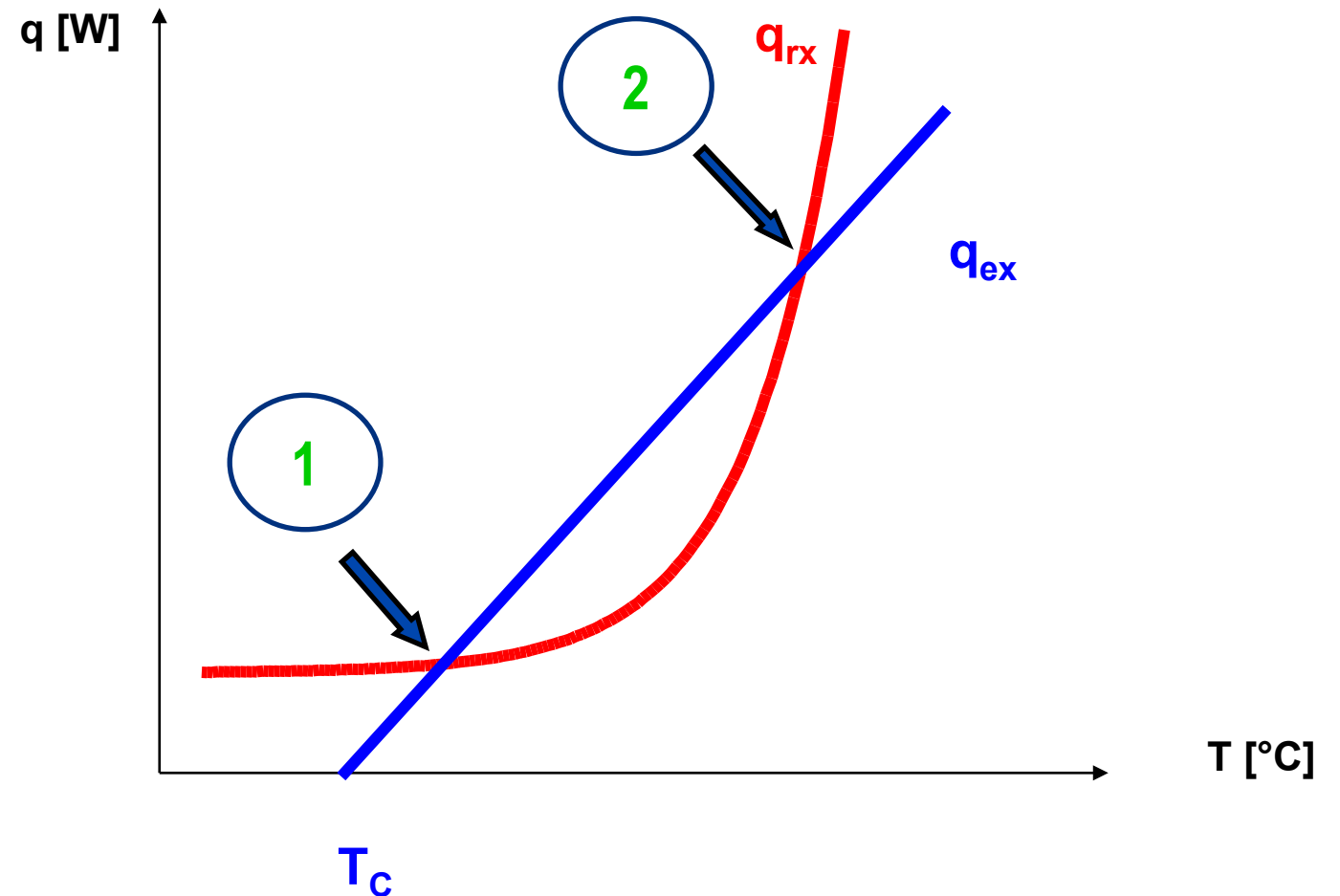
K





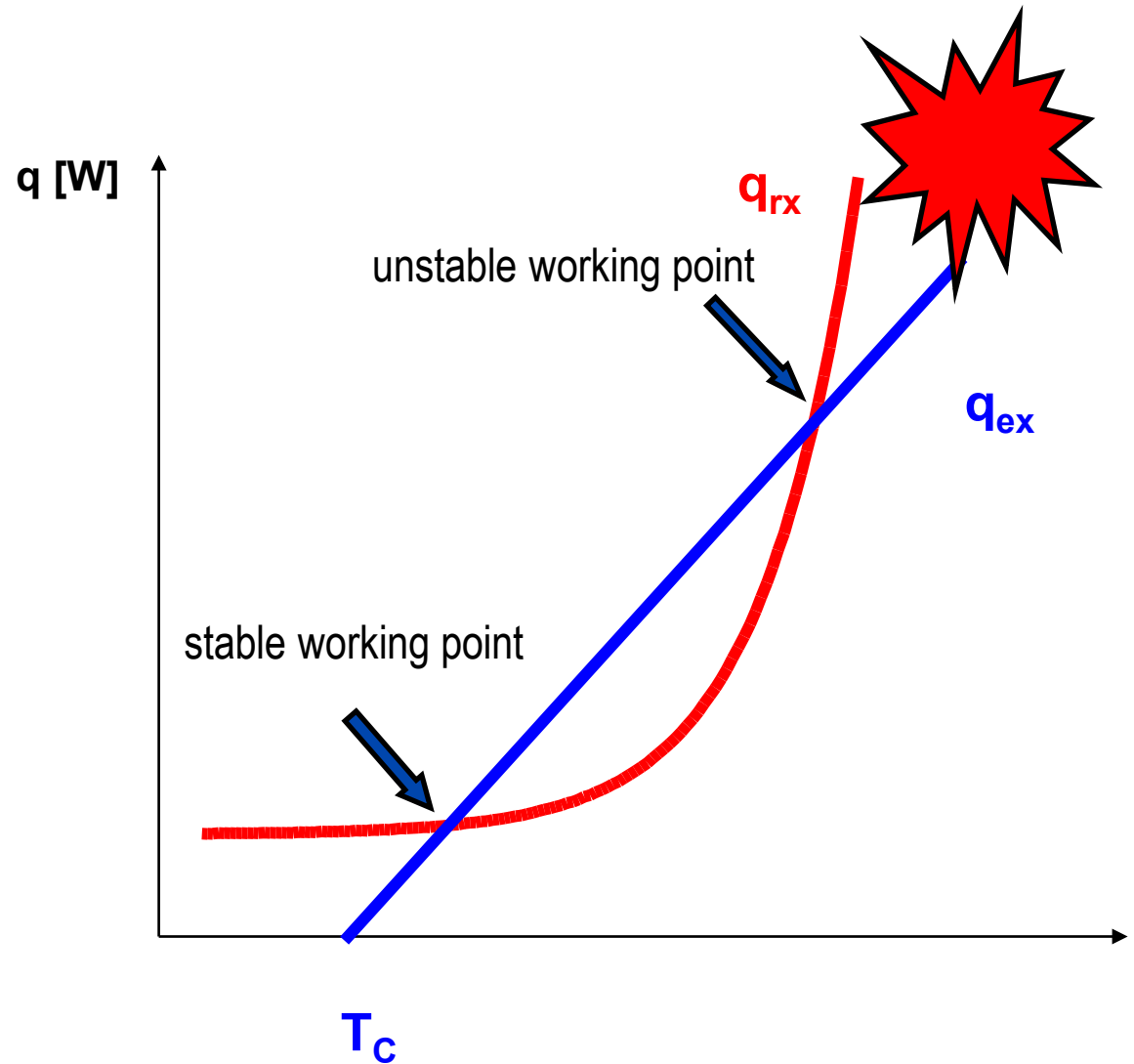
Semenov-Plot – normal operating conditions

- What is the difference between the two working points?
- Which one would you choose and why?
 - A. Point 1
 - B. Point 2
 - C. Point 1 or 2, makes no difference
- Think about it a few minutes



Semenov-Plot – normal operating conditions

15

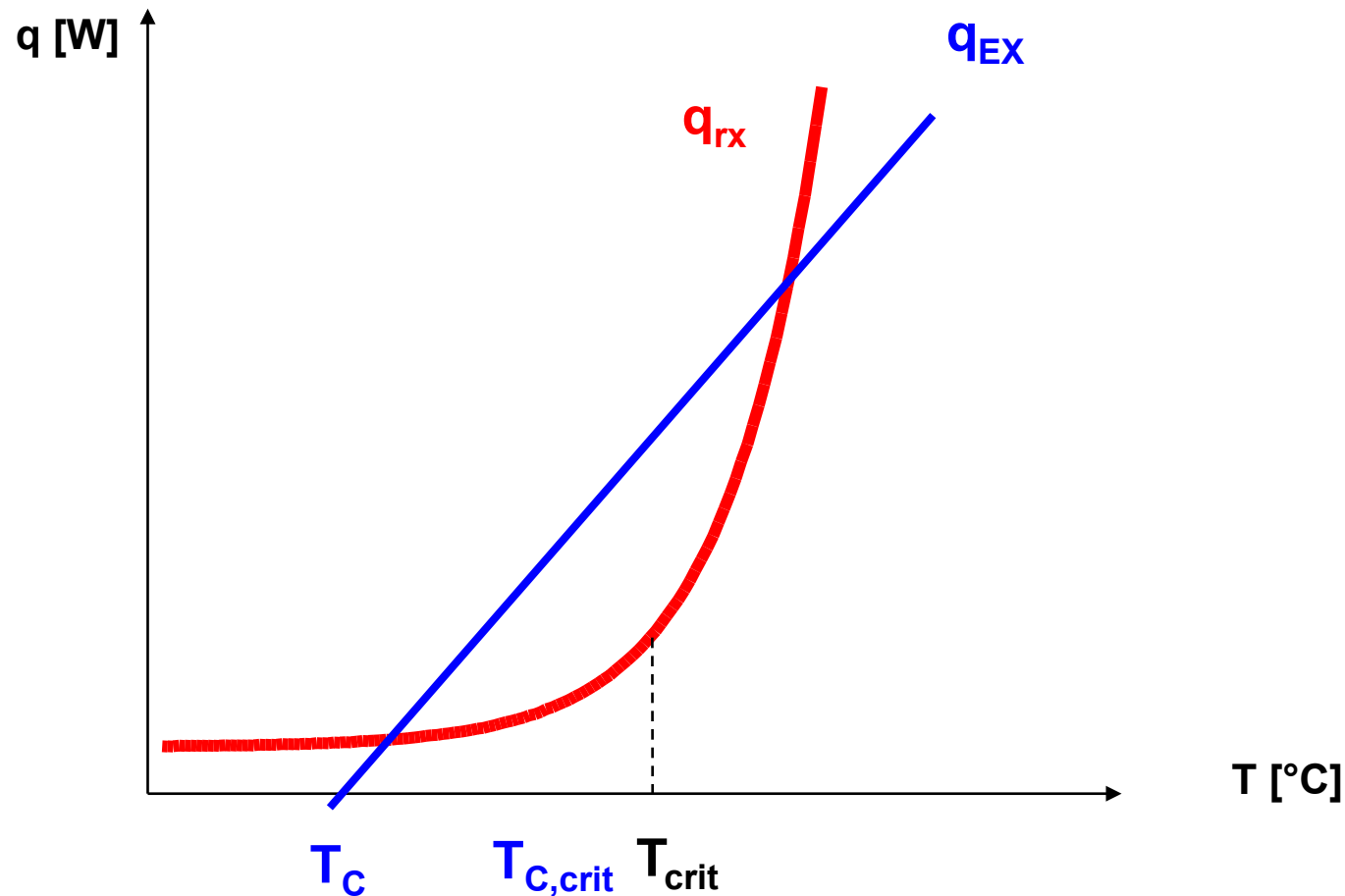


q : heat flow
 T : temperature
 T_c : temperature cooling media

rx: reaction
ex: exchange

W
°C/K
°C/K

$$q_{EX} = UA(T_C - T)$$



q : heat flow

W

T : temperature

°C/K

T_C : temperature cooling media

°C/K

$T_{C,crit}$: critical cooling media temperature

°C/K

T_{crit} : critical process temperature

°C/K

U : heat transfer coefficient

W/(m²·K)

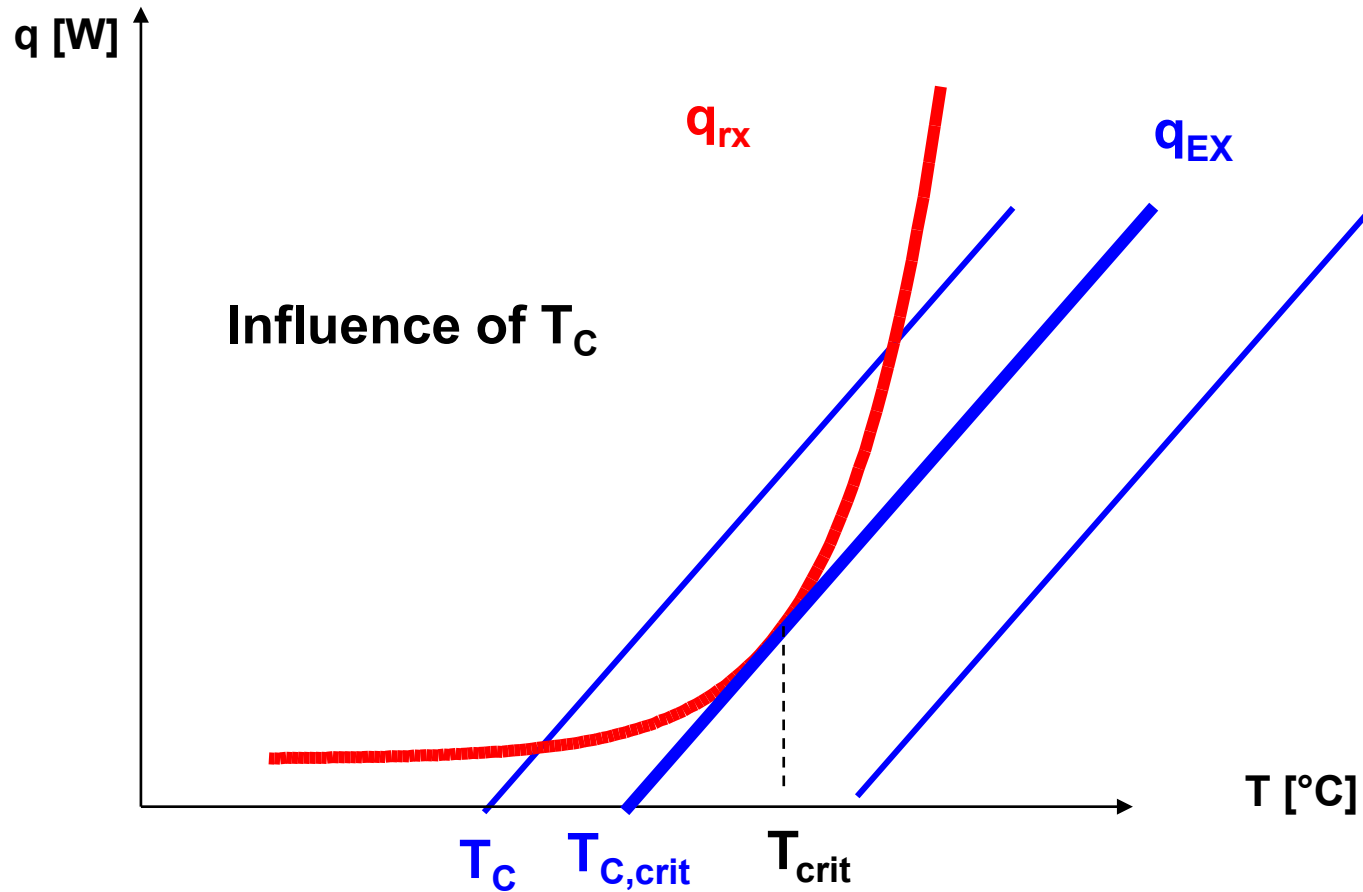
A : heat exchange area

m²

rx: reaction

ex: exchange

$$q_{EX} = UA(T_C - T)$$



q : heat flow

W

T : temperature

°C/K

T_C : temperature cooling media

°C/K

$T_{C,crit}$: critical cooling media temperature

°C/K

T_{crit} : critical process temperature °C/K

U : heat transfer coefficient

W/(m²·K)

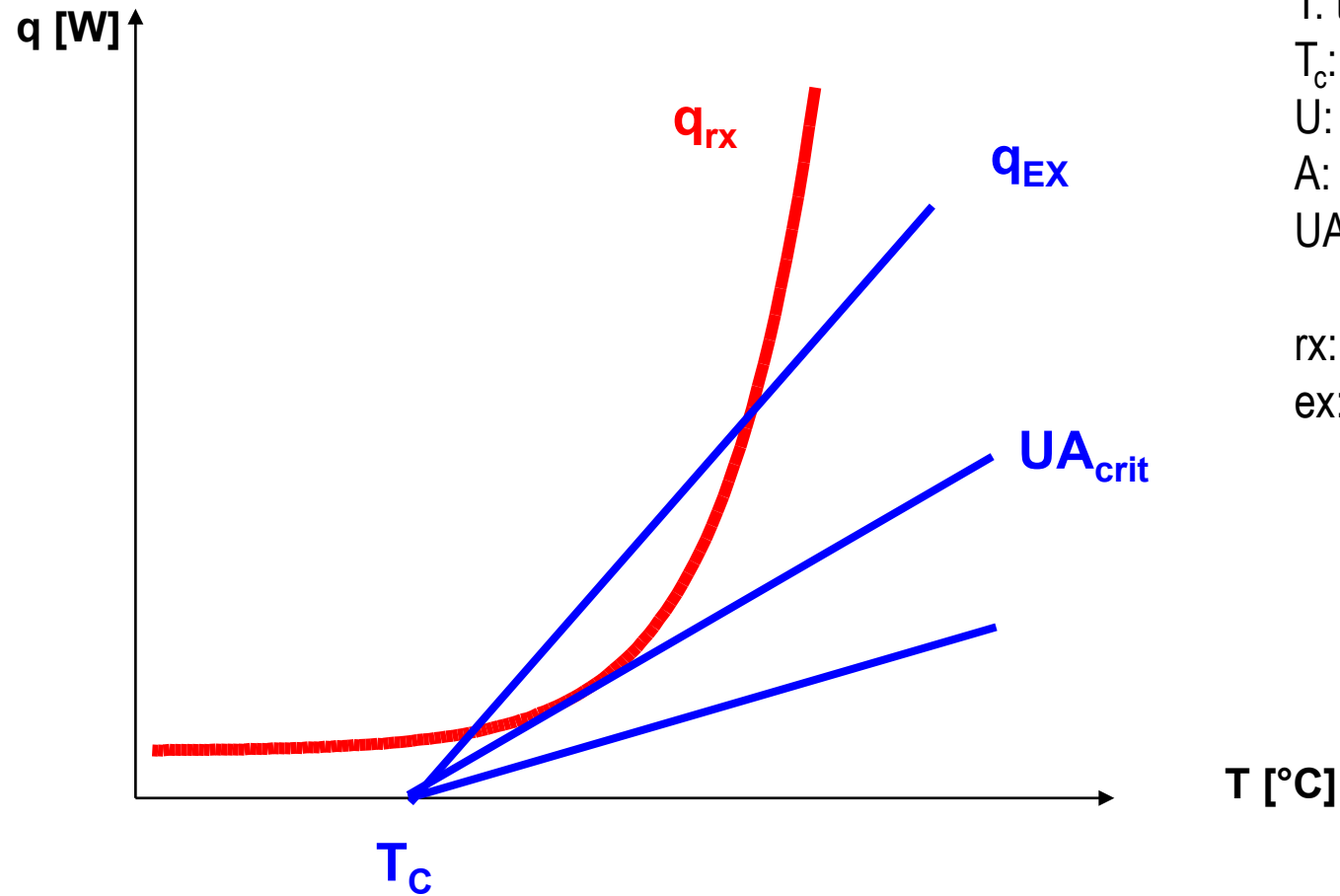
A : heat exchange area

m²

rx: reaction

ex: exchange

$$q_{EX} = UA(T_C - T)$$



q : heat flow

W

T : temperature

°C/K

T_c : temperature cooling media

U : heat transfer coefficient

W/(m²·K)

A : heat exchange area

m²

UA_{crit} : critical heat transfer coefficient-heat area

W/K

rx: reaction

ex: exchange

Key aspects Semenov Plot: normal operating conditions

- Heat production depends exponentially on T
 - Heat removal depends linearly on T
- Cooling capacity
- Heat production depends on V
 - Heat removal depends on A
- SCALE-UP
- Under normal operating conditions there is a stable and an unstable working point → need to work at the stable working point
 - Influence of UA (fouling, change of scale) and T_c (winter - summer)

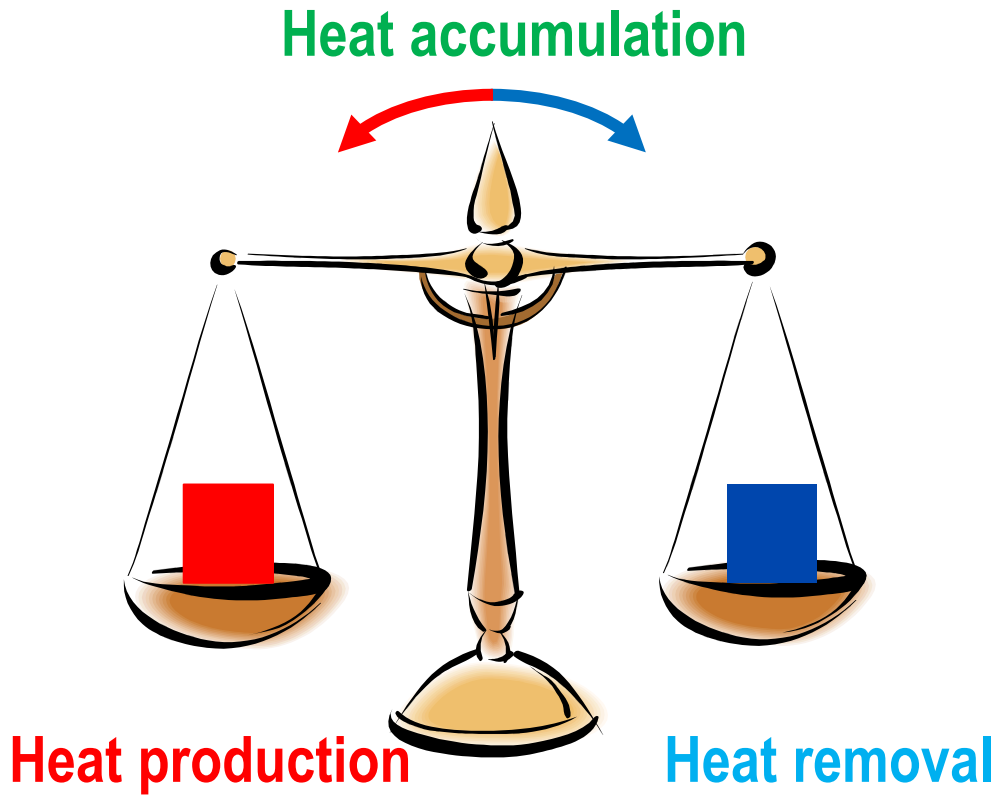
<https://youtu.be/sRuz9bzBrY>

Content Module 2

- Video/ introduction to the hazard
- Thermal Risks
 - Heat Balance
 - Failure Scenario
- Criticality
- Assessment Procedure



Chapters 2 and 3



$$\frac{dT}{dt} = k(1 - X_A)^n c_{A0}^{n-1} \Delta T_{ad} - \frac{UA(T - T_c)}{\rho V c'_p}$$

T: temperature

K

t: time

s

k: rate constant

$s^{-1} \text{mol}^{1-n} \text{l}^{n-1}$

X: conversion

-

n: order of the reaction

-

c_{A0} : starting concentration of A

mol/l

ΔT_{ad} : adiabatic temperature rise

K or °C

U: heat transfer coefficient

$\text{W}/(\text{m}^2 \cdot \text{K})$

A: heat exchange area

m^2

T_c : temperature cooling media

K

ρ : density

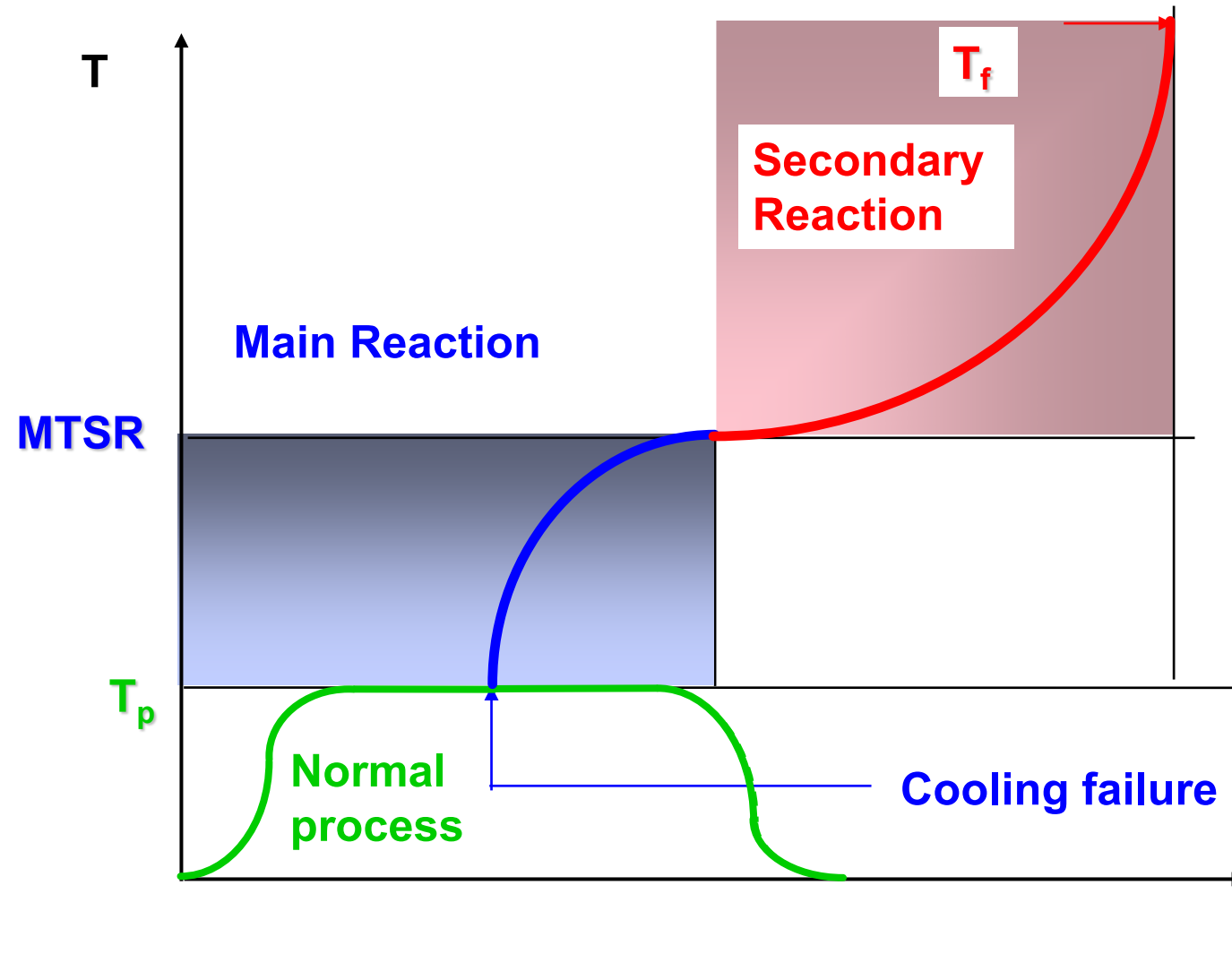
kg/l

c'_p : specific heat capacity

$\text{J}/(\text{kg} \cdot \text{K})$

V: volume

l



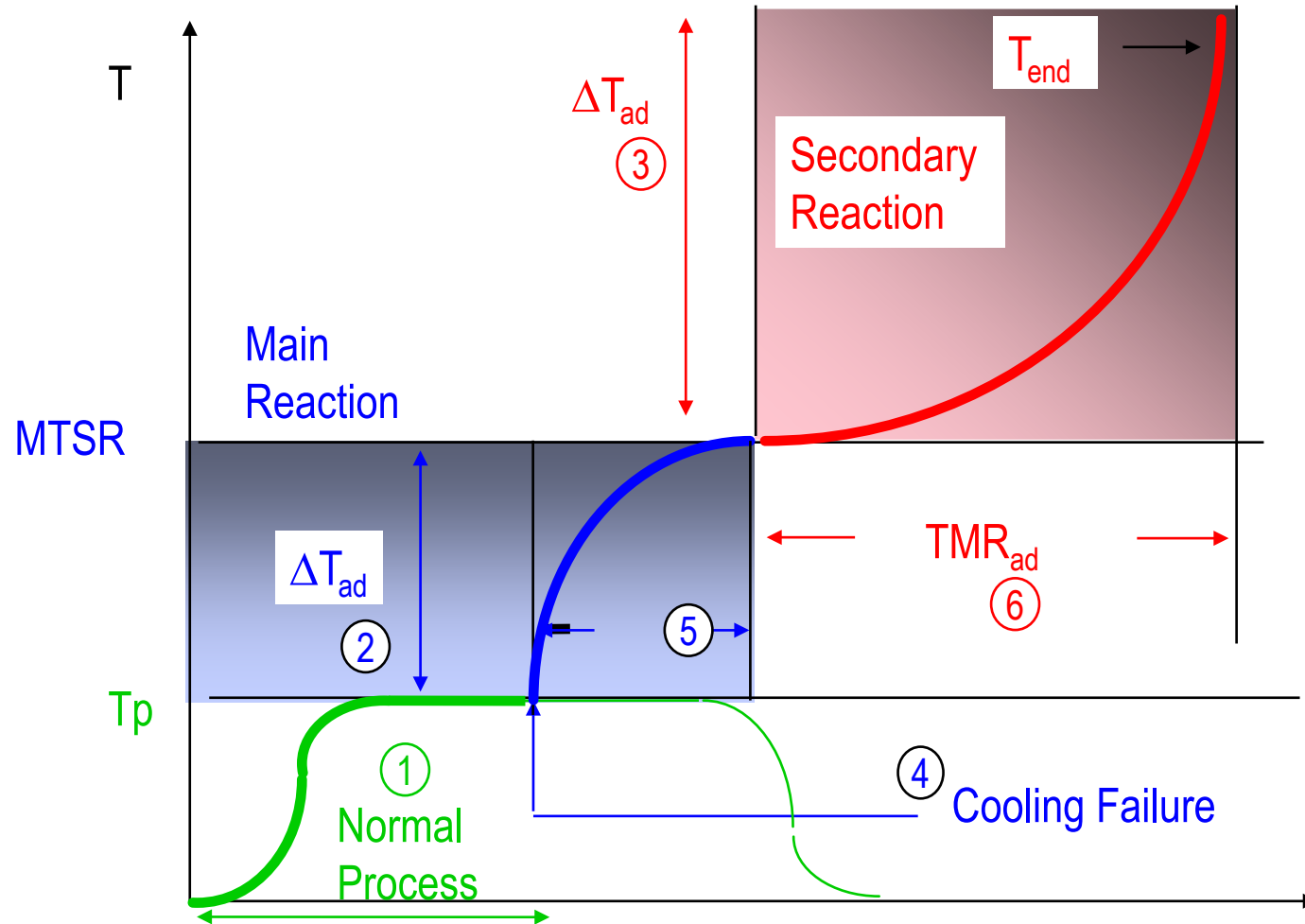
T_p : process temperature

MTSR: Maximal Temperature of the Synthesis Reaction

T_f : final temperature or end temperature T_{end}

Cooling Failure Scenario

25



T_p : process temperature

MTSR: Maximal Temperature of the Synthesis Reaction

ΔT_{ad} : adiabatic temperature rise

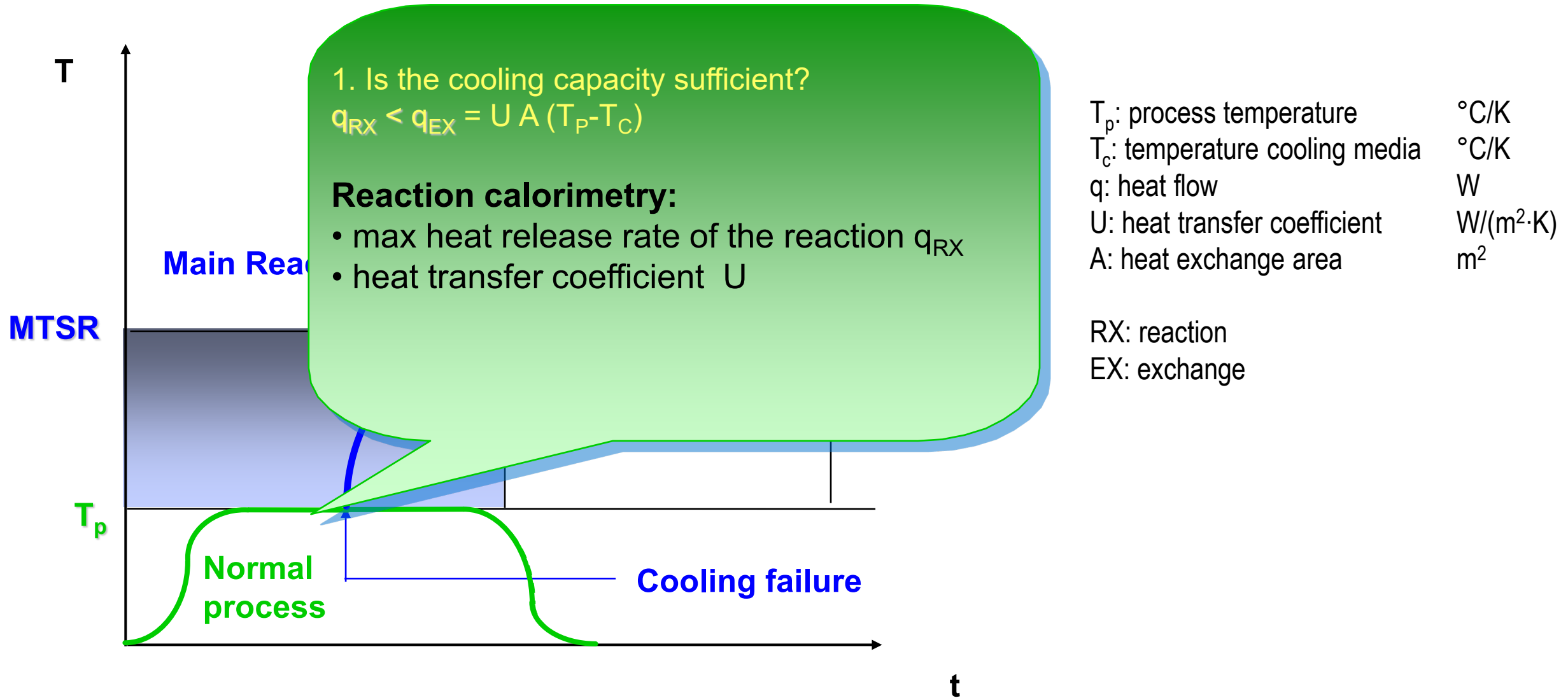
T_f : final temperature or end temperature T_{end}

TMR_{ad}: Time to Maximum Rate under adiabatic conditions

Adiabatic conditions: no heat exchange with the surrounding, the whole energy stays in the system (reaction mass) and leads to a temperature increase → neglecting heat losses of a real system during a cooling failure.

Time

1	Is the cooling capacity sufficient to remove the heat released by the reaction under normal operating conditions?	4	When does the cooling failure have the worst consequences?
2	What temperature may be reached after runaway of the main reaction ?	5	How long does the runaway of the main reaction take?
3	What temperature may be reached after runaway of secondary reaction	6	How long does the runaway of the secondary reaction take?



2. Which temperature can be reached after runaway of the main reaction

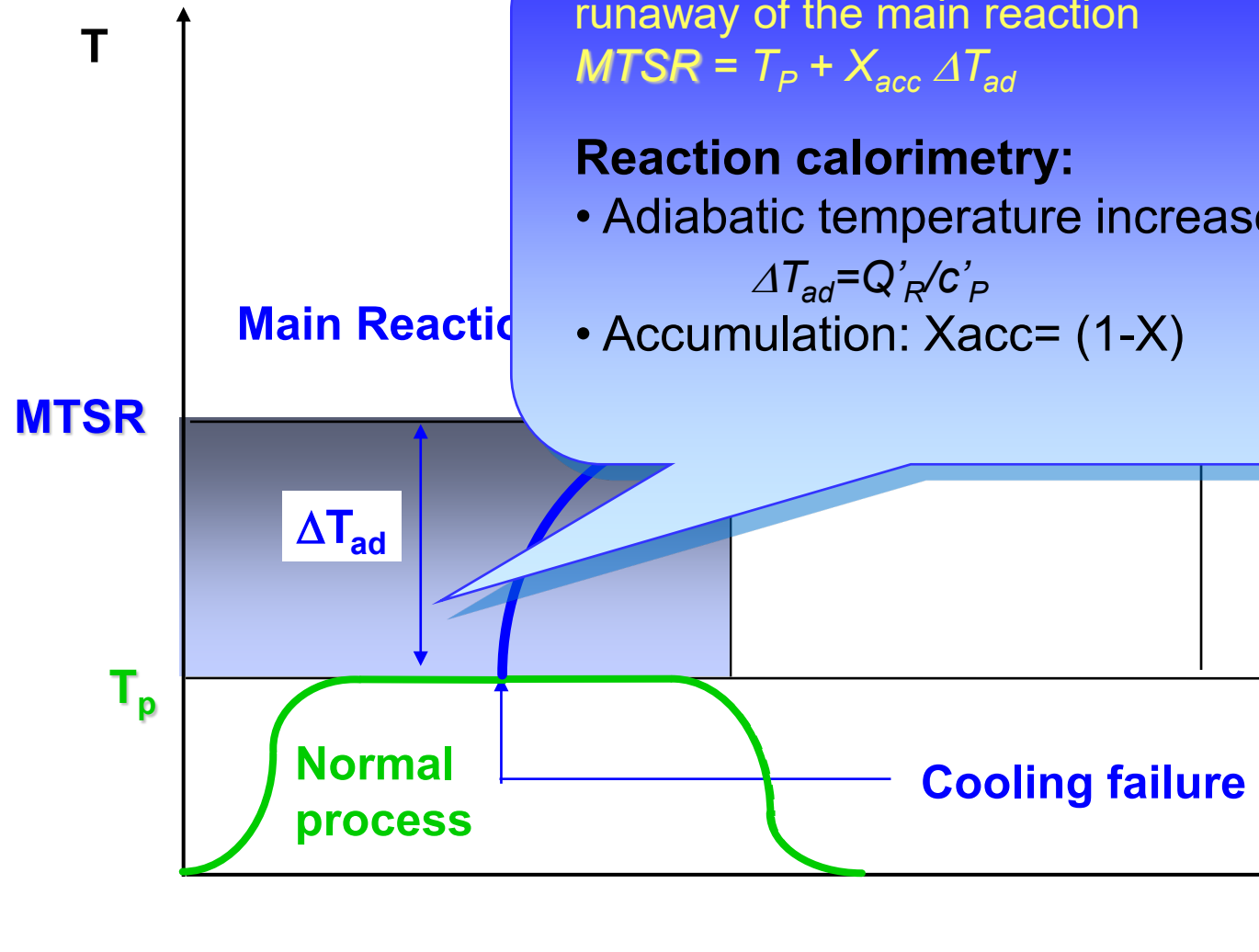
$$MTSR = T_p + X_{acc} \Delta T_{ad}$$

Reaction calorimetry:

- Adiabatic temperature increase

$$\Delta T_{ad} = Q'_R / c'_p$$

- Accumulation: $X_{acc} = (1 - X)$



MTSR: maximal temperature
of the synthesis reaction °C/K

T_p : process temperature °C/K

X_{acc} : accumulation -

ΔT_{ad} : adiabatic temperature
rise °C/K

Q'_R : specific reaction energy kJ/kg

c'_p : specific heat capacity kJ/(kg·K)

X : conversion -

Adiabatic Temperature Rise

$$\Delta T_{ad} = \frac{Q'}{c_p} \quad \left[\frac{\text{kJ} \cdot \text{kg}^{-1}}{\text{kJ} \cdot \text{kg}^{-1} \cdot \text{K}^{-1}} \right]$$

ΔT_{ad} : adiabatic temperature rise

°C/K

Q' : specific reaction energy

kJ/kg

c_p : specific heat capacity

kJ/(kg·K)

ΔH_r : molar reaction enthalpy

kJ/mol

c_{A0} : starting concentration of A

mol/m³

ρ : density

kg/m³

$$\Delta T_{ad} = \frac{(-\Delta H_R) \cdot c_{A0}}{\rho \cdot c_p} \quad \left[\frac{\text{kJ} \cdot \text{mol}^{-1} \cdot \text{mol} \cdot \text{m}^{-3}}{\text{kg} \cdot \text{m}^{-3} \cdot \text{kJ} \cdot \text{kg}^{-1} \cdot \text{K}^{-1}} \right]$$

Conclusion: ΔT_{ad} is given for one concentration of starting material. If the concentration is changed, then the adiabatic temperature rise changes accordingly

Severity: Temperature Scale: Heat Capacity

- Heat Capacity: J.K^{-1}
- Specific Heat Capacity: $\text{J.kg}^{-1}.\text{K}^{-1}$
- Mixture with i components and mass M_i

$$Cp' = \frac{\sum_i M_i \cdot Cp'_i}{\sum_i M_i}$$

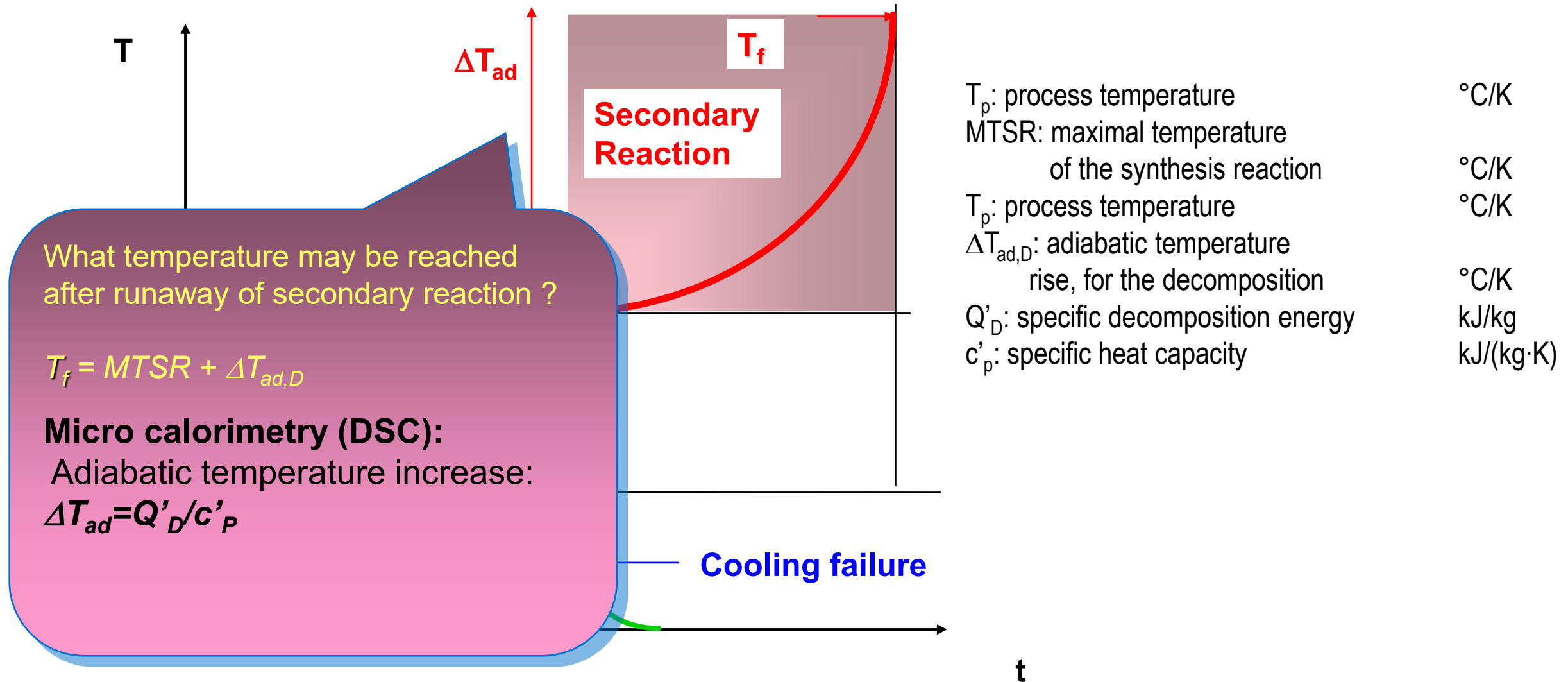
- Typical values for heat capacity

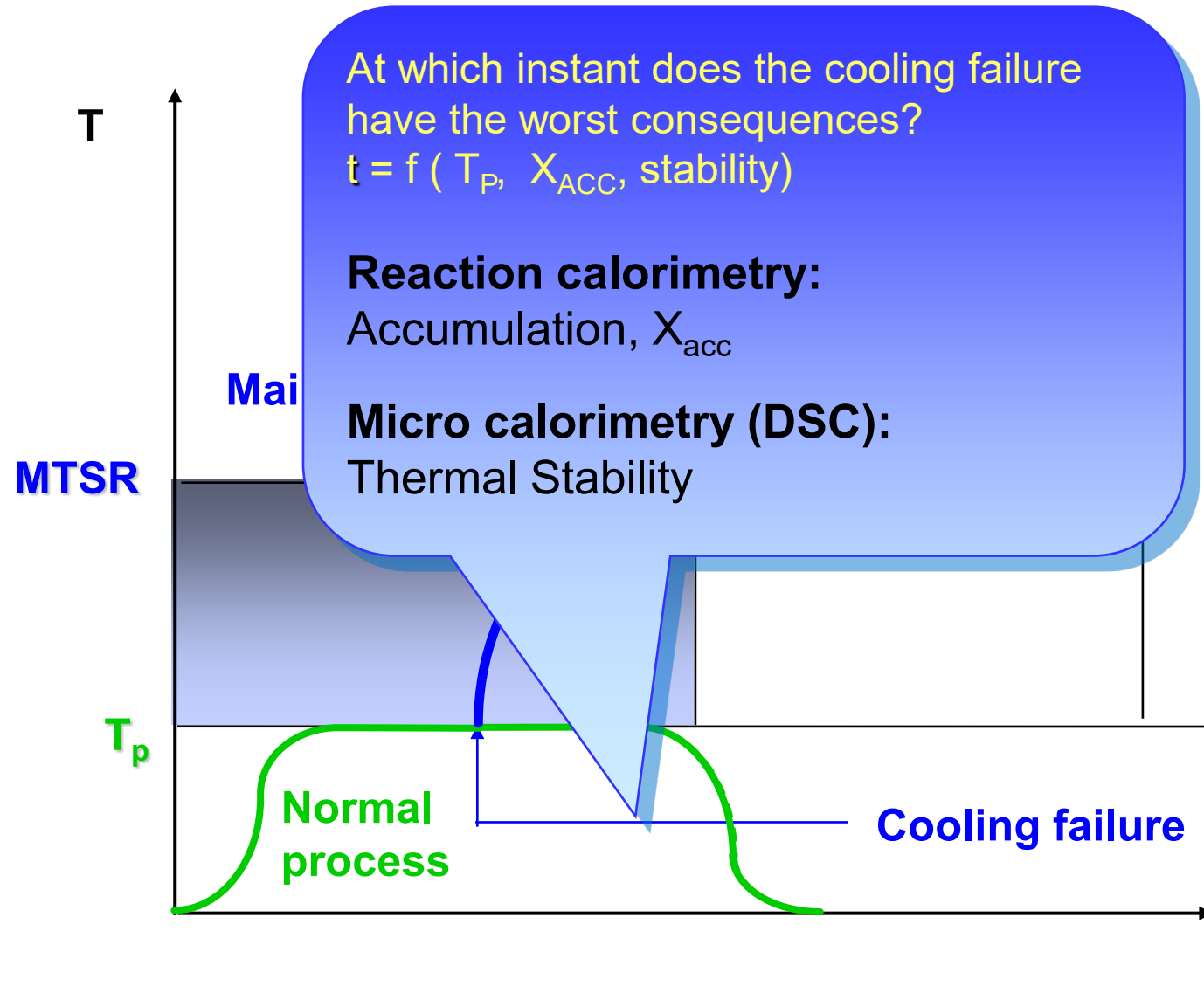
Water: $4.2 \text{ kJ.kg}^{-1}.\text{K}^{-1}$

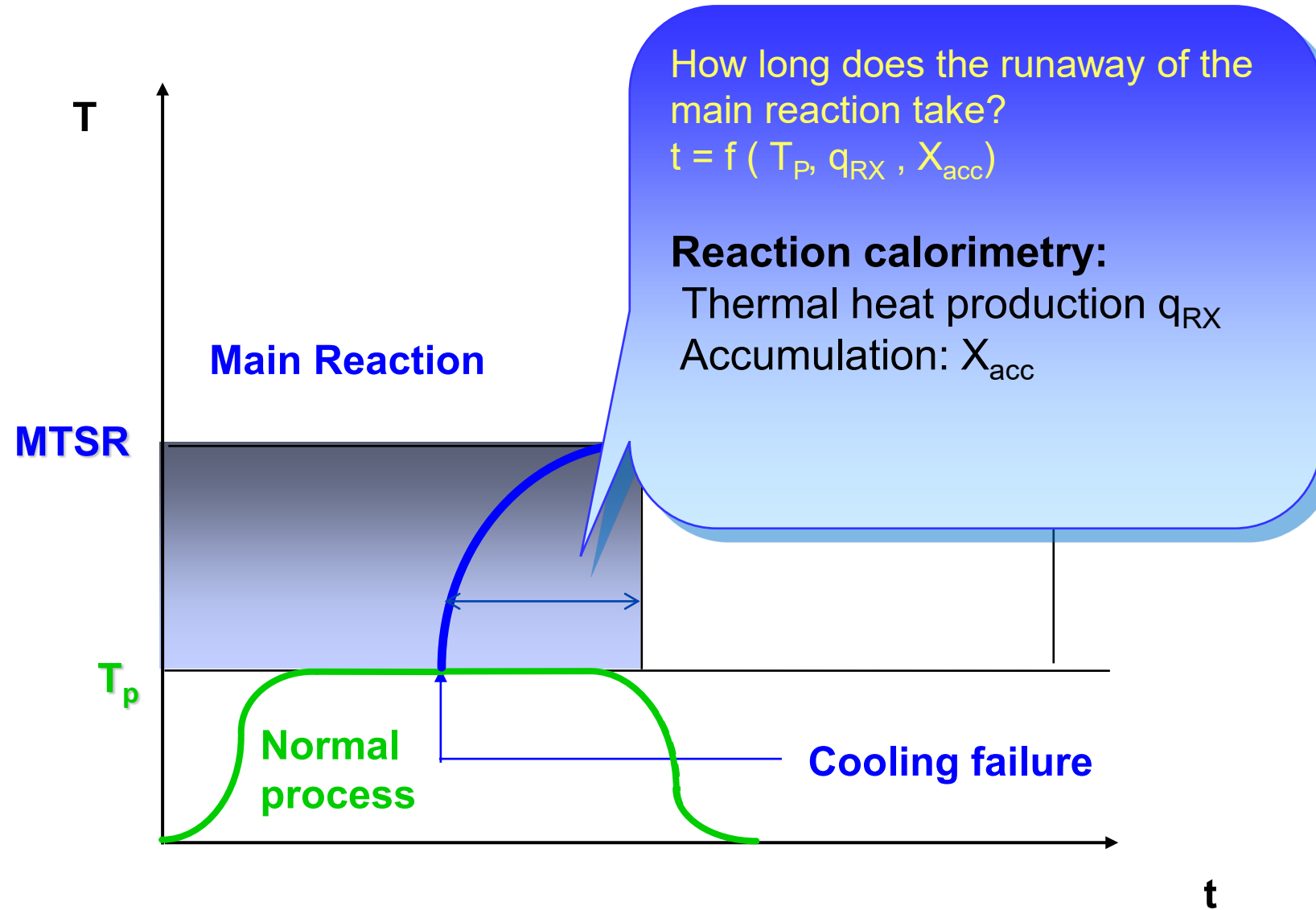
Liquid organic substances: $1.8 \text{ kJ.kg}^{-1}.\text{K}^{-1}$

Sulfuric acid: $1.3 \text{ kJ.kg}^{-1}.\text{K}^{-1}$

Solid organic substances: $1.3 \text{ kJ.kg}^{-1}.\text{K}^{-1}$





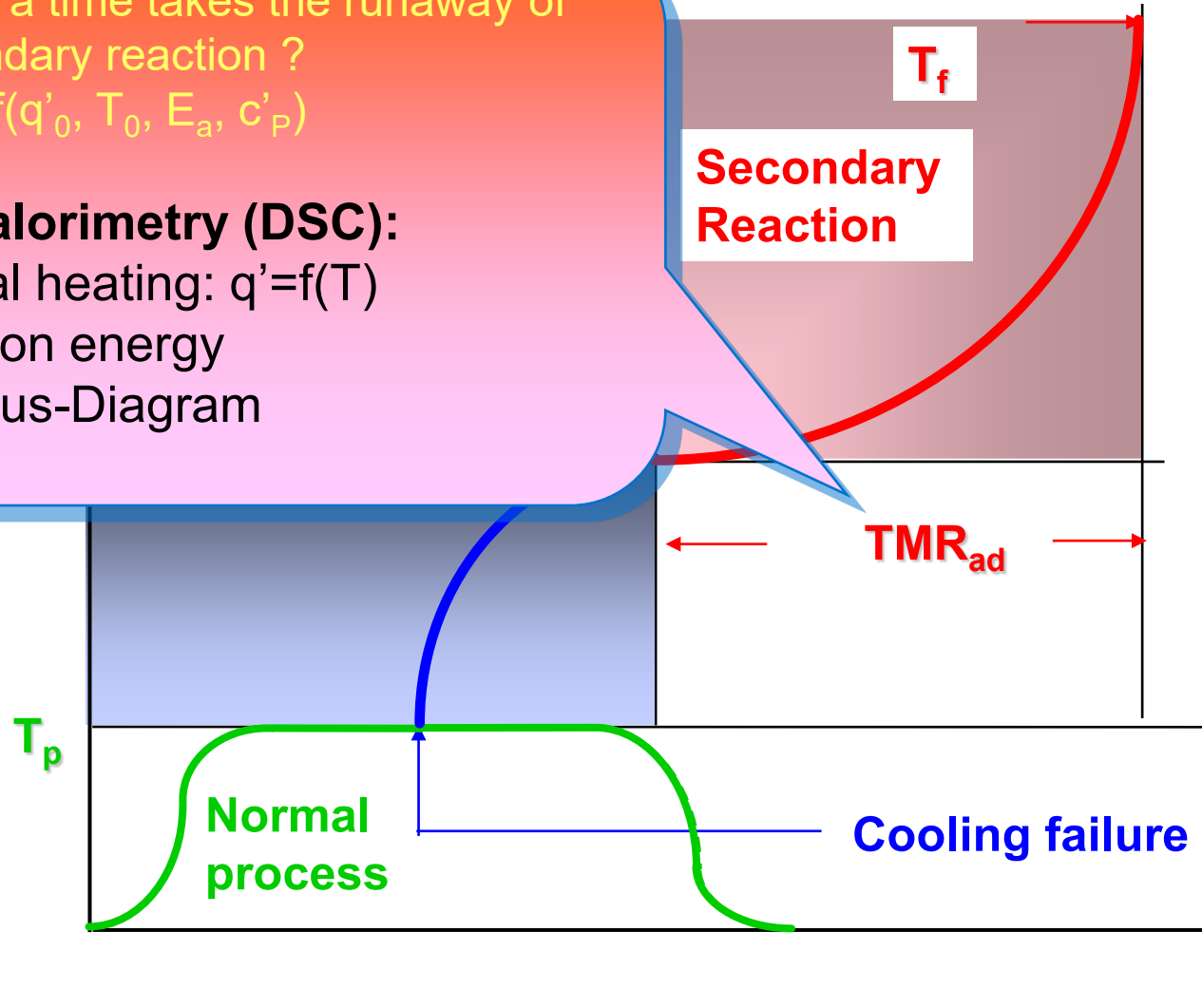


How long a time takes the runaway of the secondary reaction ?

$$\text{TMR}_{\text{ad}} = f(q'_0, T_0, E_a, c'_p)$$

Micro calorimetry (DSC):

- Thermal heating: $q' = f(T)$
- Activation energy
- Arrhenius-Diagram



TMR_{ad} : time of maximum rate
under adiabatic conditions

s or h
K

T_0 : reference temperature

q'_0 : specific heat release rate at the
reference temperature

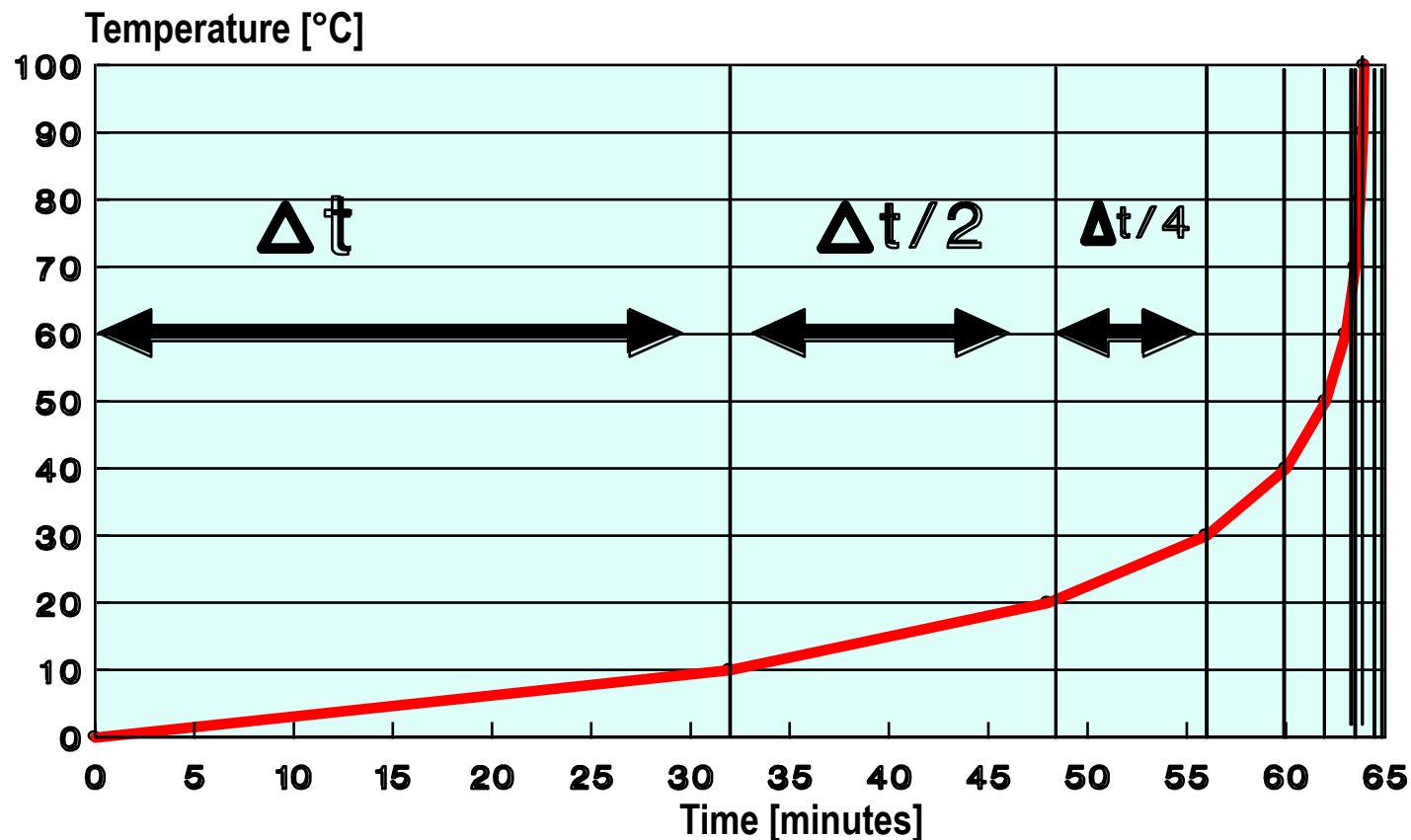
W/kg
J/mol

E_a : activation energy

c'_p : specific heat capacity

kJ/(kg·K)

Adiabatic temperature course van't Hoff rule: doubling reaction rate each 10°C



Δt : initial time interval for an increase in temperature of 10 °C, in this case 32 minutes

Very useful rule for estimations of TMRad but it is not conservative

Time to Maximum Rate under Adiabatic Conditions: TMR_{ad}

Approximate estimation in seconds

$$TMR_{ad}(T_0) = \frac{c'_P \cdot R \cdot T_0^2}{q'_{(T_0)} \cdot E_a}$$

$TMR_{ad}(T_0)$	Time to maximum rate under adiabatic conditions at T_0
c'_P	specific heat capacity [J / kg / K]
R	universal gas constant 8.314 J / (mol. K)
T_0	considered temperature (K)
$q'_{(T_0)}$	specific heat release rate at T_0 [W / kg]
E_a	activation energy [J / mol]

To draw the **cooling failure scenario**, the temperature T_0 that has to be considered is the MTSR

→ The **TMRad** is calculated for the MTSR

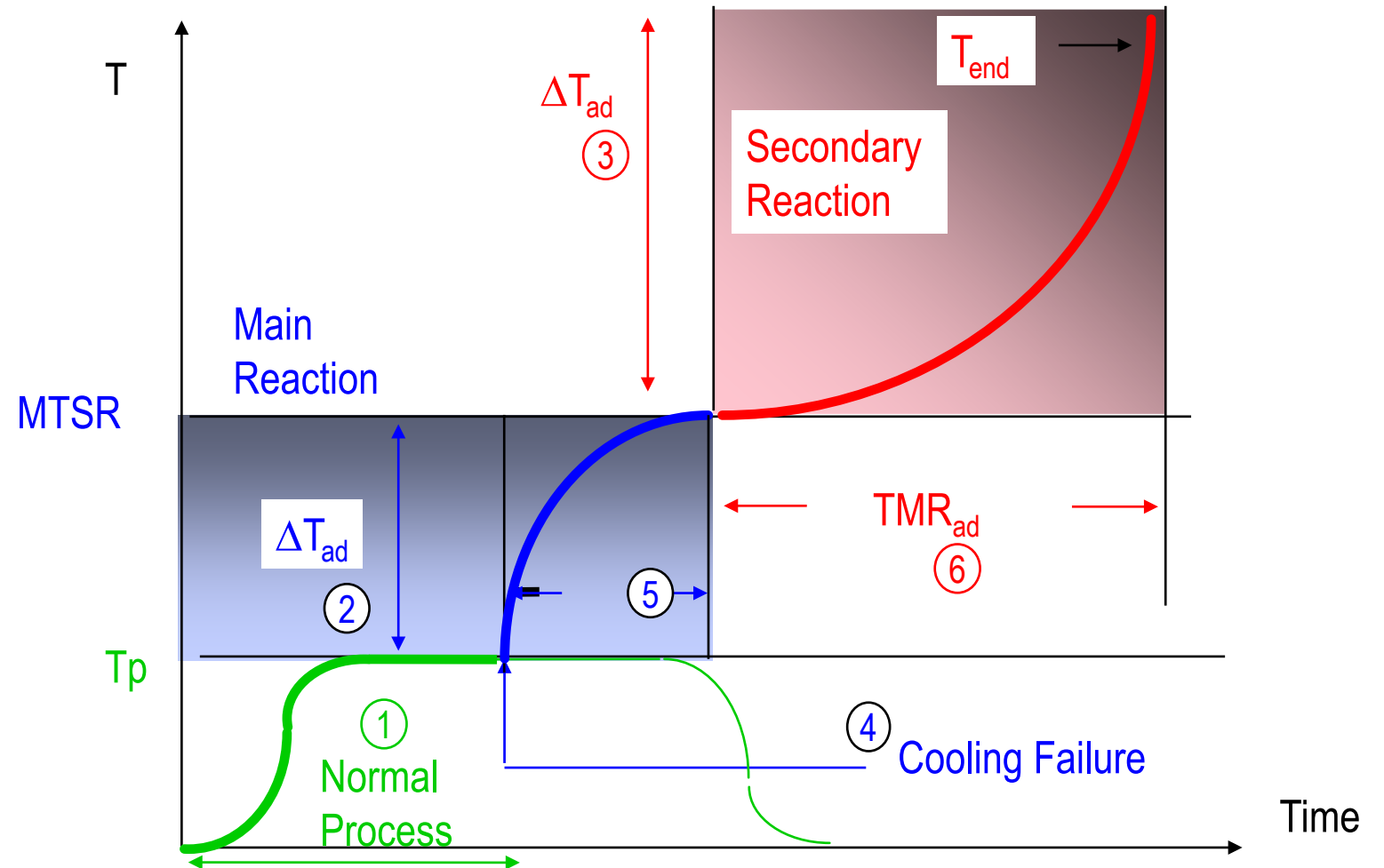
Thermal Risk and cooling failure scenario

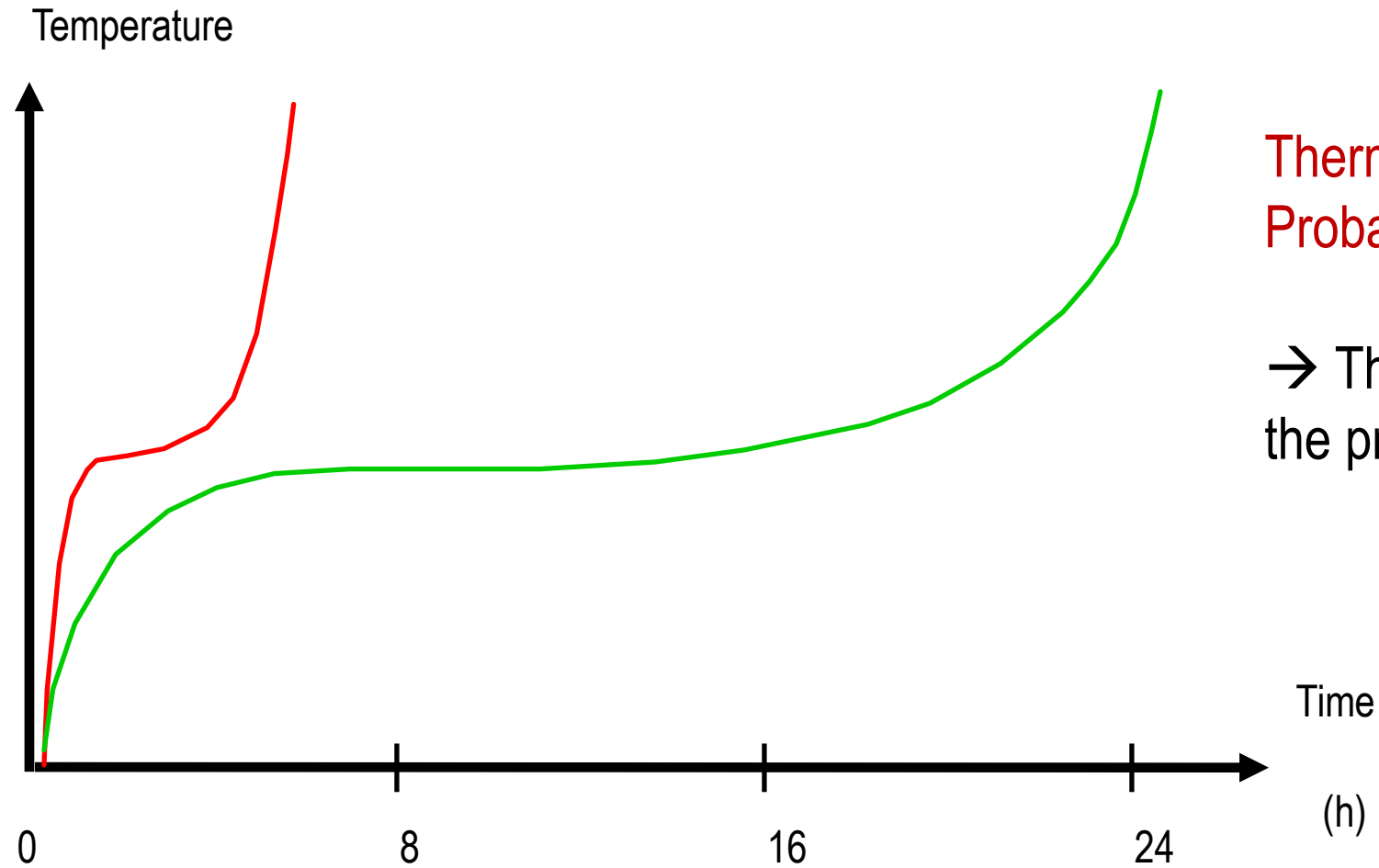
How can we evaluate the Thermal Risk?

Risk = probability x severity

Severity of a runaway = ?

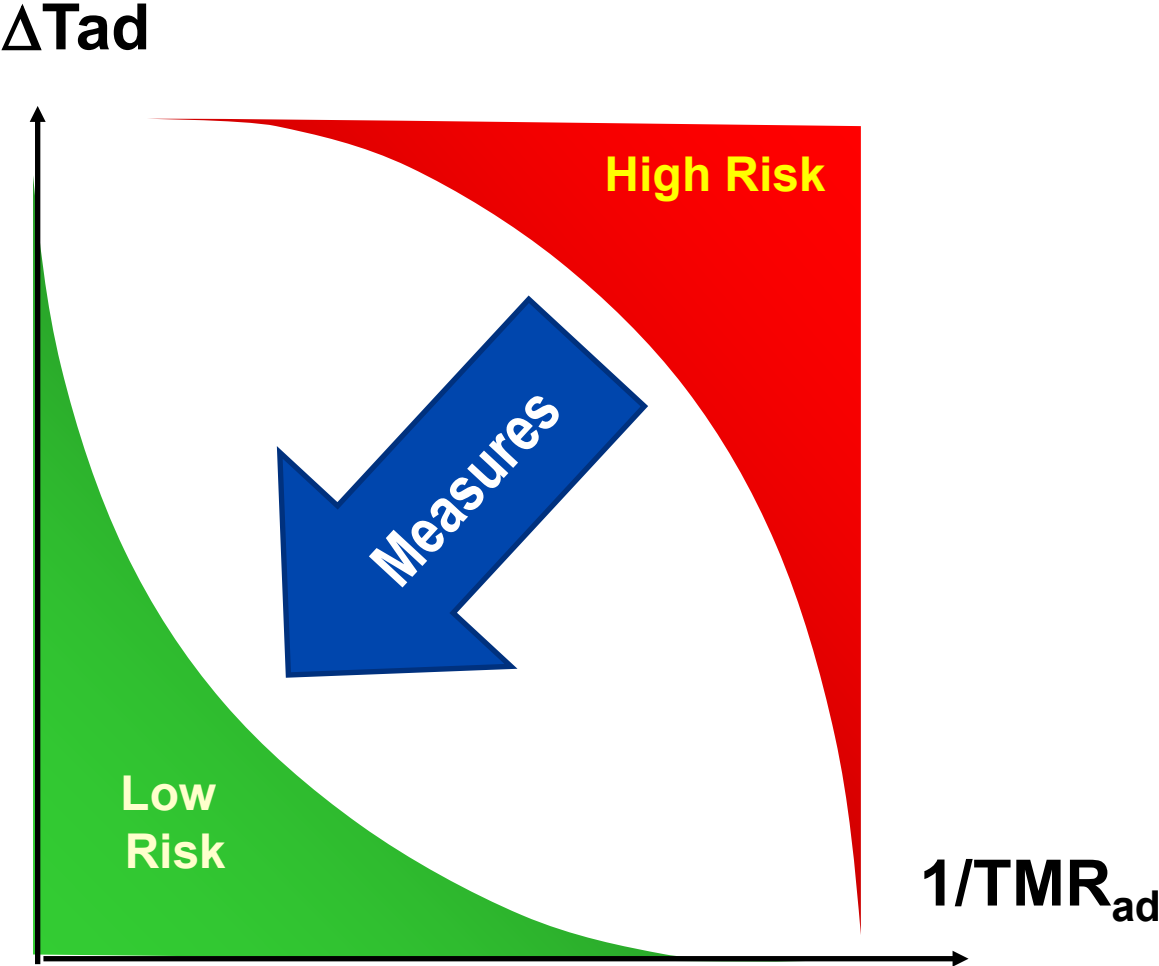
Probability of a runaway = ?





Thermal Risk:
Probability of a runaway = Time Scale

→ The longer the TMRad, the lower the probability



Criteria for probability and consequences

Criteria	Consequences	Probability
High	$\Delta T_{ad} > 200^{\circ}\text{C}$	TMRad < 8 h
Medium	$50^{\circ}\text{C} < \Delta T_{ad} < 200^{\circ}\text{C}$	8 h < TMRad < 24 h
Low	$\Delta T_{ad} < 50^{\circ}\text{C}$ and no pressure	TMRad > 24 h

Criteria based on experience

Criteria for the probability valid for controlled reaction masses (in reactors), not valid for example for storage or transport.

Criteria for risk evaluation

Consequences	High	$\Delta T_{ad} > 200K$			
	Medium	$50K < \Delta T_{ad} < 200K$			
	Low	$\Delta T_{ad} < 50K$ And no pressure			
			$TMR_{ad} \geq 24h$	$8h < TMR_{ad} < 24$	$TMR_{ad} \leq 8h$
			Low	Medium	High
			Probability		

	Low risk, risk acceptable
	Medium risk. Apply ALARP principle (ALARP: as low as reasonable practicable)
	High risk. Risk unacceptable

- A decomposition reaction with a specific energy of 500 J/g releases 10 W/kg at a temperature of 150°C.
- Translating in terms of thermal risk:
 - Consequences: determine the adiabatic temperature increase: $\Delta T_{ad} = \frac{Q'}{c_p'}$
 - Probability: determine TMR_{ad} : $TMR_{ad}(T_0) = \frac{c_P' \cdot R \cdot T_0^2}{q'_{(T_0)} \cdot E_a}$
- A decomposition, able to raise the temperature by 250 °C, leads to a severe thermal explosion within less than one hour, starting from 150 °C.

Content Module 2

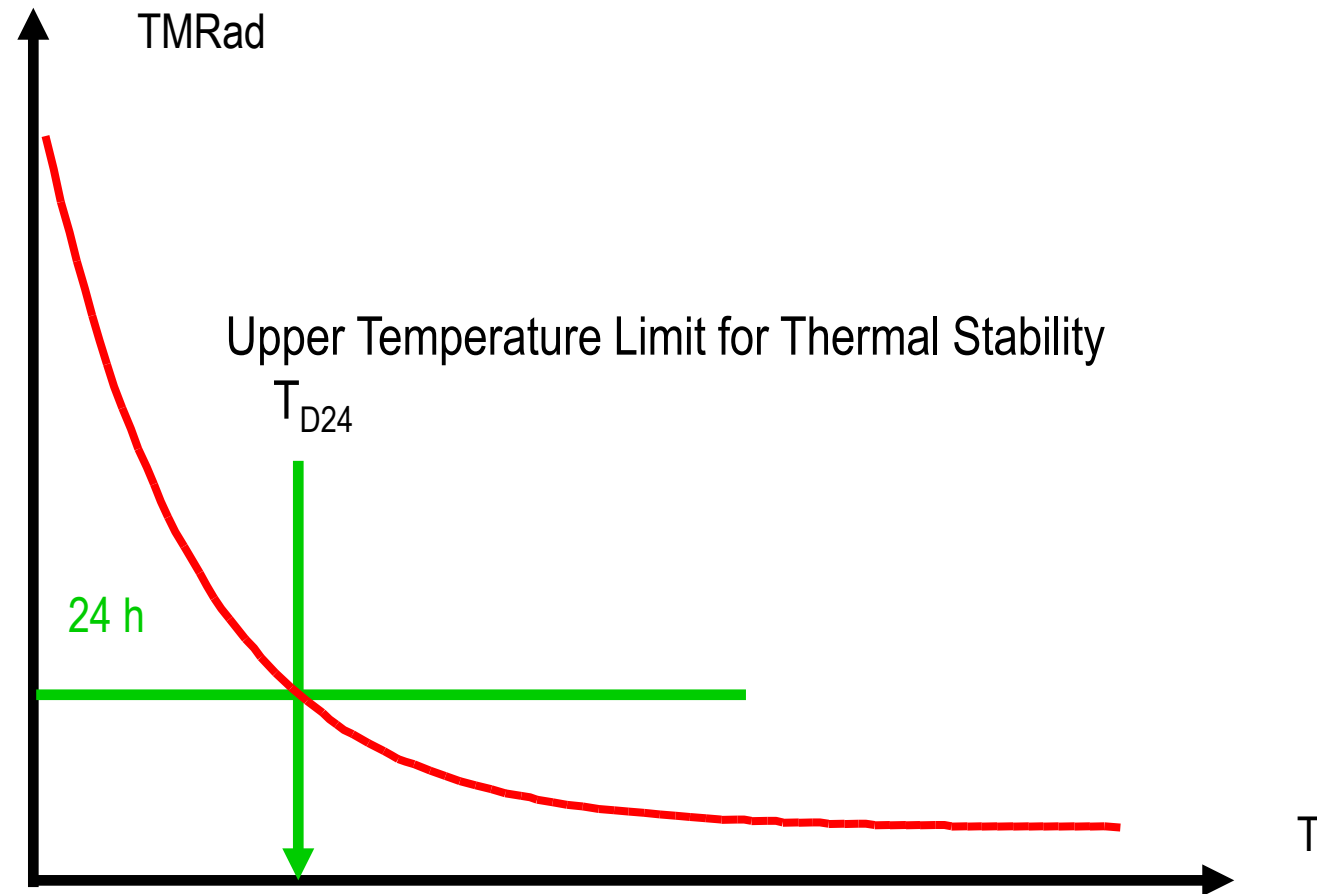
- Video/ introduction to the hazard
- Thermal Risks
 - Heat Balance
 - Failure Scenario
- Criticality
- Assessment Procedure



Chapters 2 and 3

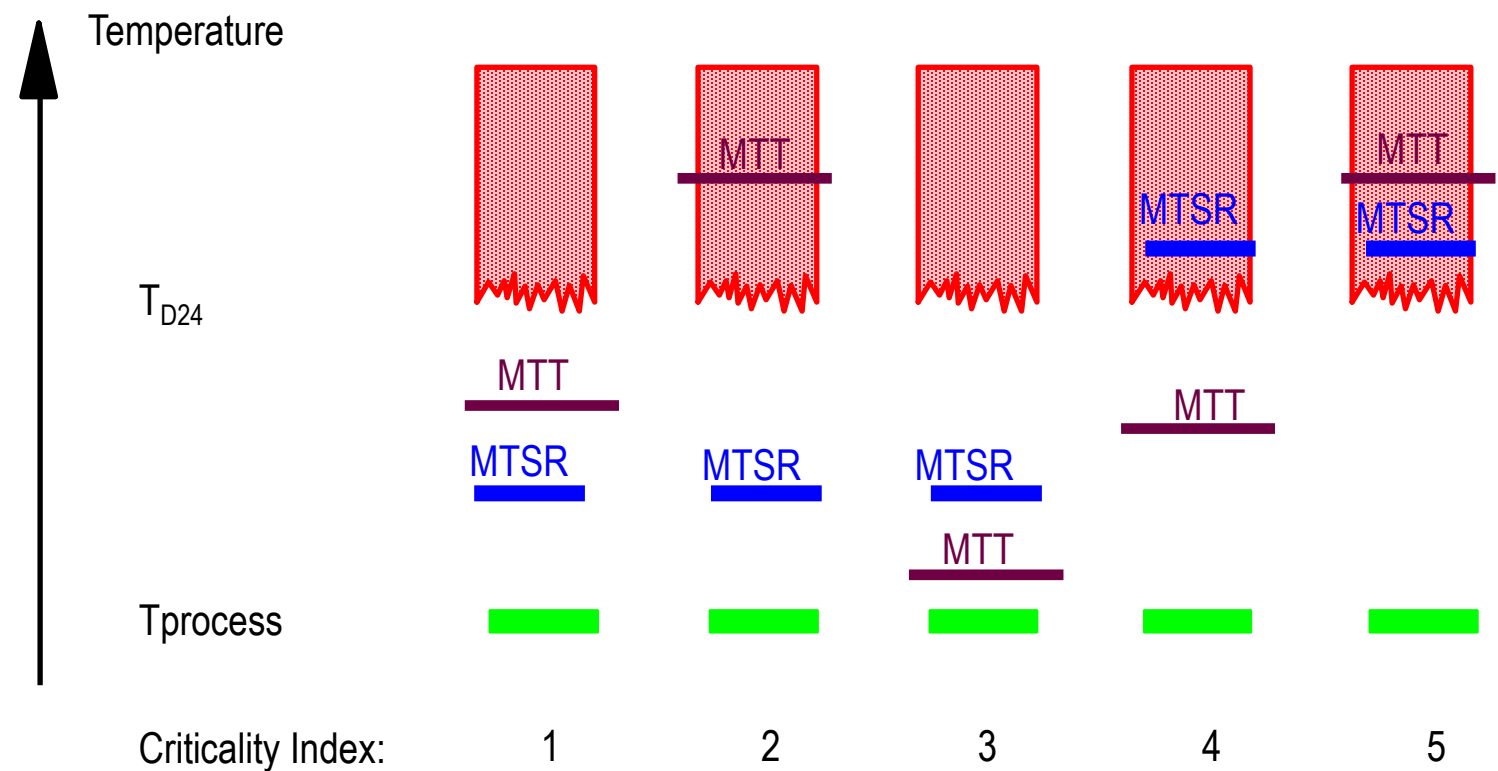
TMRad as a Function of Temperature

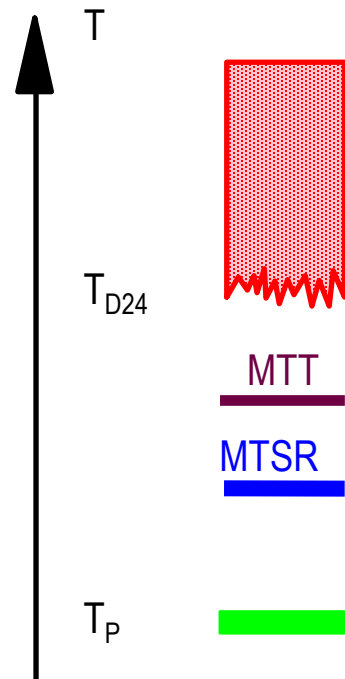
45



Characteristic Temperatures

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



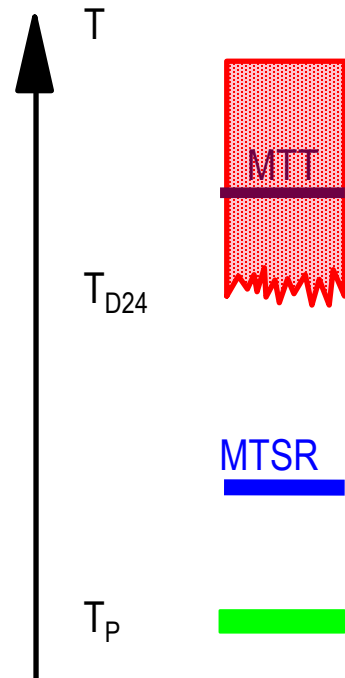


Decomposition is not triggered.

MTT is not reached

No special Measure required.

Boiling point could serve as a safety barrier

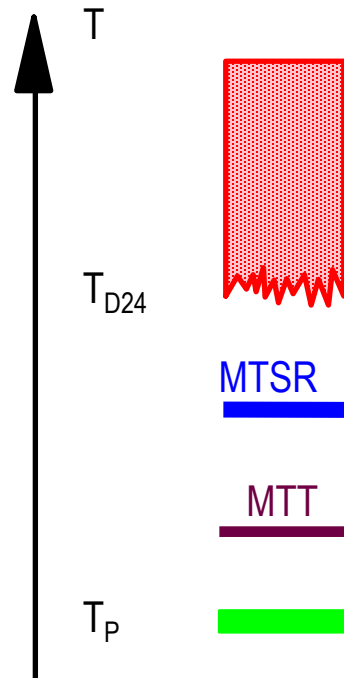


Decomposition is not triggered.

MTT is not reached

No special Measure required.

Avoid heat accumulation conditions
Boiling point could *not* serve as a safety barrier.

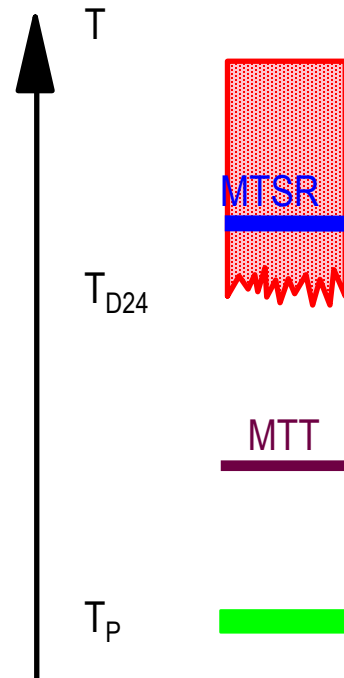


Decomposition is not triggered.

MTT is reached

Risk reducing measures are required.

**Boiling point could serve as a safety barrier.
Design system for that purpose**

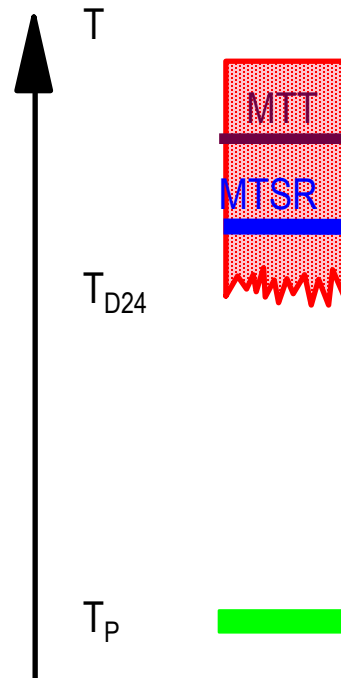


Decomposition could be triggered.

MTT is reached

Risk reducing measures required.

Boiling point could serve as a safety barrier to avoid triggering the decomposition reaction. Design system for that purpose



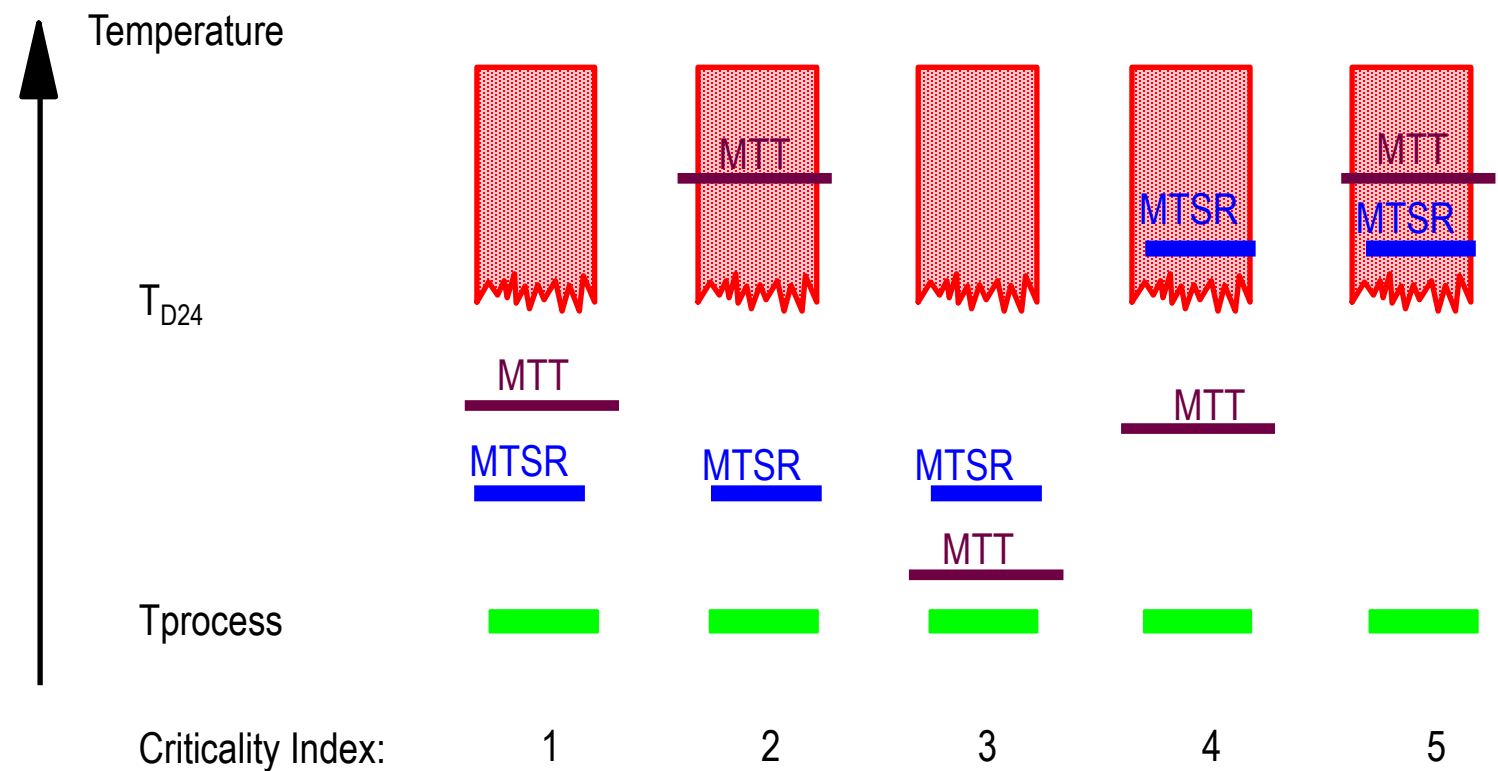
Decomposition is triggered.

MTT is reached

Risk reducing measures required.

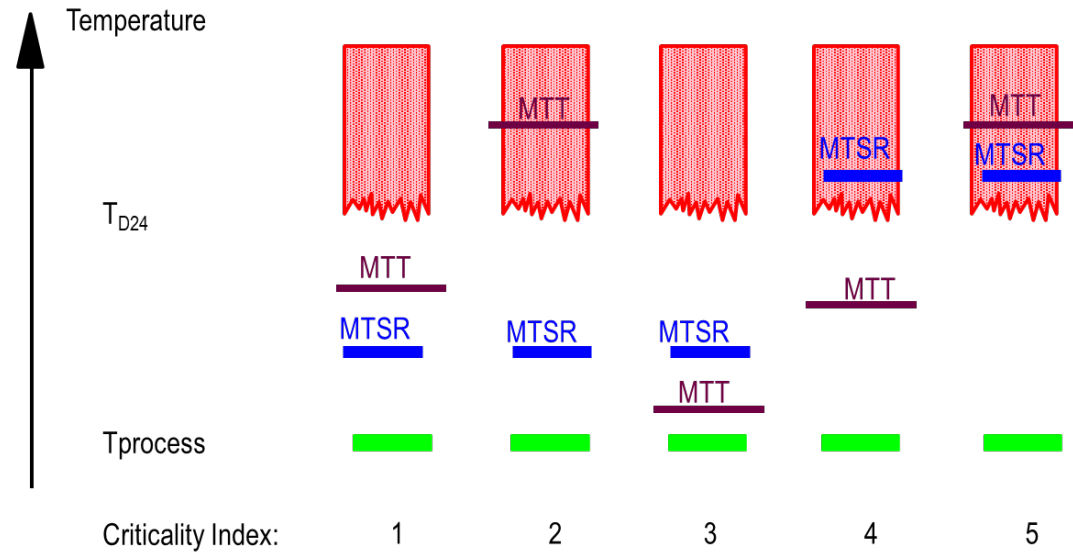
Emergency measures required.

Consider redesigning the process

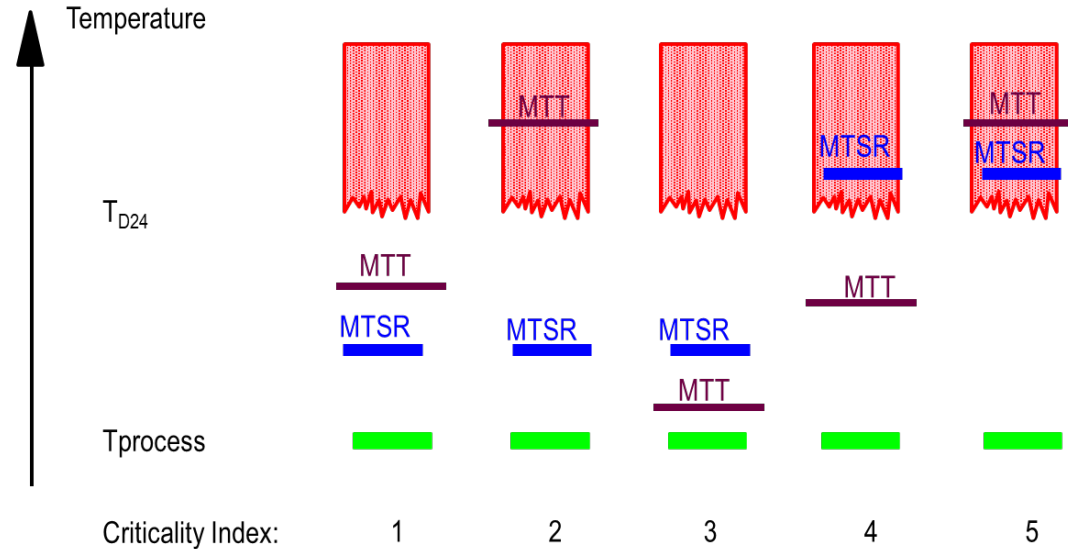


Criticality classes

- If you have a criticality class 5 process, what can you change to make it less hazardous?
- Write down 3 possible changes



- What is the hazard linked with criticality 3 processes?
- What are the benefits and disadvantages of having a boiling temperature (MTT) close to T_{process} ?
- What are the benefits and disadvantages of having a boiling temperature (MTT) close to MTSR?
- So what is best, a boiling temperature close to T_{process} or to MTSR?

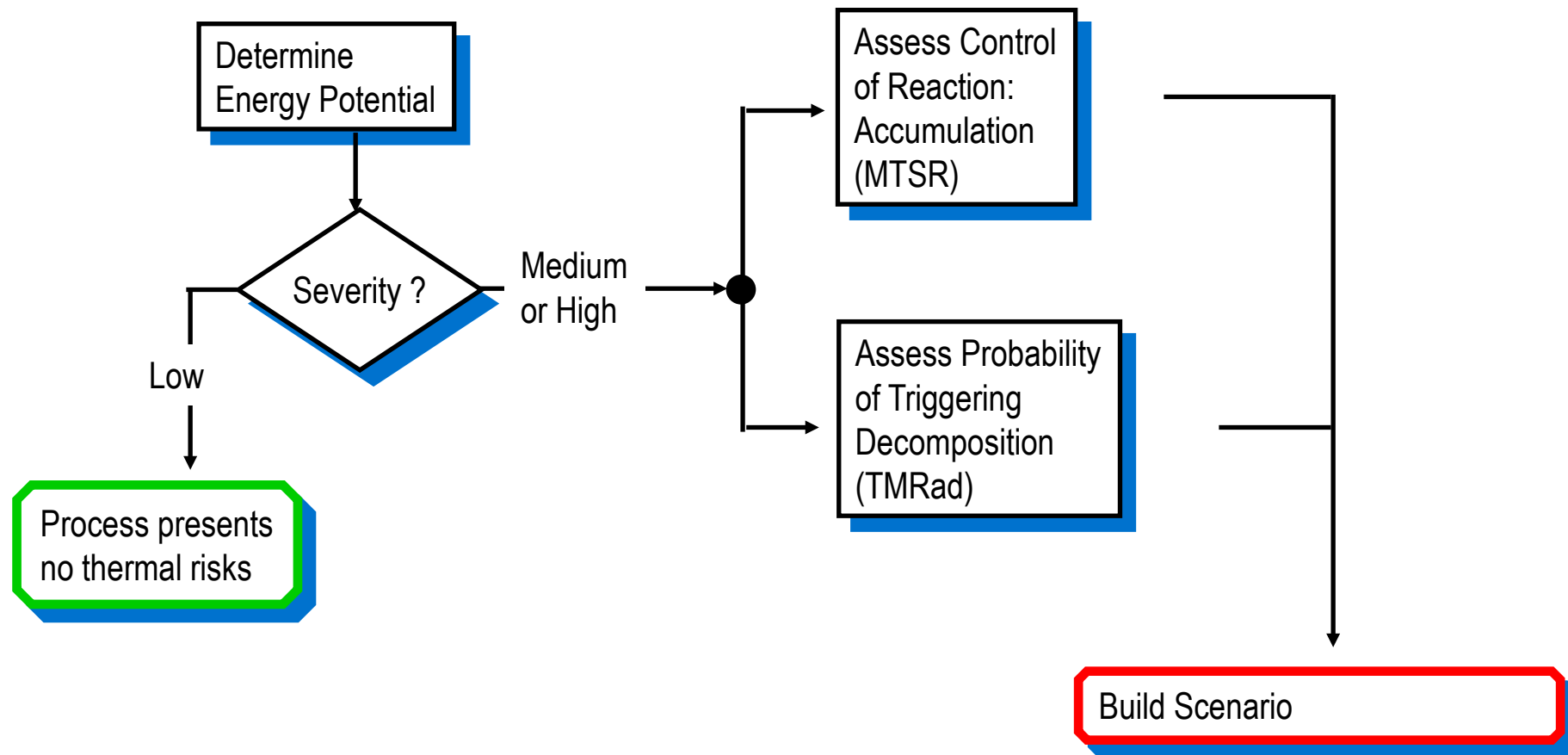


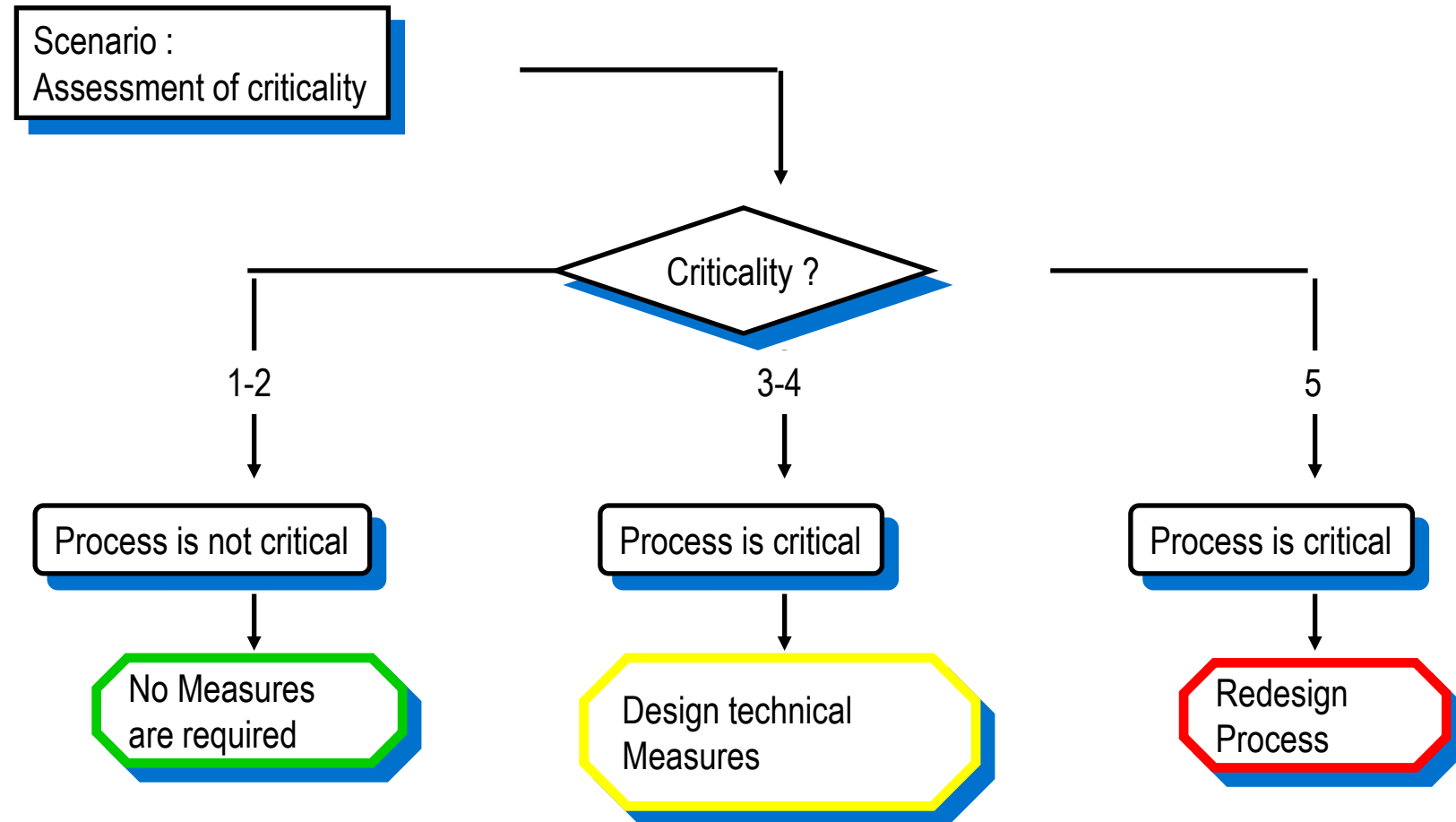
Content Module 2

- Video/ introduction to the hazard
- Thermal Risks
 - Heat Balance
 - Failure Scenario
- Criticality
- Assessment Procedure



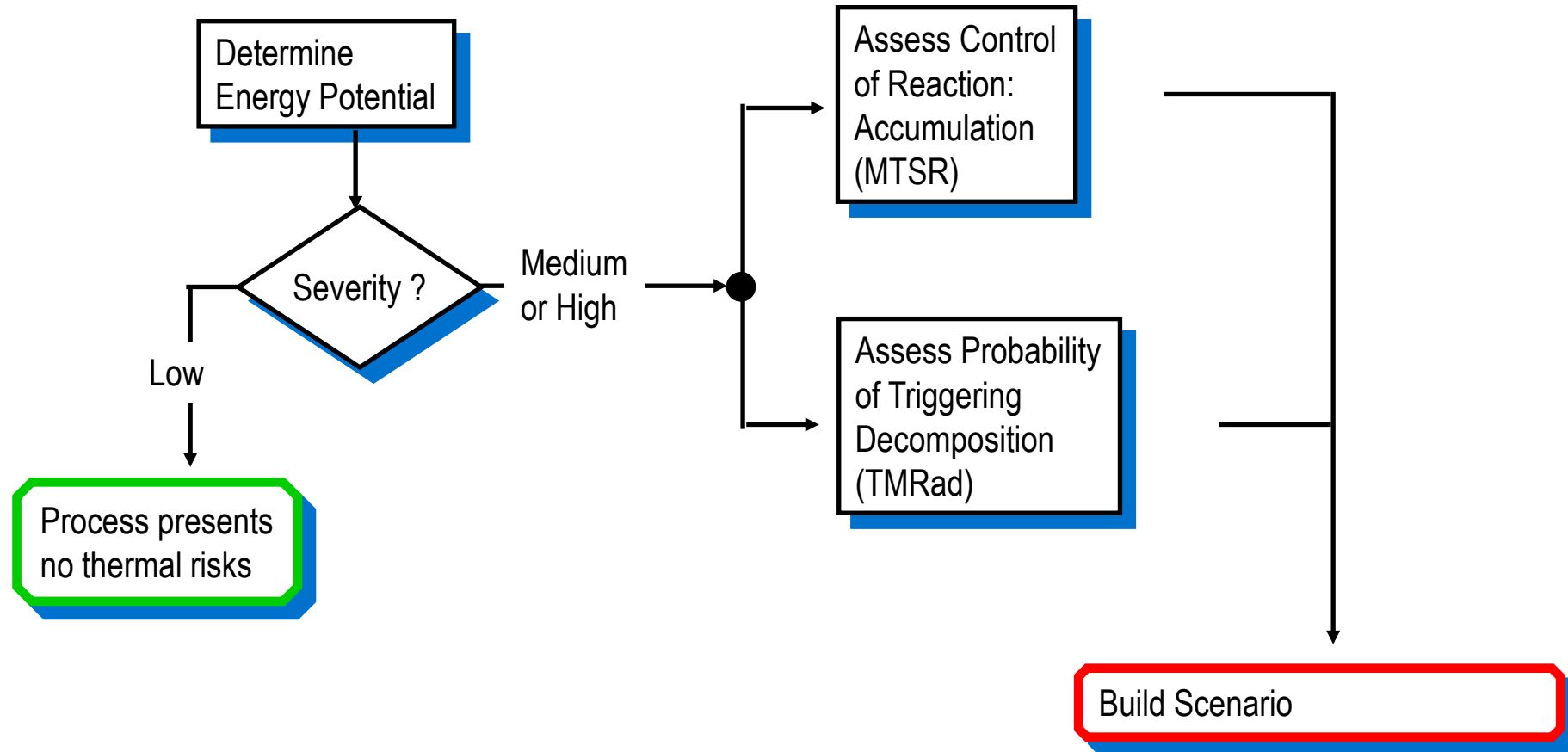
Chapters 2 and 3





Example

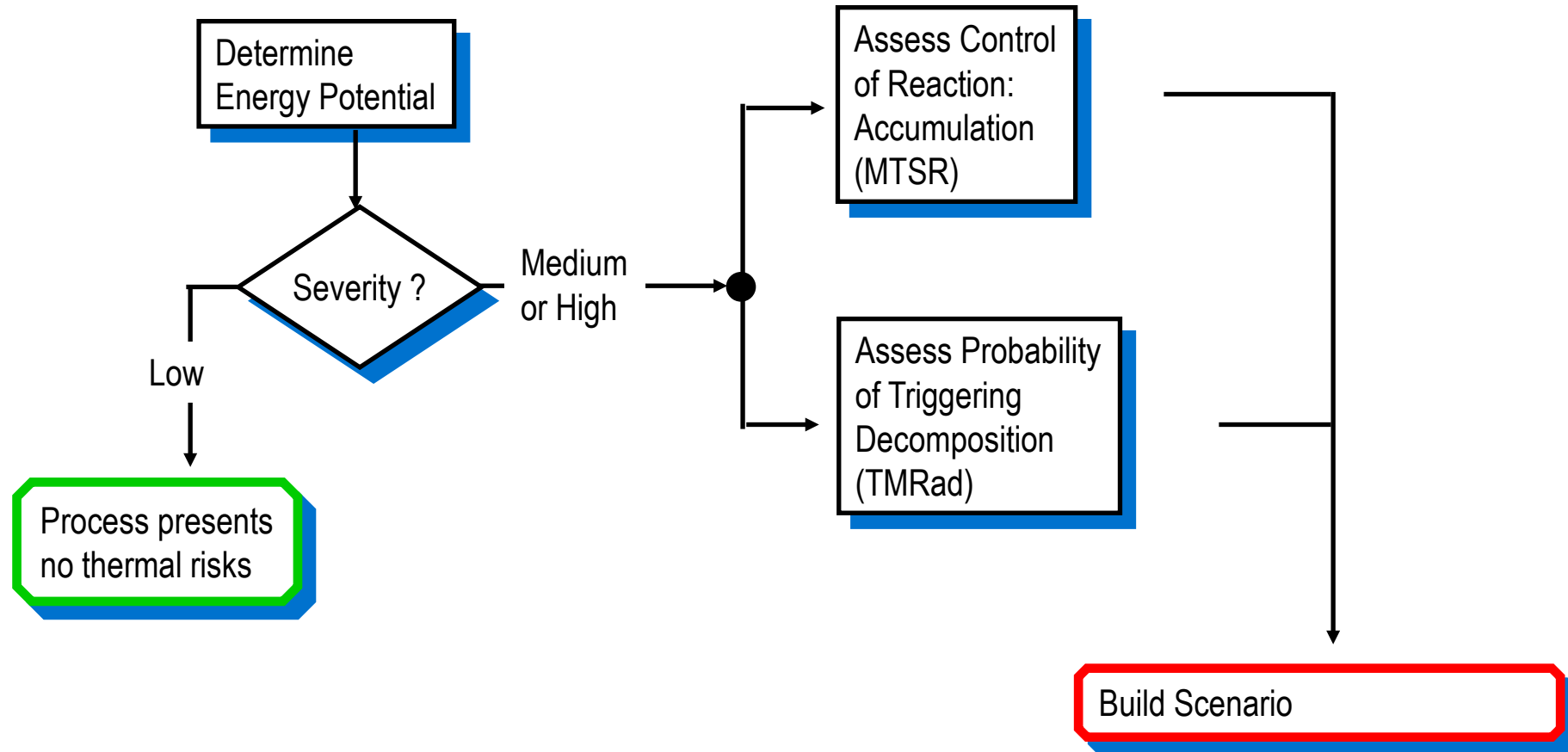
- A diazotization is performed by adding sodium nitrite to an aqueous solution of the amine (2.5 mol kg^{-1}). The industrial scale charge is 4000 kg of final reaction mass in a stirred tank reactor with a nominal volume of 4 m^3 . The reaction temperature is $5 \text{ }^{\circ}\text{C}$ and the reaction is very fast. For the safety study an accumulation of 10 % is considered realistic.
- Thermal data :
 - Reaction : $-\Delta H_r = 65 \text{ kJ/mol}$ $cp' = 3,5 \text{ kJ/(kg}\cdot\text{K)}$
 - Decomposition: $-\Delta H_{dc} = 150 \text{ kJ/mol}$ $T_{D24} = 30 \text{ }^{\circ}\text{C}$
- What is the thermal risk of this reaction?

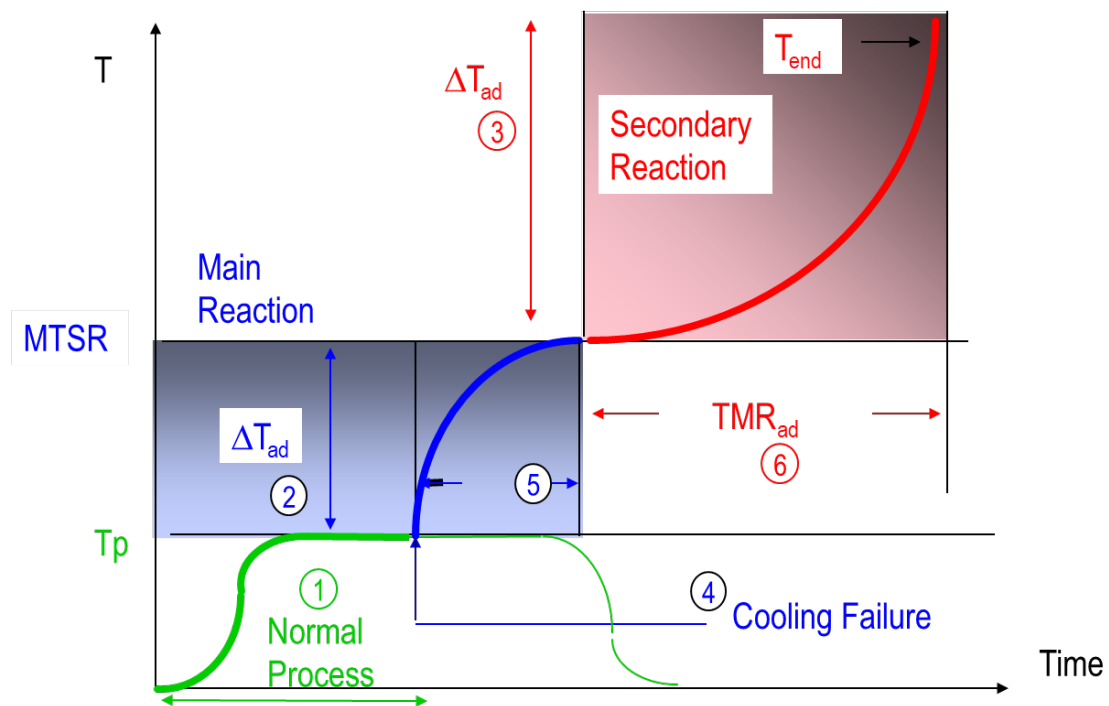


Example

- Determine energy potential
 - Reaction energy: 2.5 mol/kg is the concentration and the reaction enthalpy is $-\Delta H_r = 65 \text{ kJ/mol}$
 - Specific **reaction** energy: $Q'_{rx} = 2.5 \frac{\text{mol}}{\text{kg}} \cdot 65 \frac{\text{kJ}}{\text{mol}} = 162.5 \frac{\text{kJ}}{\text{kg}}$
 - Adiabatic temperature rise reaction $\Delta T_{ad,rxn} = \frac{Q'_{rx}}{c'_p} = \frac{162.5 \frac{\text{kJ}}{\text{kg}}}{3.5 \frac{\text{kJ}}{\text{kg} \cdot \text{K}}} = 46 \text{ K}$
 - Specific **decomposition** energy: $Q'_{dec} = 2.5 \frac{\text{mol}}{\text{kg}} \cdot 150 \frac{\text{kJ}}{\text{mol}} = 375 \frac{\text{kJ}}{\text{kg}}$
 - Adiabatic temperature rise decomposition $\Delta T_{ad,dec} = \frac{Q'_{rx}}{c'_p} = \frac{375 \frac{\text{kJ}}{\text{kg}}}{3.5 \frac{\text{kJ}}{\text{kg} \cdot \text{K}}} = 107 \text{ K}$
- Overall $\Delta T_{ad} 151^\circ\text{C}$: medium consequences

Criteria	Consequences	Probability
High	$\Delta T_{ad} > 200^\circ\text{C}$	TMRad < 8 h
Medium	$50^\circ\text{C} < \Delta T_{ad} < 200^\circ\text{C}$	8 h < TMRad < 24 h
Low	$\Delta T_{ad} < 50^\circ\text{C}$ and no pressure	TMRad > 24 h





1 Is the cooling capacity sufficient to remove the heat released by the reaction under normal operating conditions?	4 When does the cooling failure have the worst consequences?
2 What temperature may be reached after runaway of the main reaction ?	5 How long does the runaway of the main reaction take?
3 What temperature may be reached after runaway of secondary reaction	6 How long does the runaway of the secondary reaction take?

Example

1. Is the **cooling capacity** sufficient to remove the heat released by the reaction under normal operating conditions?

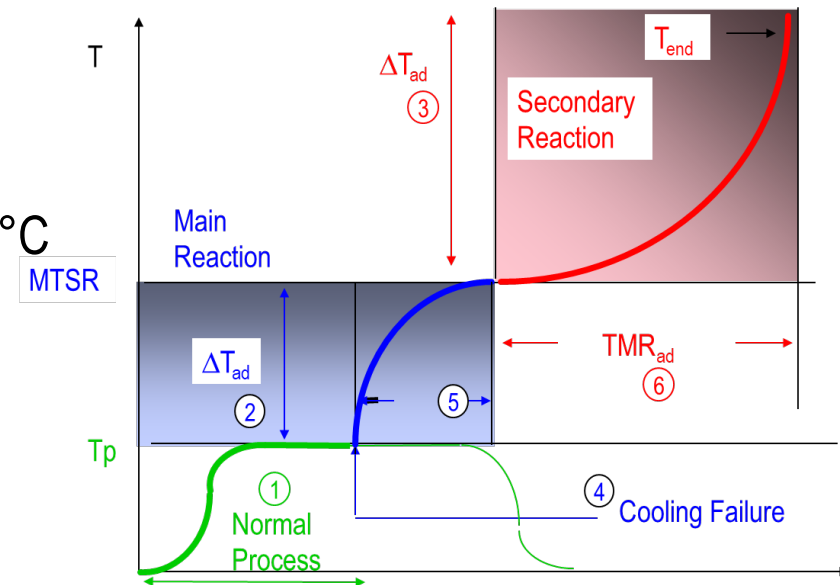
- No information on cooling capacity of the installation q_{ex}
- No information on heat release rate of the reaction q_{rx}
- Not possible to assess this question with the available data → remains an open question

2. What temperature may be reached after runaway of the main reaction?

- Calculate adiabatic temperature rise:

$$\text{Batch: } \Delta T_{ad,rxn} = \frac{Q'_{rx}}{c'_p} = \frac{162.5 \frac{kJ}{kg}}{3.5 \frac{kJ}{kg \cdot K}} = 46K \quad \text{MTSR} = T_p + \Delta T_{ad,rxn} = 5 + 46 = 51^\circ\text{C}$$

$$\text{Semi-batch 10\% accumulation: } \text{MTSR} = T_p + X_{acc} \Delta T_{ad,rxn} = 5 + 0.1 \cdot 46 = 9.6^\circ\text{C}$$



Example

3. What temperature may be reached after runaway of the secondary reaction?

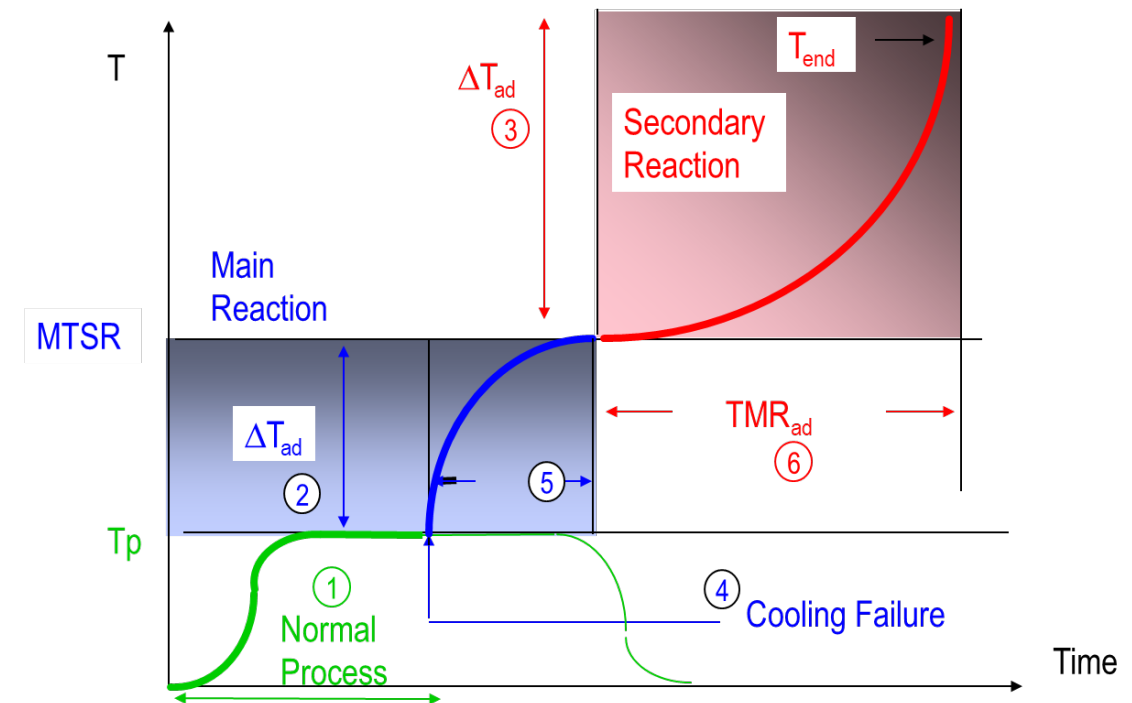
- Calculate adiabatic temperature rise:

$$- \Delta T_{ad,dec} = \frac{Q'_{rx}}{c'_p} = \frac{375 \frac{kJ}{kg}}{3.5 \frac{kJ}{kg \cdot K}} = 107 K$$

$$- T_f = MTSR + \Delta T_{ad,dec}$$

$$- \text{Batch: } T_f = 51 + 107 = 158^\circ C$$

$$- \text{Semi-batch: } T_f = 10 + 107 = 117^\circ C$$



Example

4. When does the cooling failure have the worst consequences?

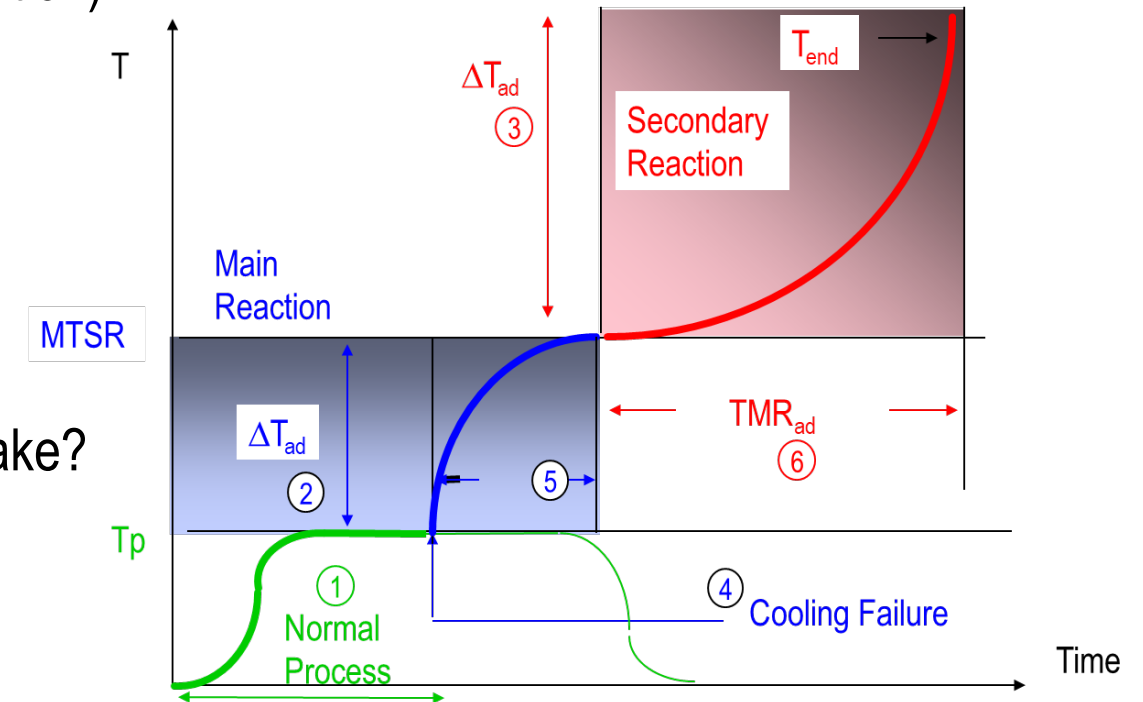
- For batch: at the beginning of the process (full accumulation)
- For semi-batch: at the maximum accumulation

5. How long does the runaway of the main reaction take?

- No information → conservative to neglect

6. How long does the runaway of the secondary reaction take?

- TMR_{ad} from the MTSR
 - MTSR Batch 51°C
 - MTSR Semi-batch 10°C
 - $TD_{24}=30^{\circ}\text{C}$
 - Batch: $\text{MTSR} > TD_{24} \rightarrow \text{TMR}_{ad} < 24\text{h}$ for Batch
 - Semi-batch: $\text{MTSR} < TD_{24} \rightarrow \text{TMR}_{ad} > 24\text{h}$ for Semi-batch



Example

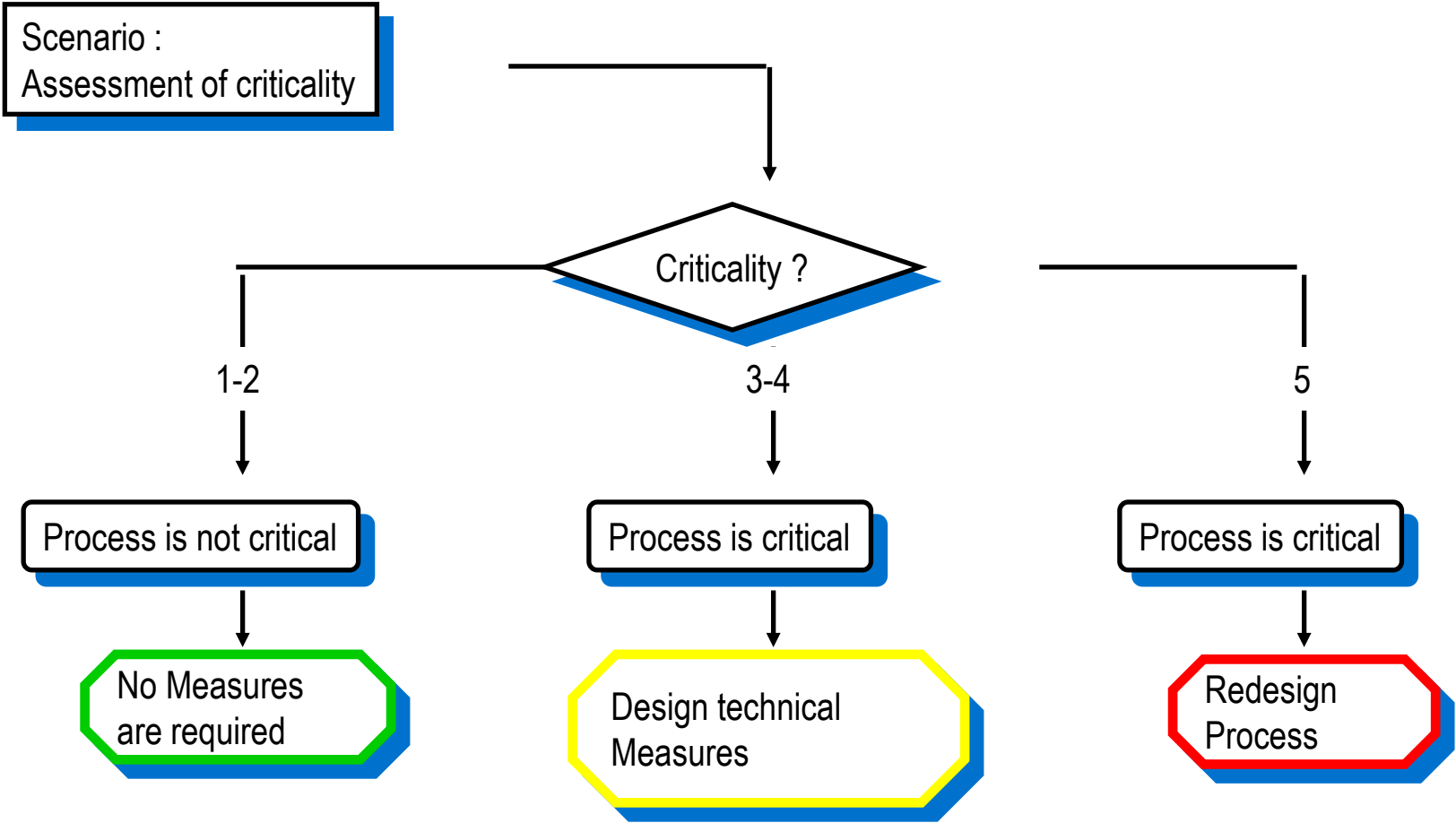
- Probability of runaway $TD_{24}=30^{\circ}\text{C}$
 - Estimation by extrapolating with van't Hoff rule
 - Batch: TMRad at 51°C : $\sim 6\text{h}$ → High probability of runaway
 - Semi-batch: TMRad at 10°C : $\sim 100\text{h}$ → Low probability of runaway

T	TMRad
0	$\sim 200\text{h}$
10	$\sim 96\text{h}$
20	$\sim 48\text{h}$
30	$\sim 24\text{h}$
40	$\sim 12\text{h}$
50	$\sim 6\text{h}$

Criteria	Consequences	Probability
High	$\Delta T_{ad} > 200^{\circ}\text{C}$	$\text{TMRad} < 8\text{ h}$
Medium	$50^{\circ}\text{C} < \Delta T_{ad} < 200^{\circ}\text{C}$	$8\text{ h} < \text{TMRad} < 24\text{ h}$
Low	$\Delta T_{ad} < 50^{\circ}\text{C}$ and no pressure	$\text{TMRad} > 24\text{ h}$

- Thermal risk

Consequences	High	$\Delta T_{ad} > 200K$			
	Medium	$50K < \Delta T_{ad} < 200K$	SEMI-BATCH		BATCH
	Low	$\Delta T_{ad} < 50K$ And no pressure			
			$TMR_{ad} \geq 24h$	$8h < TMR_{ad} < 24$	$TMR_{ad} \leq 8h$
			Low	Medium	High
			Probability		



Characteristic Temperatures

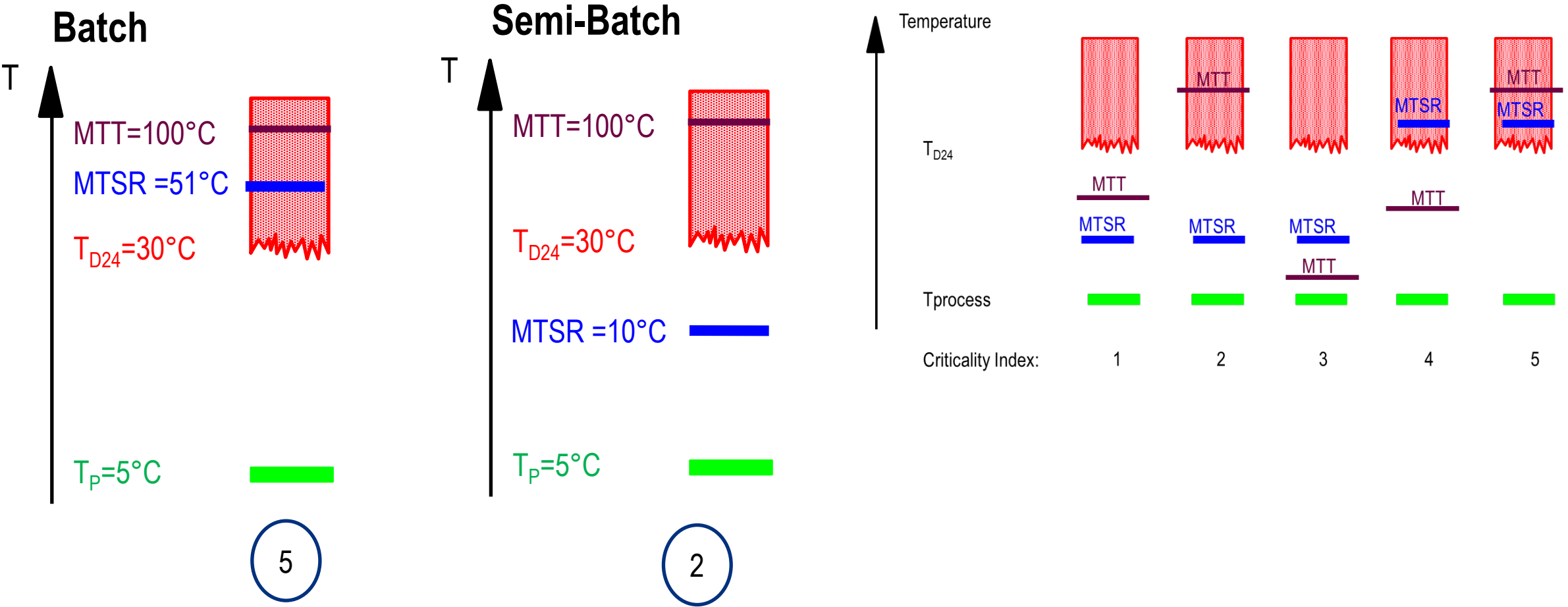
- T_p : Process Temperature
Defined by the mode of operation
- MTSR: Maximum Temperature of Synthesis Reaction
Defined by the accumulation of reactants and T_p
- T_{D24} : Temperature at which the Decomposition becomes critical $TMRad = 24$ hrs
Defined by the thermal stability of reaction mass
- MTT: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

T_p : 5°C

$MTSR_B = 51^\circ\text{C}$ $MTSR_{SB} = 10^\circ\text{C}$

$T_{D24} = 30^\circ\text{C}$

$MTT \sim 100^\circ\text{C}$ (aqueous system, boiling T)



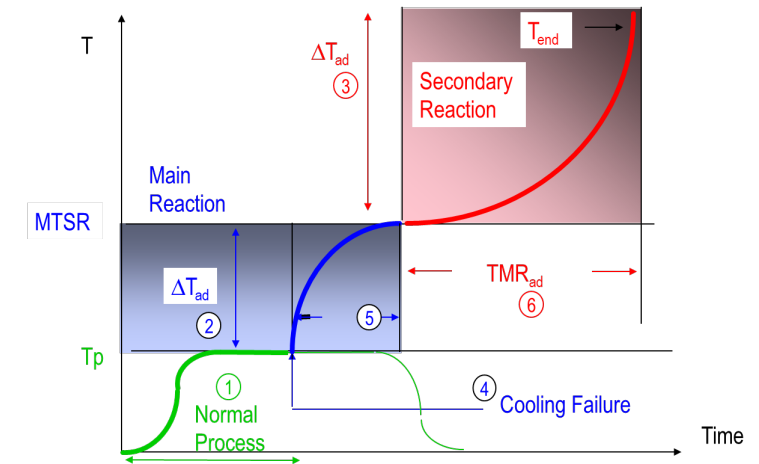
Example

- Conclusions

Key points Cooling failure and Criticality Class

- Cooling Failure Scenario is the scenario used to assess the thermal hazard of a process

- Graph (normal conditions, main reaction, secondary reaction)
- Six questions and Nomenclature
 - MTSR: maximum temperature of the synthesis reaction
 - Tf or Tend: final temperature
 - TMR_{ad} or tmr_{ad}: time to maximum rate under adiabatic conditions



- Criteria for severity and probability assessment for thermal hazard

- Consequences: adiabatic temperature increase

$$\Delta T_{ad} = \frac{Q'}{c_p'}$$

- Probability: TMRad or tmrad

Criteria	Consequences	Probability
High	$\Delta T_{ad} > 200^{\circ}\text{C}$	TMRad < 8 h
Medium	$50^{\circ}\text{C} < \Delta T_{ad} < 200^{\circ}\text{C}$	8 h < TMRad < 24 h
Low	$\Delta T_{ad} < 50^{\circ}\text{C}$ and no pressure	TMRad > 24 h

Key points Cooling failure and Criticality Class

- Thermal Risk

Consequences	High	$\Delta T_{ad} > 200K$			
	Medium	$50K < \Delta T_{ad} < 200K$			
	Low	$\Delta T_{ad} < 50K$ And no pressure			
			$TMR_{ad} \geq 24h$	$8h < TMR_{ad} < 24h$	$TMR_{ad} \leq 8h$
			Low	Medium	High
			Probability		

- Convert probability (TMRad) into a temperature (T_{D24})
- Use 4 Temperatures to build-up criticality classes: (T_p , MTSR, MTT (boiling T for an open system), T_{D24})

