Summary

Content of last lecture

- Technical reliability $R(t)$
  - Failure rate $z(t)$ with “bathtub” curve, Probability of Failure $F(t)$, Failure Density Function $f(t)$, Mean Time Between Failure (MTBF), Probability of Failure on Demand (PFD), Probability and MTBF of coincidence
- Human reliability analysis (HRA)
- Quantitative impact characterization
  - Fault and event tree of incidental substance release
  - Substance spreading
    - Heavy gas model, gas diffusion model, timescale for global mass transport
- Risk assessment and management
  - $p/i$-chart, Protection Layer Concept, Ignition sources and their avoidance, Cost efficiency of safety measures
- Assessment of residual risk
- PRA Exercise: Hydrogenation of nitrobenzene to aniline
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<th>Sem. Week</th>
<th>Topics</th>
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<tr>
<td>21.02.2017</td>
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<td>1: Introduction</td>
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<td>28.02.2017</td>
<td>2</td>
<td>2: Life-Cycle Assessment</td>
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<td>07.03.2017</td>
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<td>5</td>
<td>2: Life-Cycle Assessment, 3A: Product Risk Analysis</td>
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<td>6</td>
<td>3A: Product Risk Analysis</td>
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<td>04.04.2017</td>
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<td>25.04.2017</td>
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<td>3B: Product Risk Analysis</td>
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<td>23.05.2017</td>
<td>14</td>
<td>Risk and Ethics</td>
</tr>
<tr>
<td>30.05.2017</td>
<td>15</td>
<td>Excursion and Presentation</td>
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Risk Analysis of Chemical Processes and Products
Part 5: Thermal Process Safety

Thermal runaway

- Increase in reaction temperature
- Self-acceleration
- Increase in reaction rate
- Increase in reaction heat
Part 5: Thermal Process Safety

Safety, health and environmental risk (exemplified by human toxicity)

Aim of thermal process safety: to avoid thermal runaway accidents at a systemic level by securing

(i) a stable heat balance (in case of “as usual” scenario)
(ii) a manageable thermal risk (in case of “cooling failure” scenario)

R = f(probability, impact)
R = f(exposure, dose-effect)
R = f(contribution to effect class)
**Accident:**
Ciba Basel, 23.12.1969,
Azo-dye production K-90

Damage from a thermal explosion of a 2.8 m³ Emaille-diazotization-reactor

**Reaction:**
diazotization of 6-chloro-2,4-dinitro-aniline

\[
\begin{align*}
\text{Cl} & \quad \text{NH}_2 \\
\text{NO}_2 & \quad \text{NO}_2
\end{align*}
\]

\[
\text{Cl} \quad \text{NH}_2 \\
\text{NO}_2 & \quad \text{NO}_2
\]

\[
\text{287 kg} \quad \text{384 kg}
\]

\[
1.34 \text{ kmol} \quad \text{(40% NSA)}
\]

\[
\text{NaNO}_2/\text{H}_2\text{SO}_4 \quad \text{T}=30 \text{ to } 50 \degree \text{C}
\]

\[
\text{Q}_r = 60 \text{ kJ/kg}
\]
**Diazotization of 6-chloro-2,4-dinitro-aniline in sulfuric acid/nitrosyl sulfuric acid (40% NSA)**

**reactant mixture**

Microthermal analysis

<table>
<thead>
<tr>
<th>Temperature °C</th>
<th>Heat Flow W/kg</th>
</tr>
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<tbody>
<tr>
<td>200</td>
<td>1500</td>
</tr>
<tr>
<td>250</td>
<td>1000</td>
</tr>
<tr>
<td>300</td>
<td>500</td>
</tr>
<tr>
<td>350</td>
<td>0</td>
</tr>
</tbody>
</table>

**Heat of Reaction**

- **Diazo-decomposition**: -380 kJ/kg
- **Nitro-decomposition**: -360 kJ/kg
- **Diazotization**: -60 kJ/kg

**Thermodynamic Parameters**

- \( c_p = 1.75 \text{ kJ/kg K} \)
- \( T_{ad} \text{ (diazotization)} = 35°C \)
Thermal Process safety

Thermal process safety as part of process risk analysis

Thermal process data
(ΔH_R, ΔH_{dec}, c_p, therm. reactor power etc.)

Definition of safe thermal process conditions

I  normal case: therm. reactor stability
(focus: desired reaction)
- mass and heat balance; stability criteria

II  accidental case: thermal runaway – scenario
after cooling failure (focus: decomposition reaction)
- characterization of risk by impact and probability

safety measures (primarily inherently safe process conditions)
“As usual” and “runaway” scenario as starting points for thermal risk analysis.

(I) Thermal reactor stability
“as usual” scenario for desired reaction in normal operation (batch-/semibatch process etc.)

(II) Thermal runaway
“cooling failure” scenario resulting in adiabatic decomposition reaction

risk = f(impact, probability)

where

\[ \Delta T_{ad} : \text{adiabatic temperature increase (proxy measure for impact)} \]
\[ \text{TMR}_{ad} : \text{time to maximum rate under adiabatic conditions (proxy measure for probability)} \]
I Thermal Reactor Stability

Batch/semibatch process

1) desired reaction
2) decomposition reaction

630-Liter reactor. Stainless steel with
- double-walled heating (cooling)
- stirring system
- distillation system
(Pharma Pilotplant Novartis Basel)
a) Batch reactor

Definition of batch reaction process:
All reactants are fed into the reactor. The start of the reaction is carried out by:
- increasing the temperature or
- adding catalyst or
- adding reaction components simultaneously

Assumptions:
- **reactor**: no heat storage capacity
- **reactor content**: neither axial nor radial concentration or temperature gradient
- **cooling jacket**: no temperature gradient between input and output
- **process parameter**: $\rho$, $c_p$, $\Delta H_R$ and $U$

\[
\begin{align*}
T_c &\quad [K] \\
A &\quad [m^2] \\
U &\quad [W/m^2/K] \\
V &\quad [m^3] \\
T &\quad [K] \\
c_p &\quad [J/kg/K] \\
\rho &\quad [kg/m^3] \\
k &\quad \text{kinetic constant} \\
\dot{n}_{evap} &\quad \text{evaporation rate} \\
r_A &\quad \text{reaction rate for } A \\
T &\quad \text{reaction temperature} \\
T_c &\quad \text{cooling temperature} \\
U &\quad \text{heat transfer coefficient} \\
V &\quad \text{reaction volume} \\
\rho &\quad \text{density of reaction mixture} \\
\end{align*}
\]
I Thermal Reactor Stability

1. Mass balance (for A)

\[
\frac{1}{\rho} \left( - \frac{dC_A}{dt} \right) = \frac{1}{\rho} \left( -r_A \right) \quad \text{[mol kg}\cdot\text{s}^{-1}]
\]

where

\[
-r_A = k(T) \cdot f(\text{conc.}) \quad \text{[mol m}^3\cdot\text{s}^{-1}]
\]

\[
k(T) = k_0 e^{-\frac{E_A}{RT}} \quad \text{(Arrhenius equation)}
\]

e.g.: \(-r_A = k \cdot C_A^n\); \(n\): reaction order

\[
t_{1/2} = t\bigg|_{C_A=C_{A0/2}}
\]
I Thermal Reactor Stability

2. Heat balance

Batch cooled by external heat transfer

\[ c_p \frac{dT}{dt} = \frac{1}{\rho} (-r_A) (-\Delta H_R) - \frac{U A}{\rho V} (T - T_c) \]  

\[ \dot{q}_{acc} \quad \dot{q}_R \quad \dot{q}_C \]

accumulation  reaction  external cooling

where

\[ A/V \quad \text{specific heat transfer area} \quad [m^2/m^3] \]
\[ c_p \quad \text{specific heat capacity of reaction mixture} \quad [J/kg/K] \]
\[ \Delta H_R \quad \text{reaction enthalpy} \quad [J/mol] \]
\[ \dot{q} \quad \text{thermal power} \quad [W/kg] \]
\[ r_A \quad \text{reaction rate for A} \quad [mol/m^3/s] \]
\[ t \quad \text{time} \quad [s] \]
\[ T \quad \text{temperature of reaction mixture} \quad [K] \]
\[ T_c \quad \text{temperature of cooling material} \quad [K] \]
\[ U \quad \text{heat transfer coefficient} \quad [W/m^2/K] \]
\[ \rho \quad \text{density of reaction mixture} \quad [kg/m^3] \]

Semenov diagram:
(reaction versus cooling power)

Assumption:
\[ \rho, \ c_p, \ \Delta H_R, \ U \neq f(T) \]

p. 177/179
### Heat exchange during cooling process

\[
\frac{1}{U} = \left( \frac{1}{\alpha_{\text{int}}} + \frac{d}{\lambda_w} + \frac{1}{\alpha_{\text{ext}}} \right)
\]

where

- \( d \) wall thickness of the reactor [m]
- \( U \) heat transfer coefficient [W/m²/K]
- \( \alpha_{\text{ext}} \) heat transfer coefficient external [W/m²/K]
- \( \alpha_{\text{int}} \) heat transfer coefficient internal [W/m²/K]
- \( \lambda_w \) heat conductivity of the wall [W/m/K]

### Orders of magnitude for the heat transfer (liquid/liquid)

<table>
<thead>
<tr>
<th></th>
<th>( \alpha_{\text{int}} ) [W/(m²·K)]</th>
<th>( \lambda/d ) [W/(m²·K)]</th>
<th>( \alpha_{\text{ext}} ) [W/(m²·K)]</th>
<th>( U ) [W/(m²·K)]</th>
</tr>
</thead>
<tbody>
<tr>
<td>normal case</td>
<td>(~ 1000)</td>
<td>(~ 5000)</td>
<td>(~ 2000)</td>
<td>(~ 600)</td>
</tr>
<tr>
<td>accidental case*</td>
<td>(~ 100)</td>
<td>(~ 800)</td>
<td>(~ 100)</td>
<td>(~ 50)</td>
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</tbody>
</table>

* e.g. stirring failure
I Thermal Reactor Stability

Batch cooled by solvent reflux

(at boiling temperature $T_b$ of reaction solvent)

$$q_R = \frac{1}{\rho} (-r_A)(-\Delta H_R) = \frac{m_{\text{evap}}}{\rho V} Q_{\text{evap}} \left[ \frac{W}{kg} \right]$$

Total heat of reaction ($Q_{\text{react,tot}}$) is equal to total heat of evaporation:

$$Q_{\text{react,tot}} = m \int_0^\infty \dot{q}_R \, dt = V \cdot c_{AO} \cdot (-\Delta H_R) = m_{\text{evap,tot}} \cdot Q_{\text{evap}} \quad [J]$$

$$m_{\text{evap,tot}} = V \cdot c_{AO} \cdot (-\Delta H_R) / Q_{\text{evap}} \quad [kg]$$

where

- $m$ reaction mass
- $\dot{m}_{\text{evap}}$ solvent reflux stream [kg/s]
- $m_{\text{evap,tot}}$ total mass of evaporated solvent [kg]
- $Q_{\text{evap}}$ specific evaporation heat of solvent [J/kg solvent]
I Thermal Reactor Stability

Mass and heat balance in dimensionless form

- Mass:
  \[
  \frac{dX_A}{d\tau} = D^* \cdot e^{\gamma\left(\frac{\Theta-1}{\Theta}\right)} (1-X_A)^n
  \]

- Heat:
  \[
  \frac{d\Theta}{d\tau} = B^* \cdot D^* \cdot e^{\gamma\left(\frac{\Theta-1}{\Theta}\right)} (1-X_A)^n - S^* \cdot (\Theta-\Theta_C)
  \]

( for n\textsuperscript{th} order reaction with \(C_A = C_{A,0}(1-X_A)\) )

Dimensionless parameters:

- \(\Theta = \frac{T}{T_0}, \quad \Theta_C = \frac{T_C}{T_0}, \quad \tau = \frac{t}{t_0}\)
- \(B^* = \frac{(-\Delta H_R)C_{A,0}}{\rho c_p \cdot T_0}\)
- \(D^* = t_0 \cdot k(T_0)C_A^{n-1}_A = t_0 \cdot k_0 \cdot e^{-\frac{E_A}{RT_0}} \cdot C_A^{n-1}\)
- \(S^* = \frac{UAt_0}{\rho V \cdot c_p}\)
- \(\gamma = \frac{E_A}{RT_0}\)

Ratio between:

- two temperature or time scales
- heat of reaction and thermal capacity of the fluid
- time of process and time of reaction
- heat transferred and thermal capacity of the fluid
- activation energy and potential energy along the reaction path
**b) Semibatch reactor**

Definition of semibatch reaction process:

At least one reactant is fed into or one product removed from the reactor. For reaction start and control at least one other reactant is subsequently added over a certain time period (usually evenly dosed).

**Assumptions:**

- **reactor:** no heat storage capacity
- **reactor content:** neither axial nor radial concentration or temperature gradient
- **cooling jacket:** no temperature gradient between input and output
- **process parameter:** $\rho$, $c_p$, $\Delta H_R$ and $U$
- **dosing rate:** $m \neq f(t)$ for $t \leq t_{Dos}$
1. Mass balance (for B)

\[
\frac{d}{dt}(V \cdot c_B) = \frac{\dot{m}}{\rho_{\text{feed}}} c_{B,0} - V \cdot (-r_B) \quad \text{[mol]} \quad \text{[s]}
\]

\[
\frac{1}{\rho} \left( -\frac{dc_B}{dt} \right) = \frac{1}{\rho} (-r_B) - \frac{\dot{m}}{\rho_{\text{feed}} \rho} \frac{1}{V} (c_{B,0} - c_B) \quad \text{[mol]} \quad \text{[kg} \cdot \text{s]}
\]

2. Heat balance

\[
\frac{d}{dt}(m \cdot c_p \cdot T) = V \cdot (-r_B)(-\Delta H_R) - U \cdot A \cdot (T - T_C) + \dot{m} \cdot c_p \cdot T_{\text{feed}} \quad \text{[W]}
\]

\[
\frac{c_p}{\rho} \frac{dT}{dt} = \frac{1}{\rho} (-r_B)(-\Delta H_R) - \frac{U \cdot A}{\rho \cdot V} (T - T_C) - \frac{\dot{m} \cdot c_p}{\rho \cdot V} (T - T_{\text{feed}}) \quad \text{[W]} \quad \text{[kg]} \]

\[q_{\text{acc}} \quad q_R \quad q_C \quad q_{\text{feed}}\]

Assumption: \( c_{p,RM} = c_{p,\text{feed}} = c_p \) \( (\rho = \rho_{RM}) \) \( (RM: \text{reaction mass}) \)

\( \dot{m} \neq f(t) \) for \( t \leq t_{\text{Dos}} \), otherwise \( \dot{m} = 0 \)
Mass and heat balance in dimensionless form

\[
\frac{dX_B}{d\tau} = D^* \cdot e^{\left(\frac{\Theta-1}{\Theta}\right)} \left(1-X_B\right)^n - Q^* \cdot X_B
\]

\[
\frac{d\Theta}{d\tau} = B^* \cdot D^* \cdot e^{\left(\frac{\Theta-1}{\Theta}\right)} \left(1-X_B\right)^n - S^* \left(\Theta-\Theta_C\right) - Q^* \left(\Theta-\Theta_{feed}\right)
\]

( for \(n^{th}\) order reaction with \(C_B = C_{B,0}(1-X_B)\) )

Dimensionless parameters:

\[
\Theta = \frac{T}{T_0}, \quad \Theta_C = \frac{T_C}{T_0}, \quad \Theta_{feed} = \frac{T_{feed}}{T_0}, \quad \tau = \frac{t}{t_0}
\]

\[
B^* = \frac{(-\Delta H_R) C_{B,0}}{\rho c_p T_0}
\]

\[
D^* = t_0 \cdot k(T_0) C_{B,0}^{n-1} = t_0 \cdot k_0 \cdot e^{-\frac{E_A}{RT_0} \cdot C_{B,0}^{n-1}}
\]

\[
S^* = \frac{U A t_0}{\rho V c_p}
\]

\[
Q^* = \frac{m \cdot t_0}{\rho V}
\]

\[
\gamma = \frac{E_A}{RT_0}
\]

Ratio between:

- two temperatures or time scales
- heat of reaction and thermal capacity of the fluid
- time of process and time of reaction
- heat transferred and thermal capacity of the fluid
- thermal capacity of dosing and thermal capacity of reaction mass
- activation energy and potential energy along the reaction path
I Thermal Reactor Stability

Semibatch cooled by solvent reflux

(at boiling temperature $T_b$ of reaction solvent)

$$q_R = \frac{1}{\rho} (-r_B)(-\Delta H_R) = \frac{\dot{m} \cdot c_p}{\rho \cdot V} (T_b - T_{\text{feed}}) + \frac{\dot{m}_{\text{evap}}}{\rho \cdot V} Q_{\text{evap}} \left[ \frac{W}{kg} \right]$$

For $T_{\text{feed}} = T_b$ total heat of reaction ($Q_{\text{react,tot}}$) is equal to total heat of evaporation:

$$Q_{\text{react,tot}} = m(t_{dos}) \int_0^{\infty} \dot{q}_R dt = \frac{\dot{m} \cdot t_{dos}}{\rho_{\text{feed}}} c_B(\Delta H_R) = m_{\text{evap,tot}} \cdot Q_{\text{evap}} \quad [J]$$

$$m_{\text{evap,tot}} = \frac{\dot{m} \cdot t_{dos}}{\rho_{\text{feed}}} c_B(\Delta H_R) / Q_{\text{evap}} \quad [kg]$$

where

- $\Delta H_{\text{evap}}$ (solvent) evaporation heat [J/mol]
- $\dot{m}_{\text{evap}}$ solvent reflux stream [kg/s]
- $m_{\text{evap,tot}}$ total mass of evaporated solvent [kg]
- $Q_{\text{evap}}$ specific evaporation heat of solvent [J/kg solvent]
I Thermal Reactor Stability

Semibatch

Concentration profile \((A + B \rightarrow P)\)

- **A:** already fed into the reactor
- **B:** addition (20 mol% excess with respect to A)

Complete dosing control
\(t_{1/2\text{ react}} \ll t_{1/2\text{ dos}}\)

Complete reaction control
\(t_{1/2\text{ react}} \gg t_{1/2\text{ dos}}\)

Partial dosing control
\(t_{1/2\text{ react}} \approx t_{1/2\text{ dos}}\)

\(n_i/n_{A_0}\): number of moles of reactant \(i\) in the reactor at time \(t\) (\(i = A, B\))

E.g. nitration:

- **A:** already fed into the reactor
- **B:** addition (20 mol% excess with respect to A)

(balance equations, see "semibatch – feed cooling")

(balance equations, see "batch")

(balance equations, see "semibatch")
Feed cooling in case of complete dosing control

\( (A + B \rightarrow P) \)

(for \( t < t_{SE} \): \( \frac{dc_B}{dt} = 0 \) and \( c_B << c_{B,0} \))

A: already fed into the reactor  
B: addition (20 mol\% excess with respect to A)  
SE: stochiometric equivalence

1. Mass balance (for B; within the period \( 0 \leq t \leq t_{SE} \))

\[
\frac{1}{\rho} (-r_B) = \frac{m}{\rho_{feed}} \cdot \frac{1}{\rho} \cdot V \cdot c_{B,0} \left[ \text{mol \ kg}^{-1} \text{s} \right] ; \\
\left\{ \begin{array}{l}
D^* \gamma \left( \frac{\Theta - \Theta_{feed}}{\Theta} \right) (1 - X_B)^n = Q^* \\
\end{array} \right.
\]

(\( \rightarrow \) reaction rate is decoupled from temperature)

2. Heat balance (isotherm, cooling only by feed stream)

\[
\frac{1}{\rho_{feed}} \cdot c_{B,0} (-\Delta H_R) = c_p (T - T_{feed}) \left[ \frac{J}{\text{kg} \cdot \text{f}} \right] ; \\
(B^* = \Theta - \Theta_{feed})
\]

(\( \rightarrow T_{feed} \) for autothermal process)

\( (\rho = \rho_{RM}) \)

Note: Symbol list, see prior dimensionless representation of the semibatch balance equations

1) ChemIng only
Heat production and thermal conversion

heat production $q_r \, [\text{W/kg}]$

Definition of thermal conversion ($X_{\text{therm}}$):

$$X_{\text{therm}}(t) = \frac{\int_{0}^{t} \dot{q}_R \, dt}{\int_{0}^{\infty} \dot{q}_R \, dt}$$

with $\dot{q}_R = \frac{1}{\rho} (\rho_B)(-\Delta H_R)$

Controlling step | $x_{\text{therm}} \, (t = t_{\text{Dos}})$
--- | ---
Complete dosing control | $\sim 1$
Complete reaction control | $\sim 0$
Partial dosing control | $0 < x_{\text{therm}} < 1$

$t_{\text{Dos}}$: dosing time (up to equimolar addition of reactants)
Alkoxylaation

reactions of fatty alcohols, fatty acids and fatty amines with ethylene oxide (propylene oxide and butylene oxide) → non-ionic surfactants

\[
\begin{align*}
R-OH + n \ CH_2CH_2 & \rightarrow R-O-(CH_2CH_2O)n-H \\
R-C-OH + n \ CH_2CH_2 & \rightarrow R-C-O-(CH_2CH_2O)n-H \\
R-N & + (x + y) \ CH_2CH_2 \rightarrow R-N-(CH_2CH_2O)x-H (CH_2CH_2O)y-H
\end{align*}
\]

\[-\Delta H_R = 100 - 200 \text{ kJ/mol}\]

Reaction procedure:
first R-OH/OOH/NH₂ is fed into the reactor, and then dosing of ethylene oxide is started
c) Comparison of different reactor types

(i) Batch/semibatch reaction mode

<table>
<thead>
<tr>
<th>type of reactor</th>
<th>$\dot{q}_R \sim r_B$</th>
<th>$\dot{q}_C \sim \frac{A}{V} \cdot U$</th>
<th>therm. scale-up effect ($\propto \frac{\dot{q}_R}{\dot{q}_C}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Batch</td>
<td>high (at $t=0$)</td>
<td>low</td>
<td>large</td>
</tr>
<tr>
<td>Semibatch</td>
<td>variable</td>
<td>low</td>
<td>medium to large</td>
</tr>
</tbody>
</table>
(ii) Continuous reaction mode

<table>
<thead>
<tr>
<th>type of reactor</th>
<th>( \dot{q}_R \sim r_B )</th>
<th>( \dot{q}_C \sim \frac{A}{V} \cdot U )</th>
<th>therm. scale-up effect (( \sim \frac{\dot{q}_R}{\dot{q}_C} ))</th>
</tr>
</thead>
<tbody>
<tr>
<td>ISTR</td>
<td>low</td>
<td>medium</td>
<td>medium</td>
</tr>
<tr>
<td>plug-flow</td>
<td>high (at the entrance)</td>
<td>high</td>
<td>small</td>
</tr>
<tr>
<td>cross flow</td>
<td>variable</td>
<td>high</td>
<td>small</td>
</tr>
</tbody>
</table>

ISTR: ideally stirred tank reactor
II Thermal runaway: basic scenario for risk analysis

Risk

\[ R = f(p,i) \]

- Probability \( p \)
- Impact \( i \)
- Temperature
- Cooling failure
- Thermal explosion

1) desired reaction
2) decomposition reaction

\[ \Delta T_{ad} \]
Adiabatic decomposition of hydrogen peroxide

\[ \text{H}_2\text{O}_2\text{(aq)} + \text{I}^-\text{(aq)} \rightarrow \text{IO}^-\text{(aq)} + \text{H}_2\text{O}(l) \]

\[ \text{H}_2\text{O}_2\text{(aq)} + \text{IO}^-\text{(aq)} \rightarrow \text{I}^-\text{(aq)} + \text{H}_2\text{O}(l) + \text{O}_2\text{(g)} \]

\[ 2\ \text{H}_2\text{O}_2\text{(aq)} \rightarrow \text{O}_2\text{(g)} + 2\ \text{H}_2\text{O}(l) \]

**Recipe:**
1. 250 ml H\(_2\)O\(_2\) 35% fed into Dewar (\(T_0 \approx 22 ^\circ\text{C}\))
2. 0.074 g KI added (@ t=0) as decomposition catalyst
3. stop of adiabatic decomposition (@ T \(\approx 80 ^\circ\text{C}\)) through addition of ice
II Thermal Runaway

a) Impact of thermal runaway

$\Delta T_{ad}$ as indicator for the impact of a thermal runaway

\[
\Delta T_{ad} = \frac{Q_{dec}}{c_p} [K] = \frac{-\Delta H_{dec} \cdot C_0}{\rho \cdot c_p}
\]

where

- $C_0$: educt concentration @ t=0 [mol/m³]
- $c_p$: specific heat capacity of reaction mass [J/kg/K]
- $H_2O$: $c_p = 4.2$ [kJ/kg/K]
- organic solvent: $c_p = \text{c.a.} 1.7$ [kJ/kg/K]
- $H_2SO_4$ (100%): $c_p = 1.3$ [kJ/kg/K]

$\Delta H_{dec}$: reaction enthalpy [J/mol]

$Q_{dec}$: specific reaction heat [J/kg] (analog for decomposition $Q_{dec}$)

$\Delta T_{ad}$: adiabatic temperature rise [K]

$\rho$: density of reaction mass [kg/m³]

Classification of $\Delta T_{ad}$ in terms of impact

<table>
<thead>
<tr>
<th>$\Delta T_{ad}$ [°C]</th>
<th>Impact</th>
</tr>
</thead>
<tbody>
<tr>
<td>&gt; 200</td>
<td>high</td>
</tr>
<tr>
<td>50 &lt; $\Delta T_{ad}$ &lt; 200</td>
<td>medium</td>
</tr>
<tr>
<td>&lt; 50*</td>
<td>low</td>
</tr>
</tbody>
</table>

* additional condition: boiling point not exceeded

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II Thermal Runaway

Calculation of standard reaction enthalpy from standard enthalpies of formation of reactants and products

\[ \Delta H_R^\theta = \sum J \nu J \cdot \Delta_b H_J^\theta \]

where

- \( J \) index for specific reactant or product
- \( \Delta H_R^\theta \) standard reaction enthalpy
- \( \Delta_b H_J^\theta \) standard formation enthalpy
- \( \theta \) standard conditions (298 K, 105 Pa)
- \( \nu \) stoichiometric coefficient

### Reaction Table

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Reaction heat ((-\Delta H_R)) [kJ/mol]</th>
</tr>
</thead>
<tbody>
<tr>
<td>neutralisation (HCl)</td>
<td>55</td>
</tr>
<tr>
<td>diazotization</td>
<td>65</td>
</tr>
<tr>
<td>amination</td>
<td>120</td>
</tr>
<tr>
<td>nitration</td>
<td>130</td>
</tr>
<tr>
<td>diazo decomposition</td>
<td>140</td>
</tr>
<tr>
<td>sulfonation (SO_3)</td>
<td>150</td>
</tr>
<tr>
<td>vinylpolymerisation</td>
<td>50-200</td>
</tr>
<tr>
<td>nitro decomposition</td>
<td>400</td>
</tr>
<tr>
<td>hydrogenation (nitroaromate)</td>
<td>560</td>
</tr>
</tbody>
</table>

Online database for standard formation enthalpy e.g. [http://webbook.nist.gov/chemistry/](http://webbook.nist.gov/chemistry/)
## II Thermal Runaway

### Typical functional groups of unstable compounds

<table>
<thead>
<tr>
<th>Chemical class</th>
<th>Unstable group</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Perchlorate</td>
</tr>
<tr>
<td>2</td>
<td>Nitro</td>
</tr>
<tr>
<td>3</td>
<td>Polynitro</td>
</tr>
<tr>
<td>4</td>
<td>Nitroso</td>
</tr>
<tr>
<td>5</td>
<td>N-oxide</td>
</tr>
<tr>
<td>6</td>
<td>Hydroxylamine, oxime</td>
</tr>
<tr>
<td>7</td>
<td>Tetrazole</td>
</tr>
<tr>
<td>8</td>
<td>Triazene, triazole</td>
</tr>
<tr>
<td>9</td>
<td>Azo</td>
</tr>
<tr>
<td>10</td>
<td>Hydrazine</td>
</tr>
</tbody>
</table>

**Polymerizable compounds**
- Olefine ($X = \text{e.g. } -\text{F}, -\text{Cl}, -\text{CN}$)
- Epoxide
- Diketene

<table>
<thead>
<tr>
<th>Chemical class</th>
<th>Unstable group</th>
</tr>
</thead>
<tbody>
<tr>
<td>11</td>
<td>Substituted hydrazine</td>
</tr>
<tr>
<td>12</td>
<td>N–N– in a ring</td>
</tr>
<tr>
<td>13</td>
<td>2 N–N– in a ring</td>
</tr>
<tr>
<td>14</td>
<td>Imidazole</td>
</tr>
<tr>
<td>15</td>
<td>Oxazole</td>
</tr>
<tr>
<td>16</td>
<td>Thiazole</td>
</tr>
<tr>
<td>17</td>
<td>Acetylide</td>
</tr>
<tr>
<td>18</td>
<td>Halogen/nitrogen compounds</td>
</tr>
<tr>
<td>19</td>
<td>Nitric acid esters</td>
</tr>
<tr>
<td>20</td>
<td>Peroxides</td>
</tr>
</tbody>
</table>

### Impact

#### Reductants
(in contact with oxidizing agents)
- Metals (e.g. Na, Zn)
- Metalorganic compounds (e.g. BuLi)
- Hydride (e.g. LiAlH$_4$, NaBH$_4$)
- Silane
- Hydrogen

#### Oxidants
(in contact with reducing agents)
- HClO$_4$ (conc.) / perchlorate
- HNO$_3$ (conc.) / nitrate
- CrO$_3$ / chromate
- KMnO$_4$
- Chlorate
- Nitric/sulfuric acid (HNO$_3$/H$_2$SO$_4$)
- Alkyl nitrite
- H$_2$O$_2$
- Organic and inorganic peroxide
- SO$_3$ / oleum
- Oxygen / ozone
- Chlorine
II Thermal Runaway

Impact according to $\Delta T_{ad}$

Adiabatic decomposition of hydrogen peroxide
(35 wt %)

$$2 \text{H}_2\text{O}_2(\text{aq}) \rightarrow \text{O}_2(\text{g}) + 2 \text{H}_2\text{O}(\text{l})$$

$-\Delta H_{dec} = 98 \text{ kJ/mol}$

$$\Delta T_{ad} = \frac{Q_{dec}}{c_p} = \frac{1010 \text{ kJ}}{3.6 \text{ kJ/kg.K}} = 280 \text{ K}$$

impact = high
II Thermal Runaway

b) Probability of thermal runaway

\( \text{TMR}_{\text{ad}} \) as indicator for the probability of a thermal runaway

In case of cooling failure (at \( t_{\text{cooling failure}} \))

\( \text{TMR}_{\text{ad}} \) is defined by the temperature dependent decomposition power and the starting temperature of decomposition

decomposition power \( q_{\text{dec}} \):
dependent on decomposition rate and decomposition enthalpy

\[
\dot{q}_{\text{dec}} = \frac{1}{\rho} (-r_{\text{dec}})(-\Delta H_{\text{dec}})
\]

\[
\frac{\dot{q}_{\text{dec}}(T)}{\dot{q}_{\text{dec}}(T_0)} = \exp \left[ \frac{E_A}{R} \cdot \left( \frac{1}{T_0} - \frac{1}{T} \right) \right]
\]

starting temperature \( T_0 \) of decomposition:
determined by \( T_{\text{process}} \) and residual conversion of the desired reaction (for batch mode)

\[
T_0 \approx T_{\text{process}} + \frac{\int_{t_{\text{cooling failure}}}^{\infty} \dot{q}_R(t) \, dt}{c_p}
\]

p. 185/188

K. Hungerbühler: Risk Analysis of Chemical Processes and Products, FS 2017
1st approximation for $T_{\text{MR}_{\text{ad}}}$: 10-degree rule for doubling of reaction rate

$$T_{\text{MR}_{\text{ad}}} = 2 \times t_{T_0+10\text{K}}$$

$p. 186$
2nd approximation for $TMR_{ad}$: Adiabatic heat balance for decomposition reaction

(assumption: $0^{th}$ order reaction; $\rho$, $c_p$, $\Delta H_{dec} \neq f(T)$)

$$c_p \frac{dT}{dt} = \frac{1}{\rho} k(T) \cdot (-\Delta H_{dec}) = \dot{q}_{dec} \begin{bmatrix} W \\ kg \end{bmatrix}$$

$$T_0 + \Delta T_{ad} \int_{T_0}^{T_{TMR_{ad}}} \frac{E_A}{e^{RT}dT} = \frac{k_0 \cdot (-\Delta H_{dec})}{\rho \cdot c_p} \int_0^{T_{TMR_{ad}}} dt$$

$$TMR_{ad} \cong \frac{c_p}{\dot{q}_{dec}(T = T_0)} \frac{RT_0^2}{E_A} \begin{bmatrix} [s] \end{bmatrix}$$

p. 187

K. Hungerbühler: Risk Analysis of Chemical Processes and Products, FS 2017
Isothermal DSC measurements for parameter determination of $TMR_{ad}$

$$TMR_{ad} \cong \frac{c_p}{\dot{q}_{dec}(T = T_0)} \frac{RT_0^2}{E_A}$$

Arrhenius plot: $\dot{q}_{dec} \propto \exp(-E_A/RT)$
Adiabatic heat balance for the decomposition in dimensionless form
(For \( n^{th} \) order decomposition with \( c_A = c_{A,0} (1-x_A) \))

\[
\frac{d\Theta}{d\tau} = B^* \cdot D^* \cdot e^{\left(\frac{\Theta - 1}{\Theta}\right)}
\]

\[
\int_{1}^{\Theta_{TMR_{ad}}} e^{\left(\frac{1-\Theta}{\Theta}\right)} d\Theta = B^* \cdot D^* \int_{0}^{\tau_{TMR_{ad}}} d\tau \quad \text{(for } X_A = 0) \]

\[
\tau_{TMR_{ad}} = \int_{1}^{\Theta_{TMR_{ad}}} e^{\left(\frac{1-\Theta}{\Theta}\right)} d\Theta \approx \frac{1}{\gamma \cdot B^* \cdot D^*}
\]

With the approximations

\[
\left\{ \begin{array}{l}
\frac{1-\Theta}{\Theta} \approx (1-\Theta) \\
1-e^{-\Theta_{TMR_{ad}}} \approx 1
\end{array} \right.
\]

where

\[
\tau_{TMR_{ad}} = \frac{T_{MR_{ad}}}{t_0}, \quad \Theta = \frac{T}{T_0}, \quad \tau = \frac{t}{t_0}, \quad \gamma = \frac{E_A}{RT_0}
\]

\[
\Theta_{TMR_{ad}} = \frac{T_0 + \Delta T_{ad}}{T_0}
\]

\[
B^* = \frac{(-\Delta H_{dec})C_{B,0}}{\rho \cdot c_p \cdot T_0}
\]

\[
D^* = t_0 \cdot k_0 \cdot e^{\frac{E_A}{RT_0 \cdot C_{A,0}^{-1}}}
\]
**II Thermal Runaway**

**Example: temperature dependence of TMR_{ad}**

| $T_0$ [°C] | $\dot{q}_{\text{dec}}(T=T_0)$ [W/kg] | $dT/dt \big|_{T=T_0}$ [K/h]$^*$ | TMR_{ad} [h] |
|------------|---------------------------------|-------------------------------|------------|
| 100        | 1                               | 1.8                           | 6.4        |
| 75         | 0.1                             | 0.18                          | 56         |
| 53         | 0.01                            | 0.018                         | 490        |

assumption: $c_p=2$ kJ/kg/K, decomposition reaction $0^{\text{th}}$ order with $E_A=100$ kJ/mol

\[ * \frac{dT}{dt} \bigg|_{T=T_0} = \frac{\dot{q}_{\text{dec}}(T=T_0)}{c_p} \] (according to adiabatic heat balance)

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II Thermal Runaway

Classification for $TMR_{ad}$ in terms of risk

<table>
<thead>
<tr>
<th>$TMR_{ad}$ [h]</th>
<th>Probability</th>
</tr>
</thead>
<tbody>
<tr>
<td>&lt; 8</td>
<td>high</td>
</tr>
<tr>
<td>$8 &lt; TMR_{ad} &lt; 24$</td>
<td>medium</td>
</tr>
<tr>
<td>&gt; 24</td>
<td>low</td>
</tr>
</tbody>
</table>

$TMR_{ad}$ as critical time constant for effectiveness of safety measures

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II Thermal Runaway

Probability according to TMR\textsubscript{ad}

\textbf{Adiabatic decomposition of hydrogen peroxide:} (35 wt \%)

\textbf{1\textsuperscript{st} approximation:} 10\textdegree C rule

\[ \text{TMR}_{\text{ad}} = 2 \cdot t_{T_0+10K} = \ldots \]

\textbf{2\textsuperscript{nd} approximation:} adiabatic heat balance

\[ \text{TMR}_{\text{ad}} = \frac{c_P}{\dot{q}_{\text{dec}}(T = T_0)} \frac{RT_0^2}{E_A} = \ldots \]
c) Thermal runaway risk: classification by $\Delta T_{ad}$ and $TMR_{ad}$
Thermal runaway risk: classification by criticality classes

\[ T_0 \]: max. attainable temperature after runaway of the desired reaction

\[ T_b \]: boiling point of the reaction mixture

Example 1: DNDB

**Production of dinitrodibenzyl (DNDB)**

(from ortho-nitro-toluene (ONT); DNDB is key intermediate for pharmaceutical production)

**Goal**

a) assessment of thermal risk potential  
b) safety measures planning

**Reaction**

\[
\begin{align*}
2 
\text{ONT} & \quad \text{alcoholate} \\
\text{solvent} & \quad \rightarrow \\
\text{DNDB} & \quad \text{(ONT: ortho-nitro-toluene; DNDB: dinitrodibenzyl)}
\end{align*}
\]

**Lab process**

(at T=12 °C; isotherm; semibatch process)

1. 500 g solvent is already fed in the reactor. (bp. ~90 °C)  
2. add 1 mol alcoholate.  
3. add 0.5 mol ONT within 70 min.  
4. addition of ONT stops for 15 min.  
5. add 1 mol ONT within 140 min.
**II Thermal Runaway**

**Example 1: DNDB**

**DTA Measurements**

1. **DTA measurement 1**
   - Reaction: educts cold mixed
   - Temperature ramp: 4 °C/min
   - Heat released: -270 KJ/kg, -320 KJ/kg

2. **DTA measurement 2**
   - Reaction: educts cold mixed, residual heat after 21 hours at 0 °C
   - Heat released: -170 KJ/kg, -410 KJ/kg

* Differential Thermo-Analyser

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Heat accumulation of DNDB lab process (semibatch mode)

Isothermal heat flow reaction calorimetry at $T = 12 \degree C$

- total produced heat of reaction with ideal dosing control
- measured heat of reaction
- accumulated heat of reaction

$= 1 - 2$

Example 1: DNDB
II Thermal Runaway

Adiabatic conversion of ONT to DNDB (video clip 9)
II Thermal Runaway

Example 2: pesticide

Risk assessment after explosion of a pesticide-intermediate

A pesticide-intermediate is crystallized from a melt on a cooling belt and bottled as a granulate formulation in 20 kg containers. As a result of a technical failure on the cooling belt 2600 kg of this melt (melting point 80 °C) must be stored at 90 °C over the weekend in a heated unstirred tank.

product loss = 1% per day
storage conditions: tank= 4 m³

accident:
thermal explosion after 50 hours

How to explain the cause of this accident?
II Thermal Runaway

Example 2: pesticide

1) Impact

\[ \Delta T_{ad} = \frac{800 \text{ kJ/kg}}{2 \text{ kJ/kg} \cdot \text{K}} = 400\text{K} \]

2) Probability

with 1% decomposition per day

\[ \frac{dT}{dt} = \frac{4^\circ\text{C}}{\text{day}} \approx \frac{0.2^\circ\text{C}}{\text{h}} \text{ (@90}^\circ\text{C)} \]

Doubling the rate of decomposition when the temperature rises by 10 °C:

90 °C 0.2 °C per hour
100 °C 0.4 °C per hour
110 °C 0.8 °C per hour

Assumption: \( c_p = 2 \text{ kJ/(kg} \cdot \text{K)} \)
**Thermal Process Safety**

**II Thermal Runaway**

**Example 2: pesticide**

**TMR\textsubscript{ad}: 10-degree rule for doubling of reaction rate**

\[ 50 \text{ h} = \text{TMR}_{ad} \]

\[ 25 \text{ h} = \frac{\text{TMR}_{ad}}{2} \]

\[ 12.5 \text{ h} \]

\[ 6.25 \text{ h} \]

\[ 0.2 \degree \text{C/h} \]

\[ 0.4 \degree \text{C/h} \]

\[ 10 \text{ K} \]

1) according to upper slope (=0.4 \degree \text{C/h})

---

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Process alternative: after technical fault of the cooling belt storage of the melt in a stirred double-walled tank (4 m³) at 90°C with warm water cooling (T_c = 85°C)

decomposition power: \( \dot{q}_{\text{dec}} \approx 0.1 \text{ W/kg} \)

stirring power: \( 1 \text{ kW/m}^3 \rightarrow \dot{q}_{\text{stir}} \approx 1 \text{ W/kg} \)

with:
\[
\Delta T_{\text{max}} = 5 \text{ K} \\
U = 200 \text{ W/m}^2/\text{K} \\
m = 2600 \text{ kg} \\
A = 8 \text{ m}^2
\]

cooling power: \( q_{\text{cooling}} = U \cdot A \cdot \frac{\Delta T}{m} \approx 3 \text{ W/kg} \)

cooling power > decomposition power + stirring power
\( \rightarrow \) stable heat balance
Content of this lecture

• “As usual” and “runaway” scenario
• **Thermal reactor stability**: Batch and semibatch process
  – Mass and heat balance; Semenov diagram
  – Concentration profiles, heat production and thermal conversion (semibatch only)
• Comparison of reactor types batch, semibatch, ISTR, plug-flow and cross flow
• **Thermal runaway**: Basic scenario for risk analysis
  – $\Delta T_{ad}$ as **impact** indicator
  – Typical functional groups of unstable compounds
  – $TMR_{ad}$ as **probability** indicator. Approximation with 10-degree rule or adiabatic heat balance
  – Risk classification by criticality classes
Review questions

You should be able to answer the following questions

- Draw the “as usual” and “runaway” scenario in a time-temperature profile.
- How are batch and semibatch reaction processes defined? Sketch the two reactor types. What assumptions are made?
- Compare mass balance, heat balance and cooling process for a batch and semibatch reactor.
- How are mass and heat balances defined in dimensionless form (ChemIng only)
- Draw possible concentration profiles for a semibatch reactor. Which assumptions are made?
- Compare batch, semibatch and continuous reaction modes regarding $q_R$, $q_C$ and thermal scale-up effect.
- What parameter is an indicator for the impact of a thermal runaway? Which classes are here differentiated?
- Give some examples of typical functional groups of unstable compounds.
- What parameter is an indicator for the probability of a thermal runaway? How can this value be approximated?