Fraunhofer Institute for Solar Energy Systems ISE

Technical discussion 4: Kinetics and Modelling

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Sorption Friends III, Taormina, Sicily
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Topics

Kinetics

What needs to be measured on which level?

Which measurement setups exist and which prove helpful

- For open Adsorption?
- For closed Adsorption?
- For Absorption?

What is missing?

Topics

Modelling

What needs to be modelled on which level?

Which models exist and which prove helpful

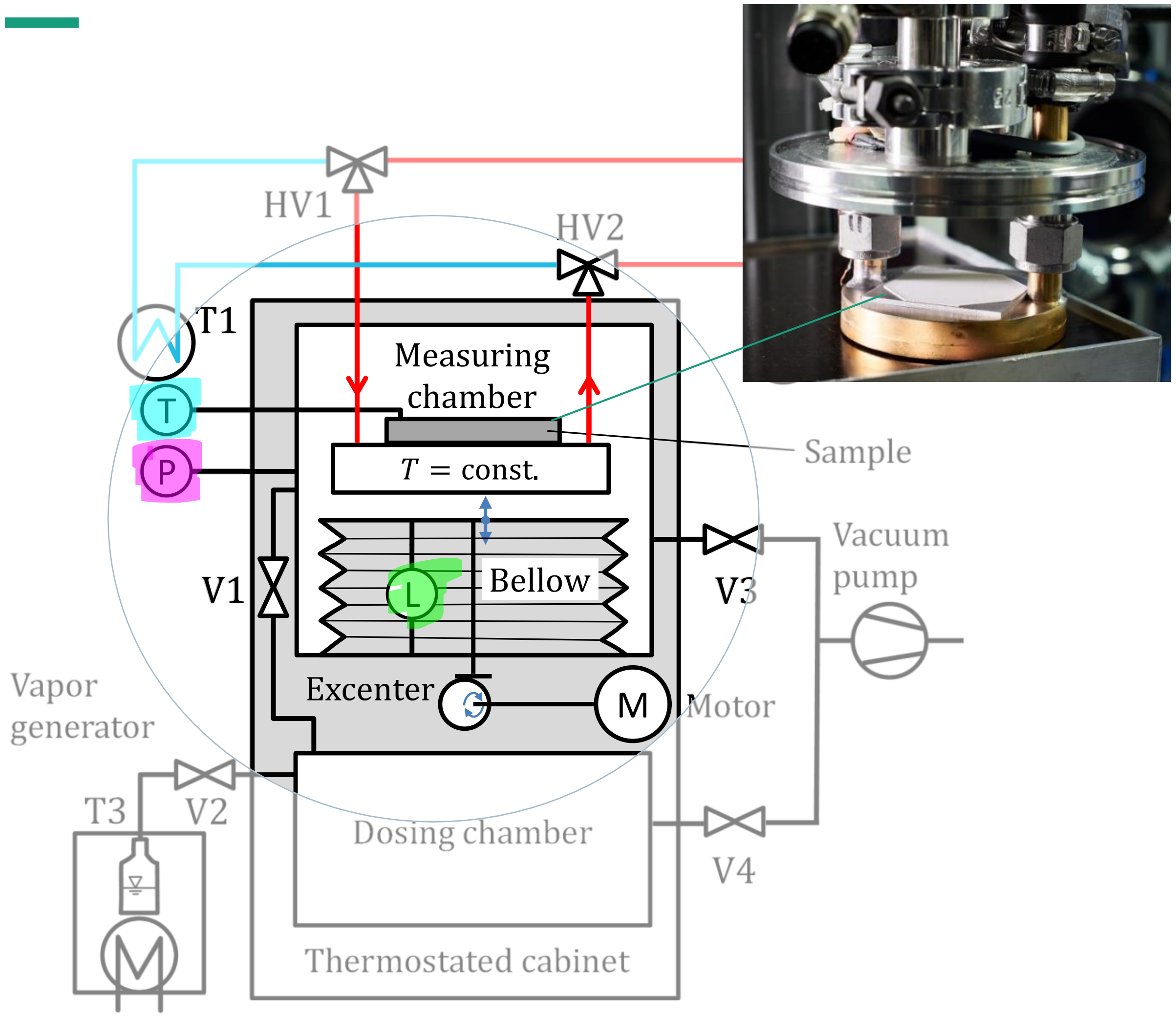
- For open Adsorption cycles?
- For closed Adsorption cycles?
- For Absorption cycles?

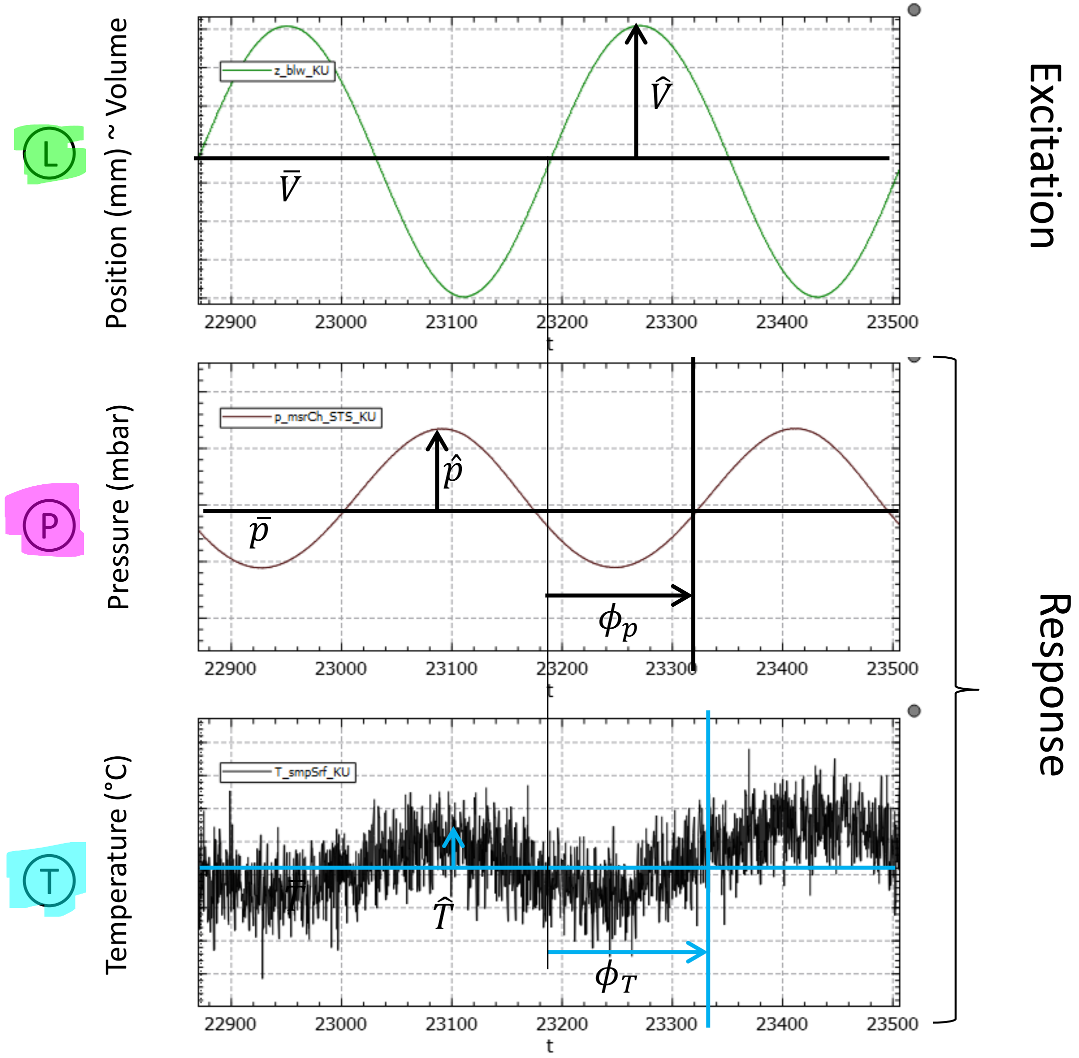
What is missing?

Hypothesis: Most modelling activities cannot be transferred neither to industry at high TRL nor to material research and development at low TRL because they are too specific, too complicated and do not address questions of technology application, but rather specific development questions.

Sorption Technology

Highlight: Frequency Response Analysis





[1] E. Laurenz *et al.*, *Int. J. Heat Mass Transf.* **2021**, *169*

Kinetics Measurement Method

Frequency Response Analysis

Excitation frequency varied: 10^{-3}…5 Hz

- Different transport effects visible at different frequencies

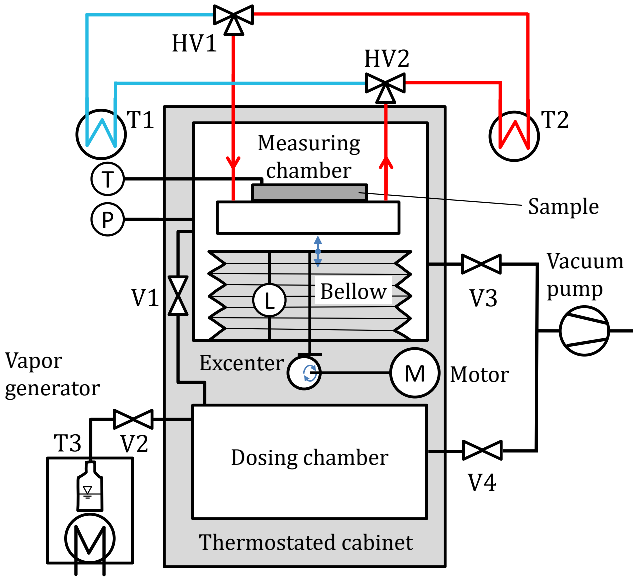
Deviation from equilibrium is small:

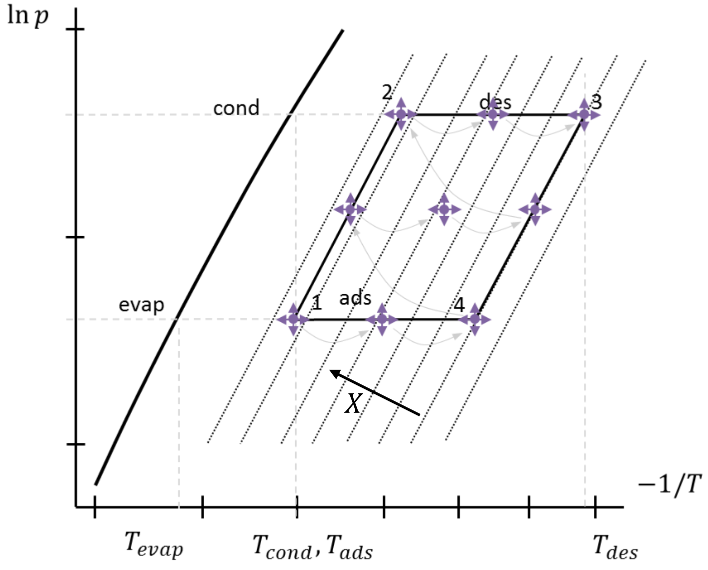
- Linear behaviour (locally constant coefficients)
- Local measurement (temperature, pressure, loading)

➢Map of measurement points in state space

Integrated pre-procedure [1]:

- Sorption equilibrium
- Differential sorption enthalpy





[1] E. Laurenz *et al.*, *Energies* **2020**, *13 (11)*, 3003

Frequency Response

Transport Model

Coupled heat and mass transfer

- Contact resistance coating/wall (h) 🟪
- Heat conduction in the coating (λ) 🟦
- Mass transfer at particle scale (k) 🟩

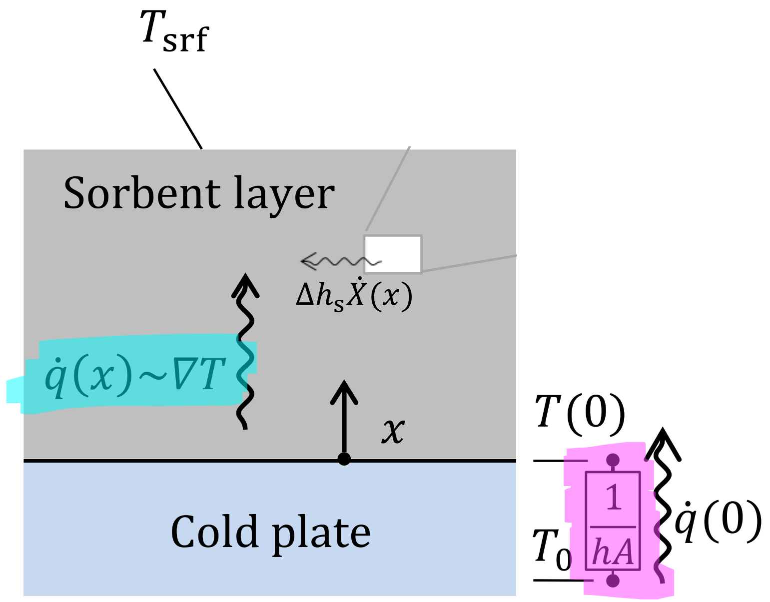
Modelling as system of ODE/PDE

- Transf. into frequency domain (Laplace)
- Constant coefficients (linearized)
- Solved analytically(!) for FR boundary conditions

Identification of h, λ and $D_{\mathrm{mi}} \approx \frac{r^2}{3}k$ [2]

- Model fitted to experimental results

only variables fitted



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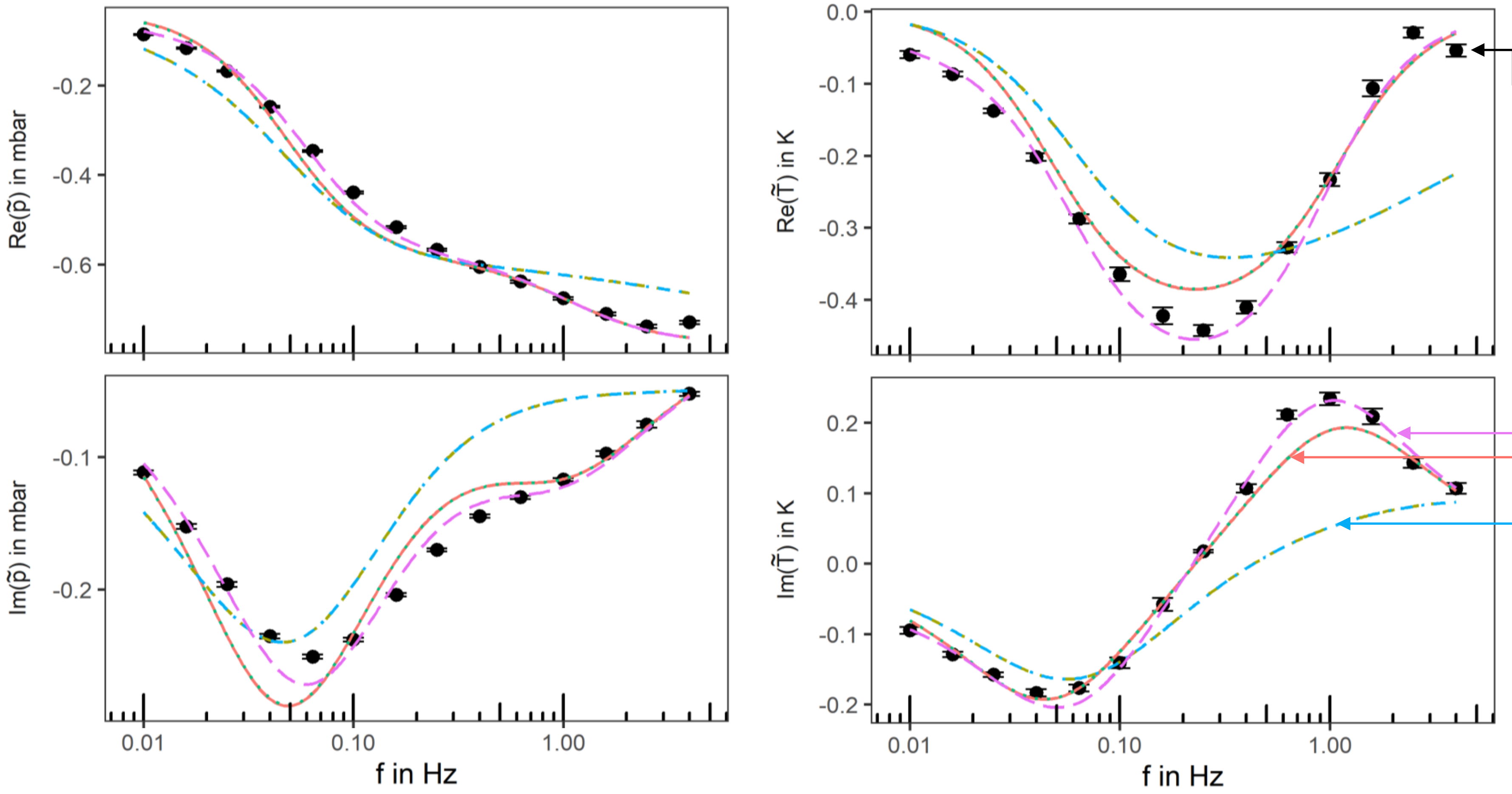
[2] E. Laurenz *et al.*, *Int. J. Heat Mass Transf.* **2021**, *169,* 120921

Frequency Response

Results



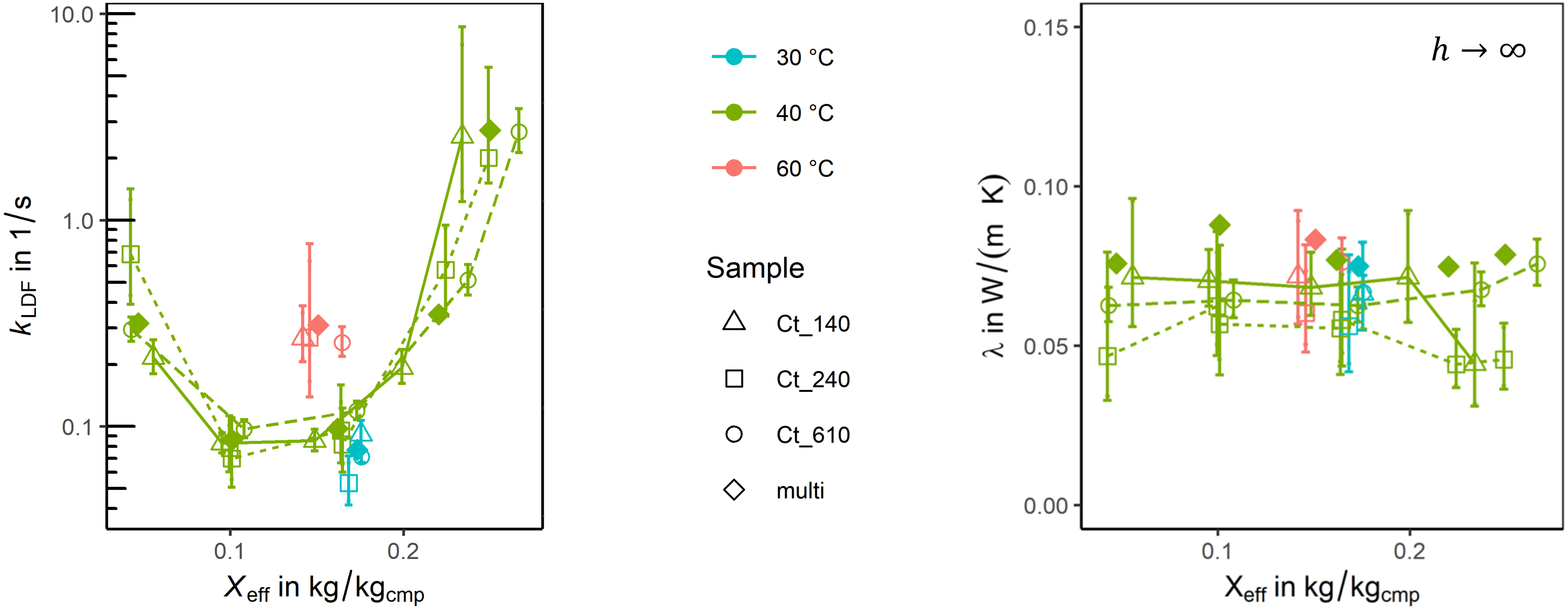
- Measurement
  610 µm, 40 °C,
  0.09 g/g, 18.5 mbar
- "Best Fits" for different Models:
  - Model just shown
  - Lumped heat & mass transfer
  - Discretised mass transfer & lumped heat transfer

Laurenz et al., *Int. J. Heat Mass Transf.* **2021**, *169*, 120921

Frequency Response

Identified Parameters

Parameters identified with „best fit“
$(h \to \infty)$



Laurenz et al., *Int. J. Heat Mass Transf.* **2021**, *169*, 120921

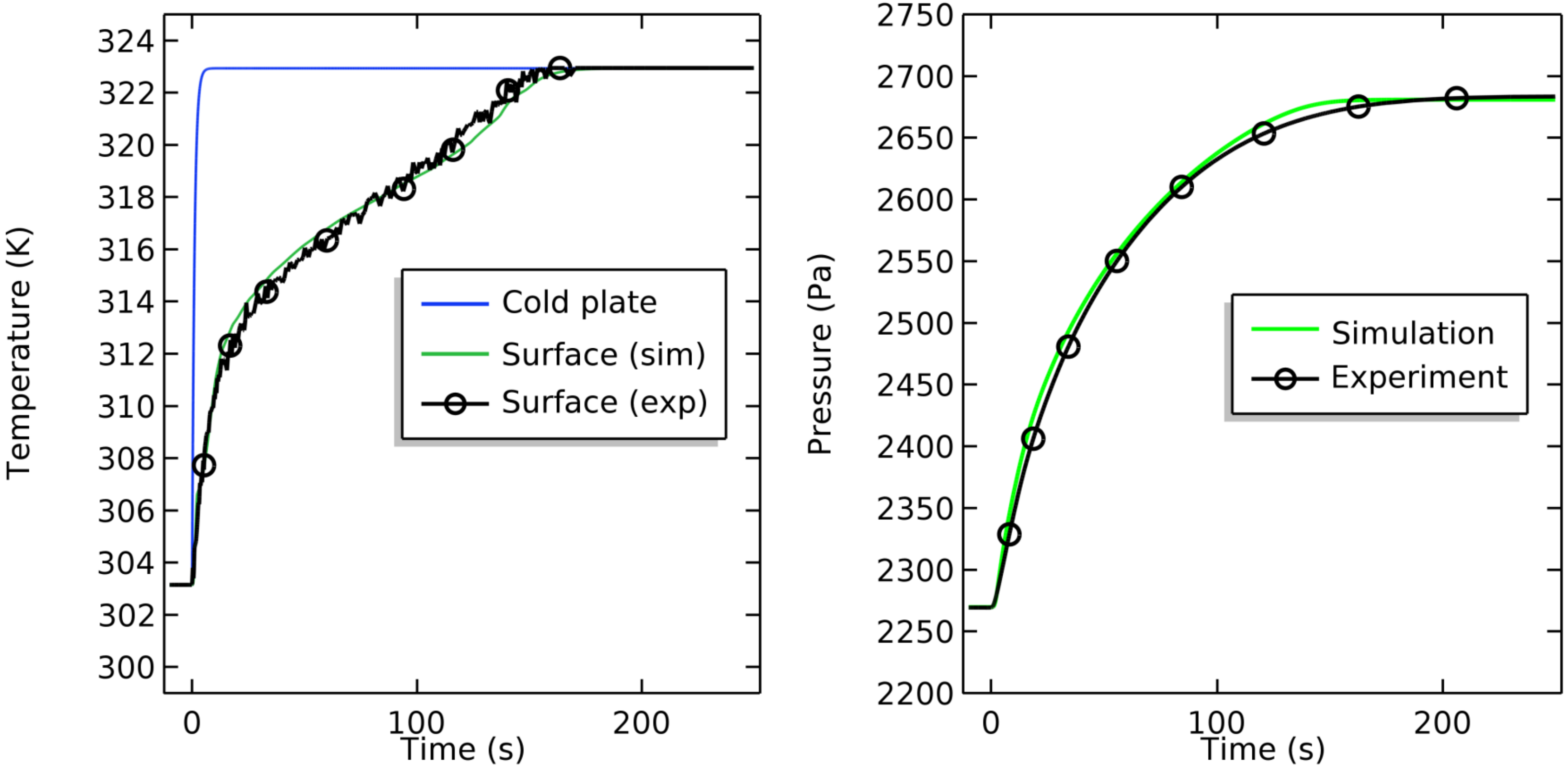
Modelling with parameters from FR

Non-linear validation

Strongly non-linear measurement [1]:
20 K temperature jump

Non-linear time-domain model [2]:

- Transport parameters: Function of temperature and loading, obtained from FRA results
- Sorption equilibrium and enthalpy from integrated pre-procedure
- No time-domain fitting!



[1] Laurenz et al., *25th IIR ICR*. Montreal **2019**
[2] Velte et al., *Energies* **2017**, *10 (8)*, 1130

Adsorption Modelling

Modelling in Simplified Model

Pressure p_{mod} is measured

Equilibrium temperature T_{eqi}

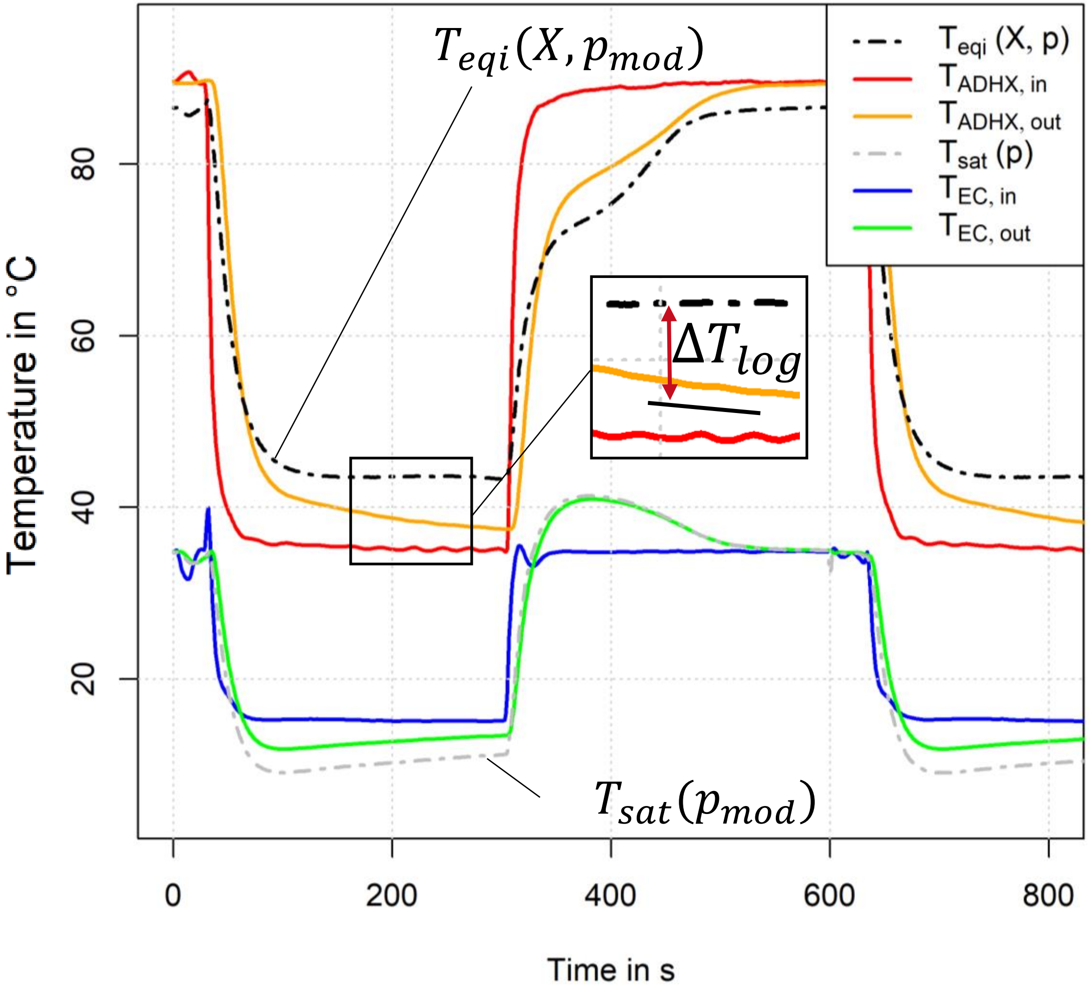
Saturation temperature T_{sat}

Basic heat exchanger theory (ε-NTU for stationary temperatures)

$$\dot{Q} = \Delta T_{log} \cdot UA$$

Overall heat and mass transfer resistance

$$\mathrm{R} = UA^{-1} = \frac{\Delta T_{log}}{\dot{Q}}$$



#6 | 15/35/90 °C, 300 s

Adsorption Modelling

Modelling in Simplified Model

Pressure p_{mod} is measured

Equilibrium temperature T_{eqi}

Saturation temperature T_{sat}

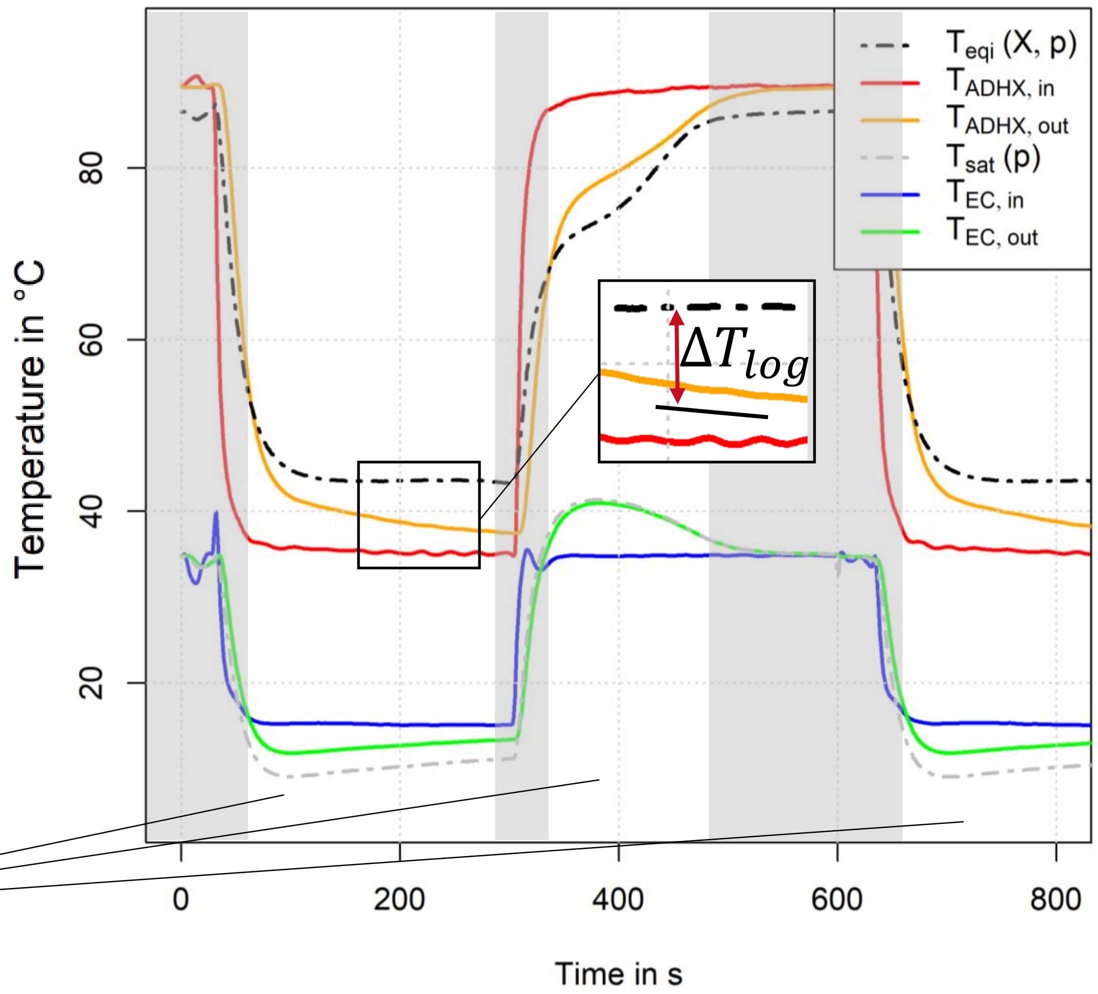
Basic heat exchanger theory (ε-NTU for stationary temperatures)

$$\dot{Q} = \Delta T_{log} \cdot UA$$

Overall heat and mass transfer resistance

$$\mathrm{R} = UA^{-1} = \frac{\Delta T_{log}}{\dot{Q}}$$

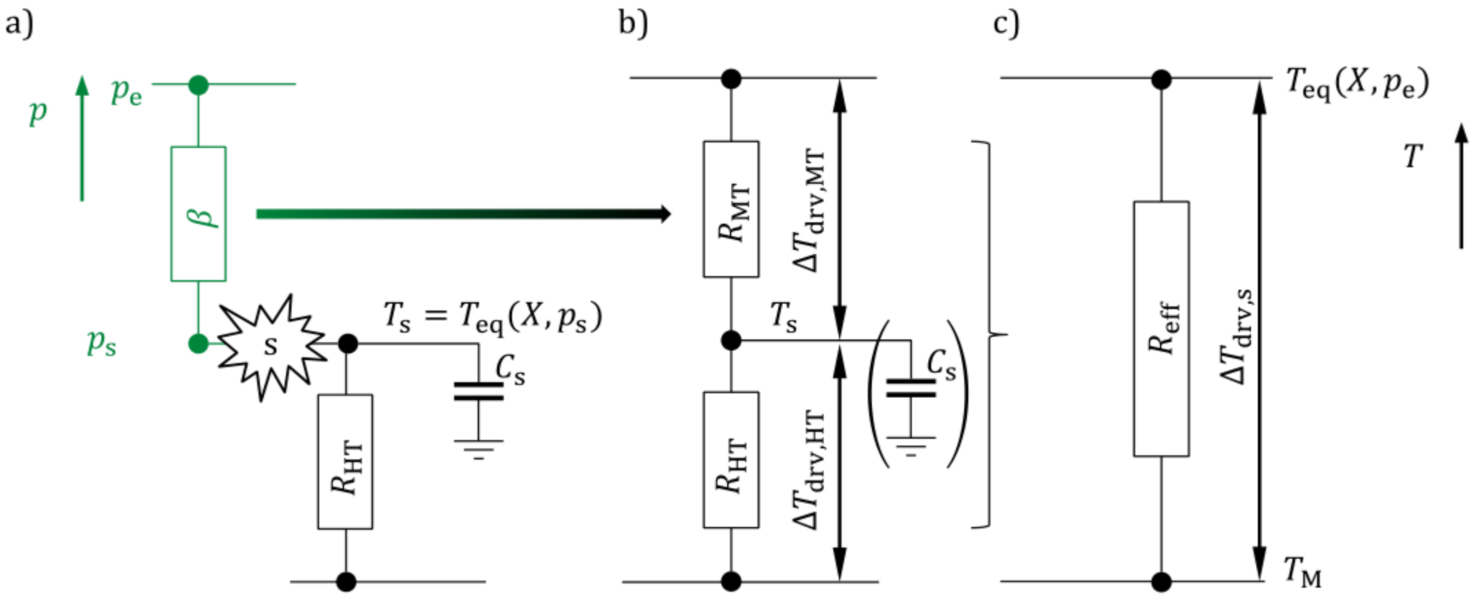
„quasi-stationary“ states



#6 | 15/35/90 °C, 300 s

Simplified model: Application to Adsorber and Evaporator

Effective resistances: equivalence between heat and mass transfer



$$R_{MT} = \frac{\Delta T_{drv,MT}}{\dot{Q}_s} = \frac{T_{eq}(X, p_e) - T_s}{m_s \Delta h_s \dot{X}}.$$

$$R_{HT} = \frac{\Delta T_{drv,HT}}{\dot{Q}_s} = \frac{T_s - T_M}{m_s \dot{X} \Delta h_s},$$

$$R_{eff} = R_{MT} + R_{HT} = \frac{\Delta T_{drv,s}}{\dot{Q}_s}.$$

$$UA_{eff} = \frac{1}{R_{eff}}$$

Important assumption: $\mathrm{d}T \cdot C \ll \mathrm{d}X \cdot m_s \Delta h_s$

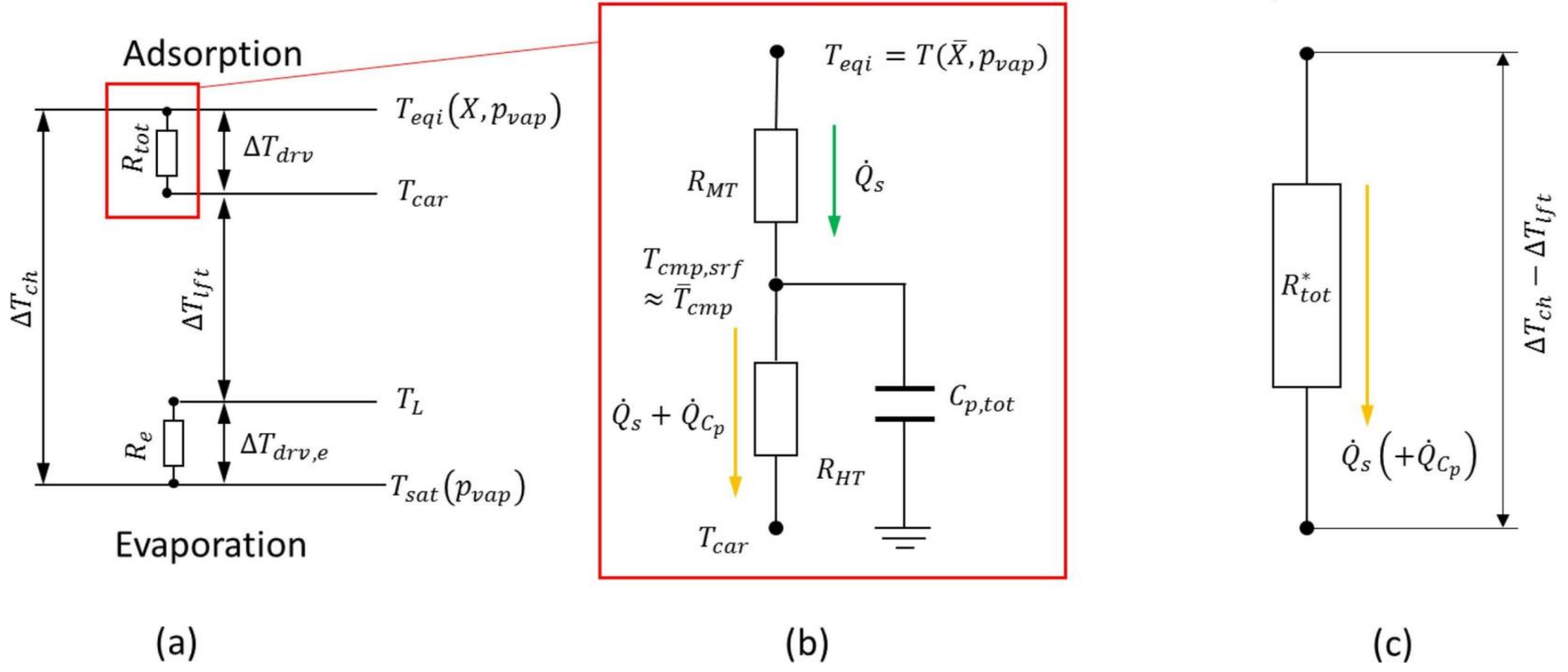
i.e. quasi isothermal

-> Heating and cooling phases to be considered separately!

Simplified model: Application to Adsorber and Evaporator

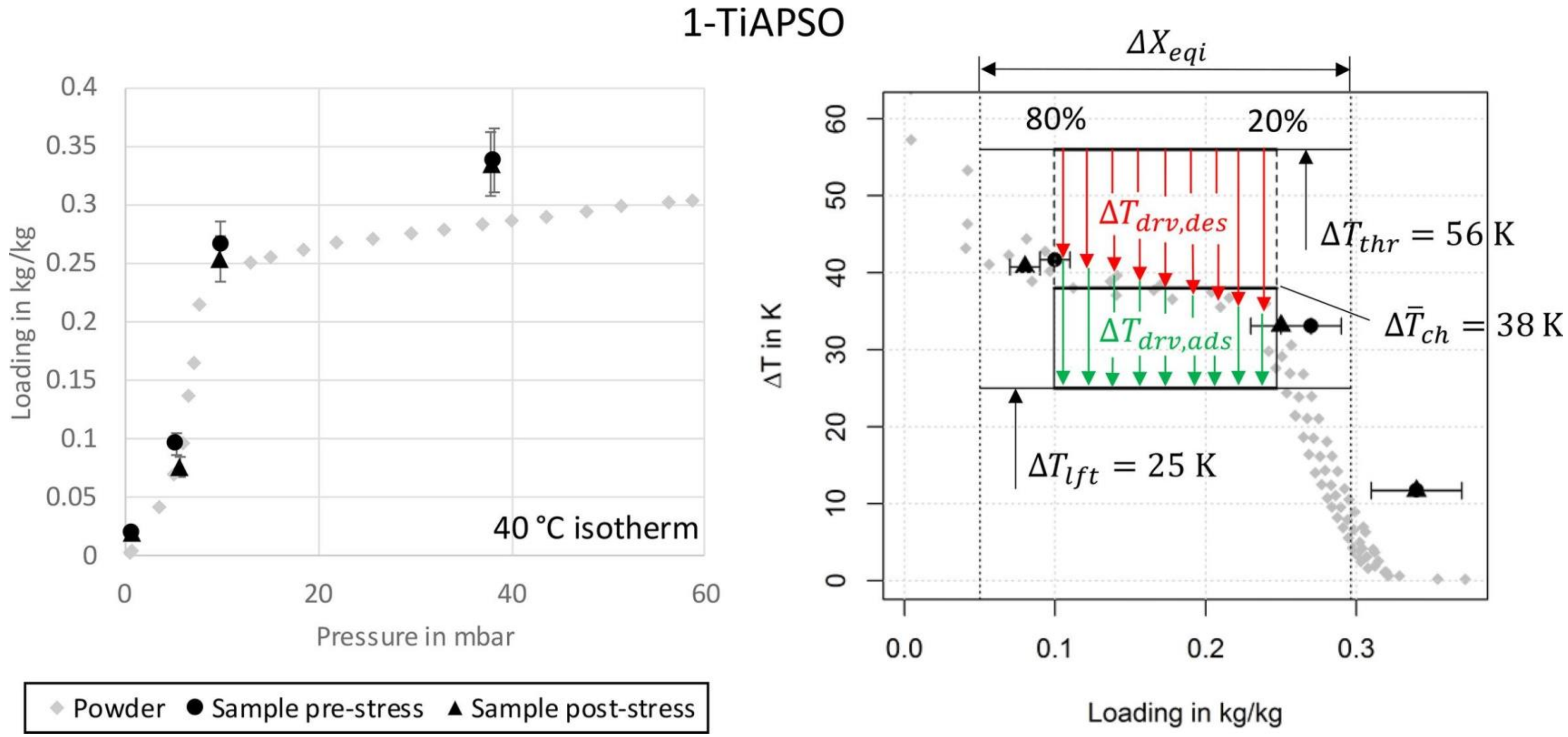
Effective resistances: temperature differences

$$R_e \rightarrow 0, T_L \rightarrow T_{sat}$$
$$\Delta T_{ch} = T_{eqi} - T_{sat}(p_{vap})$$
$$\Delta T_{lft} = T_{car} - T_{sat}(p_{vap})$$



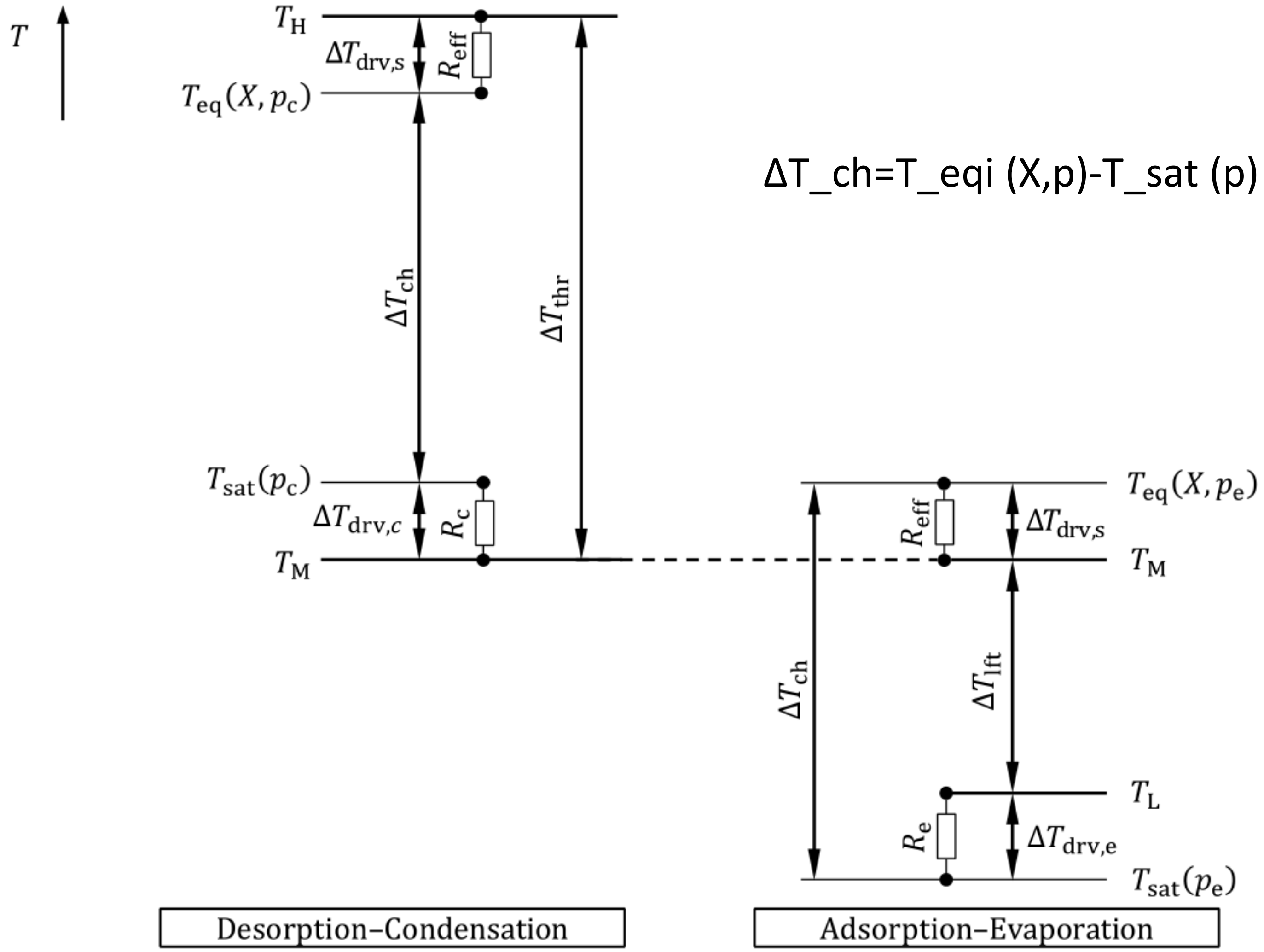
Simplified model: Application to Adsorber and Evaporator

Effective resistances: temperature differences



Simplified model: Application to Adsorber and Evaporator

Effective resistances: temperature differences



ΔT_ch=T_eqi (X,p)-T_sat (p)

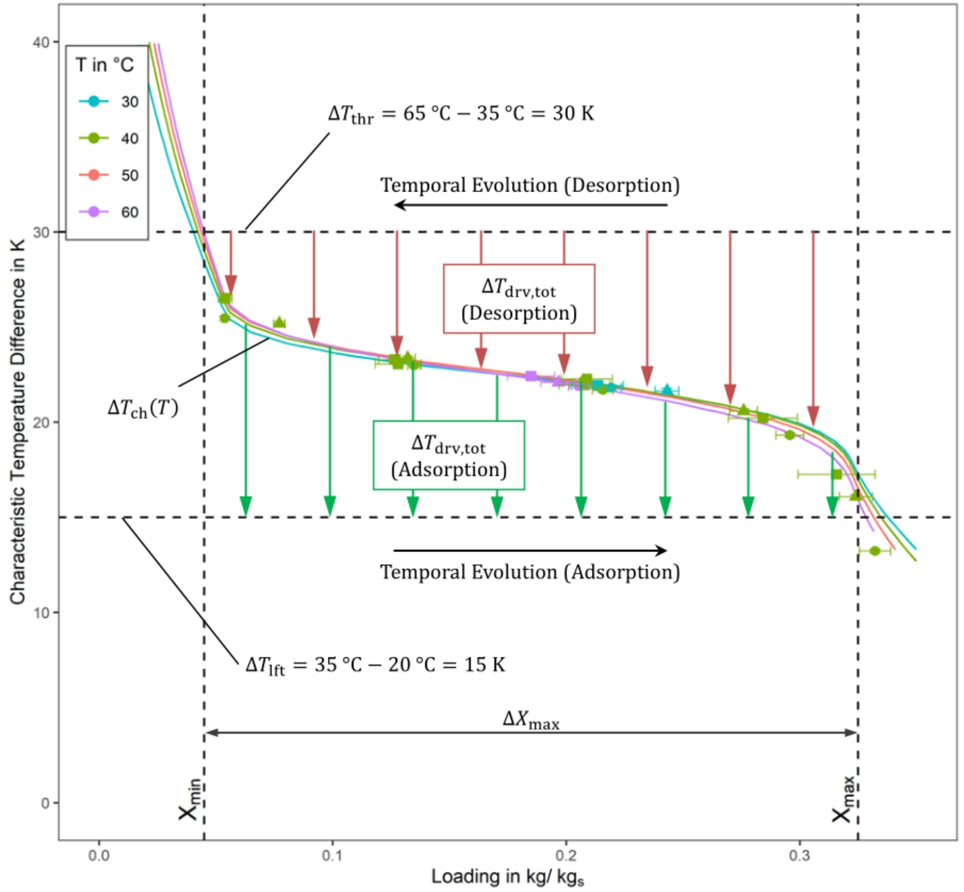
$$\dot{Q}_{\mathrm{M}}(T_{\mathrm{s}}, X) = \frac{\Delta T_{\mathrm{ch}}(T_{\mathrm{s}}, X) - \Delta T_{\mathrm{lft}}}{R_{\mathrm{e}} \frac{\Delta h_{\mathrm{v}}}{\Delta h_{\mathrm{s}}} + R_{\mathrm{s}}},$$

$$\dot{Q}_{\mathrm{L}}(T_{\mathrm{s}}, X) = \frac{\Delta T_{\mathrm{ch}}(T_{\mathrm{s}}, X) - \Delta T_{\mathrm{lft}}}{\underbrace{R_{\mathrm{e}} + R_{\mathrm{s}} \frac{\Delta h_{\mathrm{s}}}{\Delta h_{\mathrm{v}}}}_{R_{\mathrm{e,tot}}}}$$

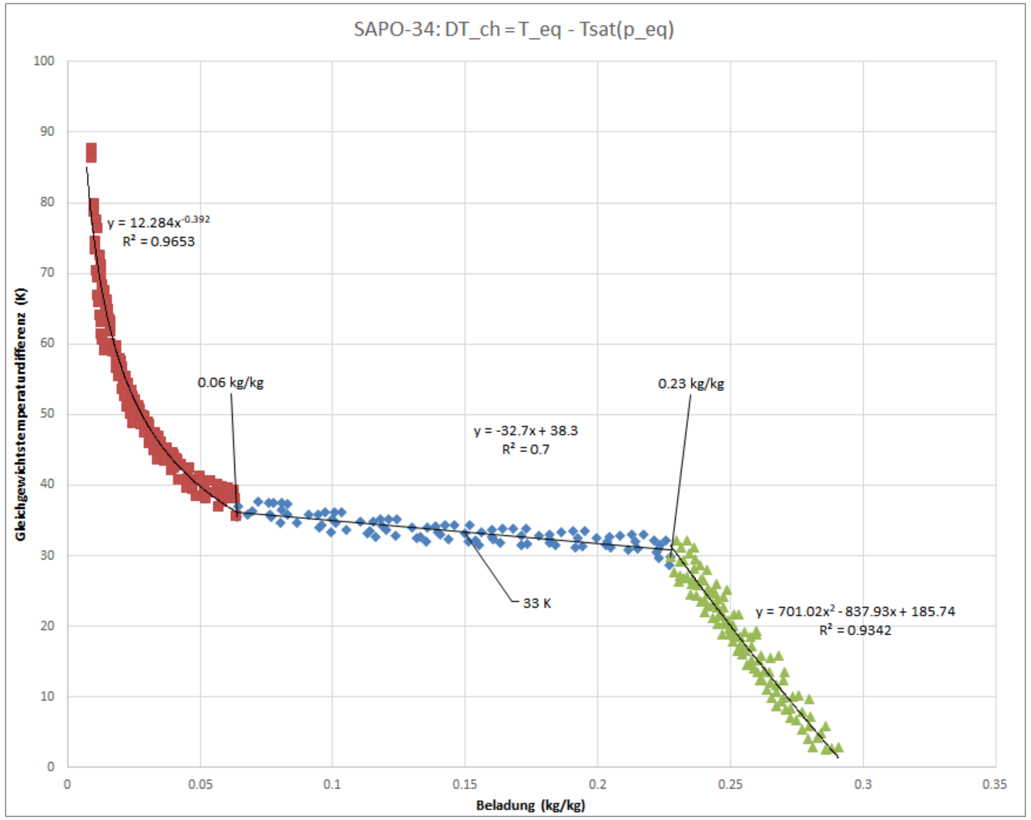
$$\mathrm{VSCP} = \frac{\Delta T_{\mathrm{ch}}(T_{\mathrm{M}}, X) - \Delta T_{\mathrm{lft}}}{R^{V}_{\mathrm{e,tot}}}$$

Simplified model: Application to Adsorber and Evaporator

Effective resistances: temperature differences



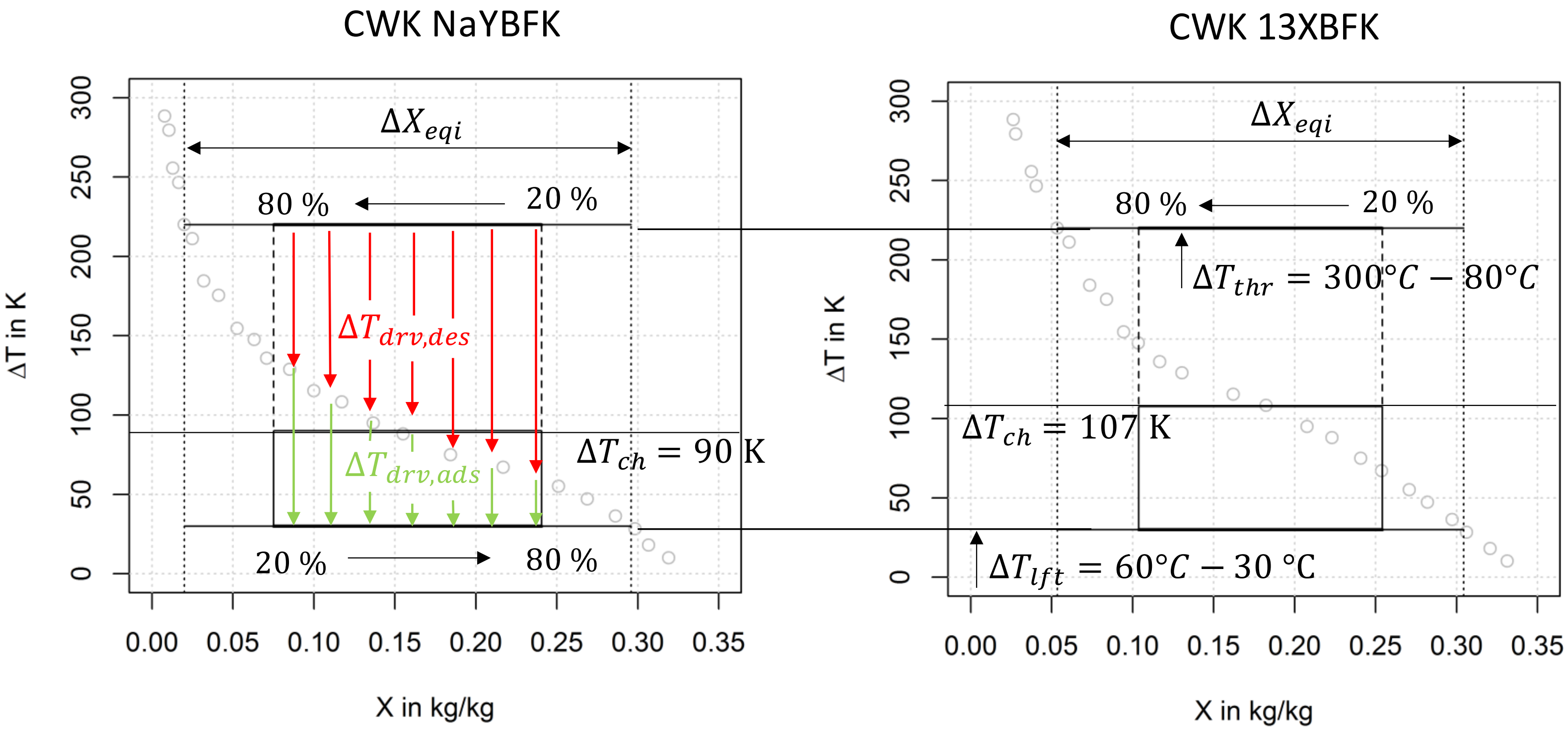
Aluminiumfumarat
(Daten ISE, mit Prozessbedingungen 20/35/65 °C)



SAPO-34
(Daten Fahrenheit)

Simplified model: Application to Adsorber and Evaporator

Effective resistances: temperature differences



(a)

(b)

Translating application boundary conditions into material performance

Difference between „idealized“ COP estimations and COPs taking into account necessities for heat and mass transfer.

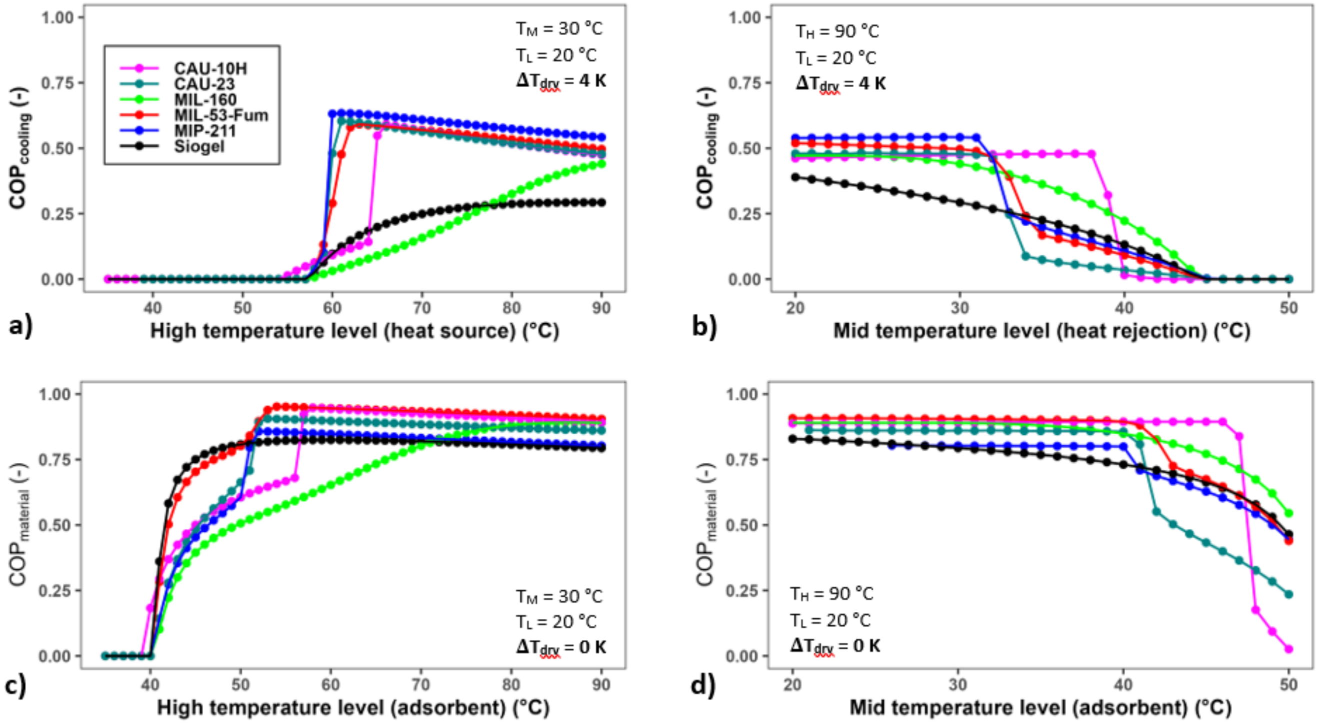


Figure 5 Estimated cooling-COP under typical application conditions (top) and ideal material-COP (bottom) for variations for variations of the high temperature level (left) and the mid temperature level (right) for MIP-211 compared to selected MOFs and a state-of-the-art silica gel (Siogel), showing a superior performance of the novel MIP-211 as long as a low-enough temperature for heat rejection can be provided. Note that for cooling-COPs the temperatures of the exploited heat sink/source differ from the temperatures at material level (driving temperature difference) whereas for material-COPs this difference is neglected resulting in drastic overestimations possible mid temperature levels and underestimation of required high-temperature levels. Negative COPs are set to zero.

[1] Matemb Ma Ntep TJ, Wahiduzzaman M, Laurenz E et al. When Polymorphism in Metal-Organic Frameworks Enables Water Sorption Profile Tunability for Enhancing Heat Allocation and Water Harvesting Performance. Adv Mater. **2023** doi: 10.1002/adma.202211302

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