Investigation of sorption characteristics of technical adsorbens by dynamic methods

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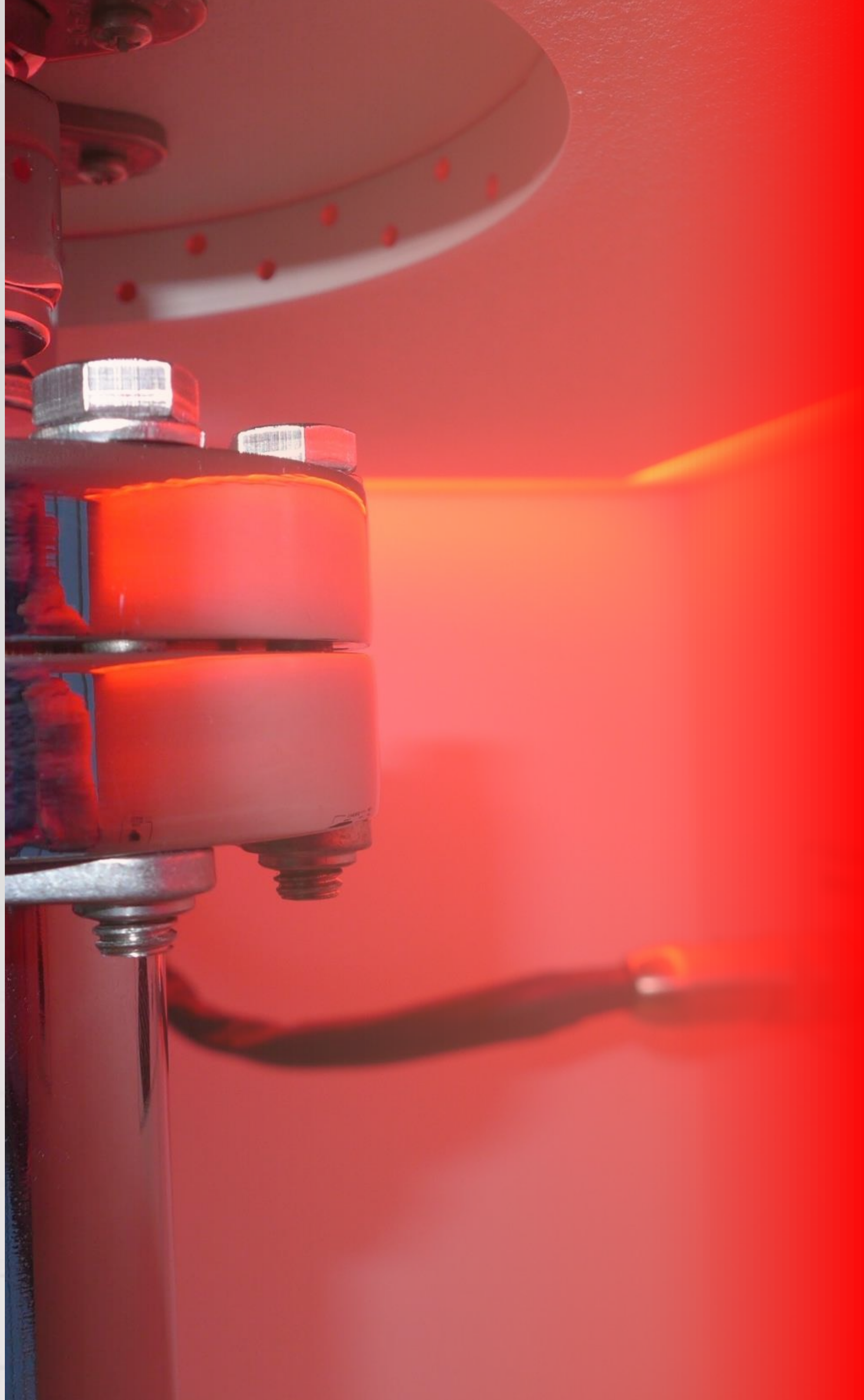
Quantachrome INSTRUMENTS

Schedule

1. Introduction
2. Experimental Setup
3. Specification of **dyna**Sorb BT
4. Measurement capabilities
5. Breakthrough curves-Theory
6. Applications
7. Interpretation of Results
8. Examples
9. Summary



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1. Introduction

Importance of dynamic Methods (measurement on fixed bed)

Why is the determination of sorption characteristic with dynamic methods so important?

- Most technical separation processes by adsorption under dynamic conditions
- Different Kinetics of guest molecules can be play a key-role during separation
- In technical separation always gas mixtures are present
  - Therefore the selectivity of adsorbent is very important
- Downscaling of technical processes possible
  - Investigation of adsorbents under relevant gas velocities
  - Investigation of cycle stability of materials
- Results can better transferred into technical processes.

Questions which can be answered with dynamic experiments:

Cycle stability
technical usable sorption capacity
Optimal gas velocity
Regeneration conditions
Influence of other adsorptives (Co-adsorption phenomena)
Proof of suitability of different adsorbens

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1. Introduction

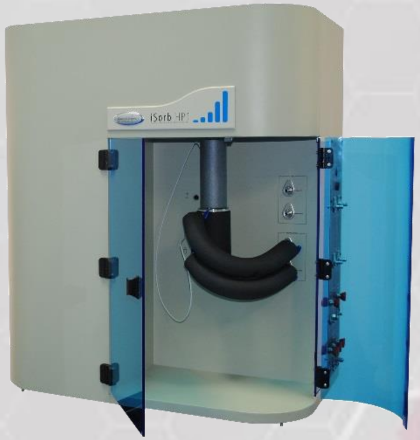
Static Methods versus dynamic Methods

Static volumetric measurements:

- Sorption takes place in an enclosed chamber
- Pressure is recorded over time
- Single component only by now. Measurement of mixtures not possible with commercial instruments. Mixture adsorption difficult.
  - ➢ Standard characterization (BET, pore volume, pure component isotherms …)

Dynamic method:

- Sorption takes place in open system.
- Pressure is constant.
- Outlet composition is recorded over time.
- Mixtures only. Measurement of single components hardly possible.
- Downscaling of technical processes possible
  - ➢ Investigation of technical relevant parameters (selectivity, sorption kinetics, regeneration conditions …)



iSorb HP 1

dynaSorb BT

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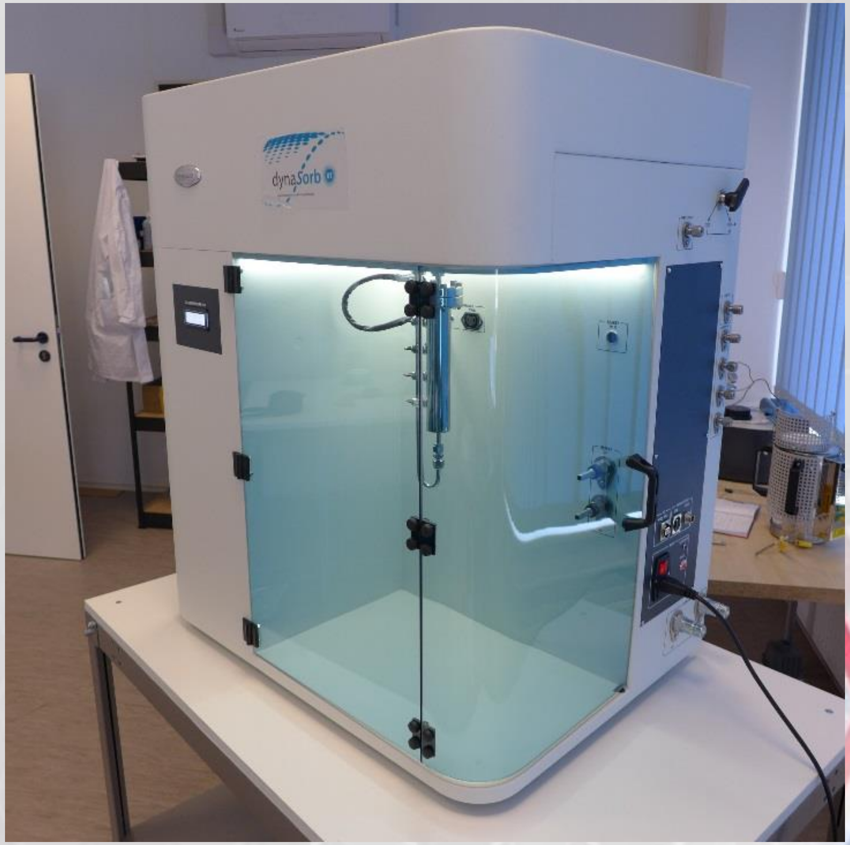
2. Experimental Setup



Automated physisorption analyzer, capable of:

- **Dynamic** flow adsorption, desorption
- Capable of high gas flow rates up to 40 L/min
- Determination of **breakthrough** curves
- Investigation of **kinetic performance** of adsorbents
- Investigation of **co-adsorption** and displacement phenomena
- Determination of sorption **selectivities**
- Automated built-in **gas mixing** with high precision mass flow controllers
- Downscaling of technical separation processes

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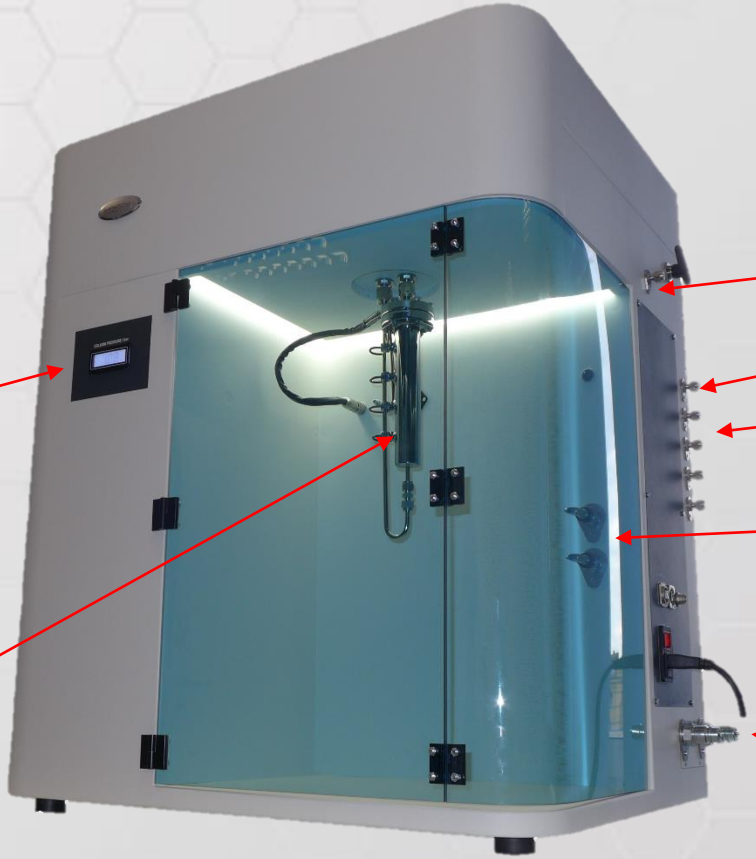
2. Experimental Setup

Visible Parts of **dynaSorb BT**



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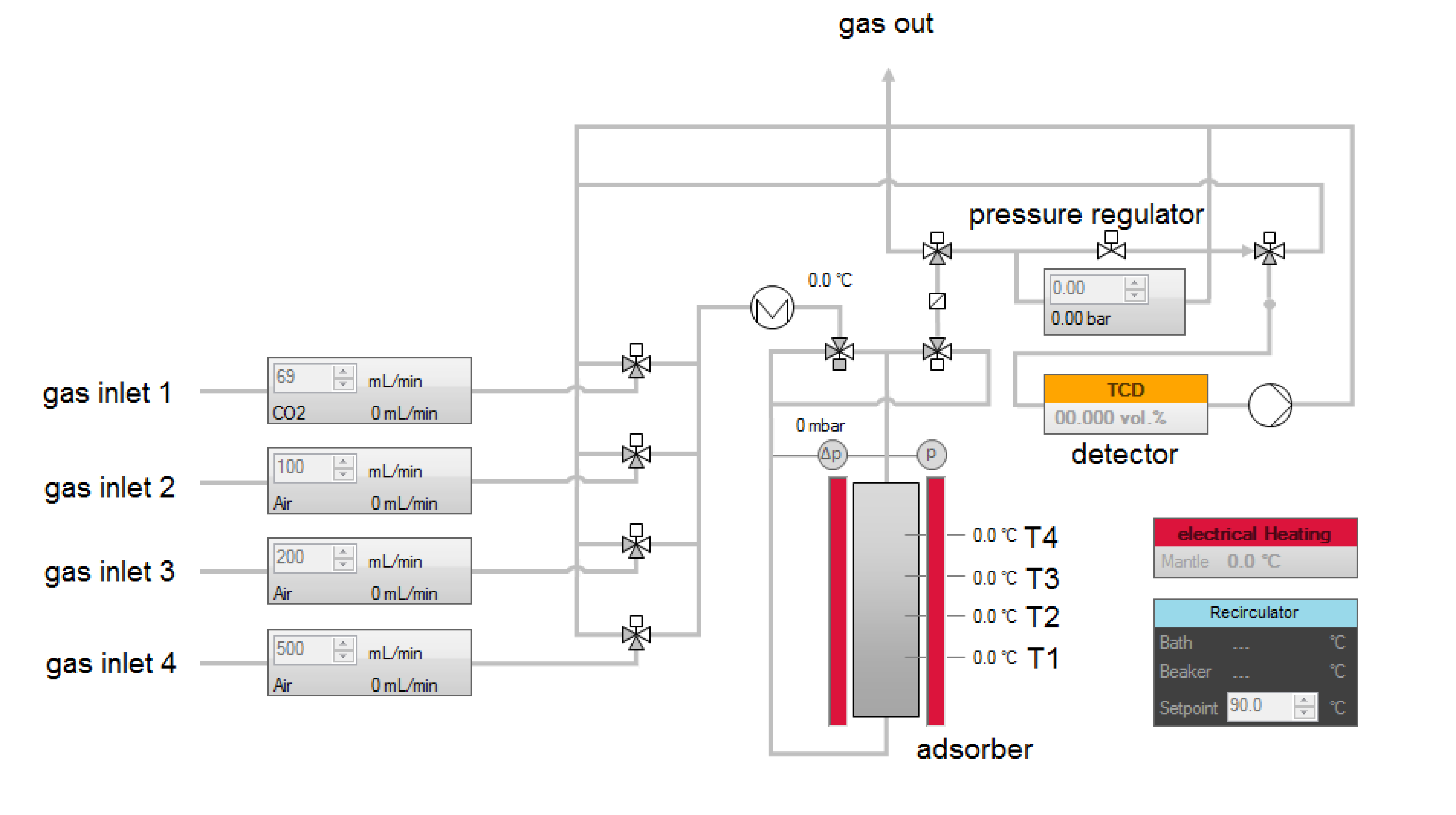
Adsorbers available:

~150 cm^3 column with 4 temperature sensors
~ 5 cm^3 column with 1 temperature sensor

2. Experimental Setup

Flow Chart of the Setup - Overview



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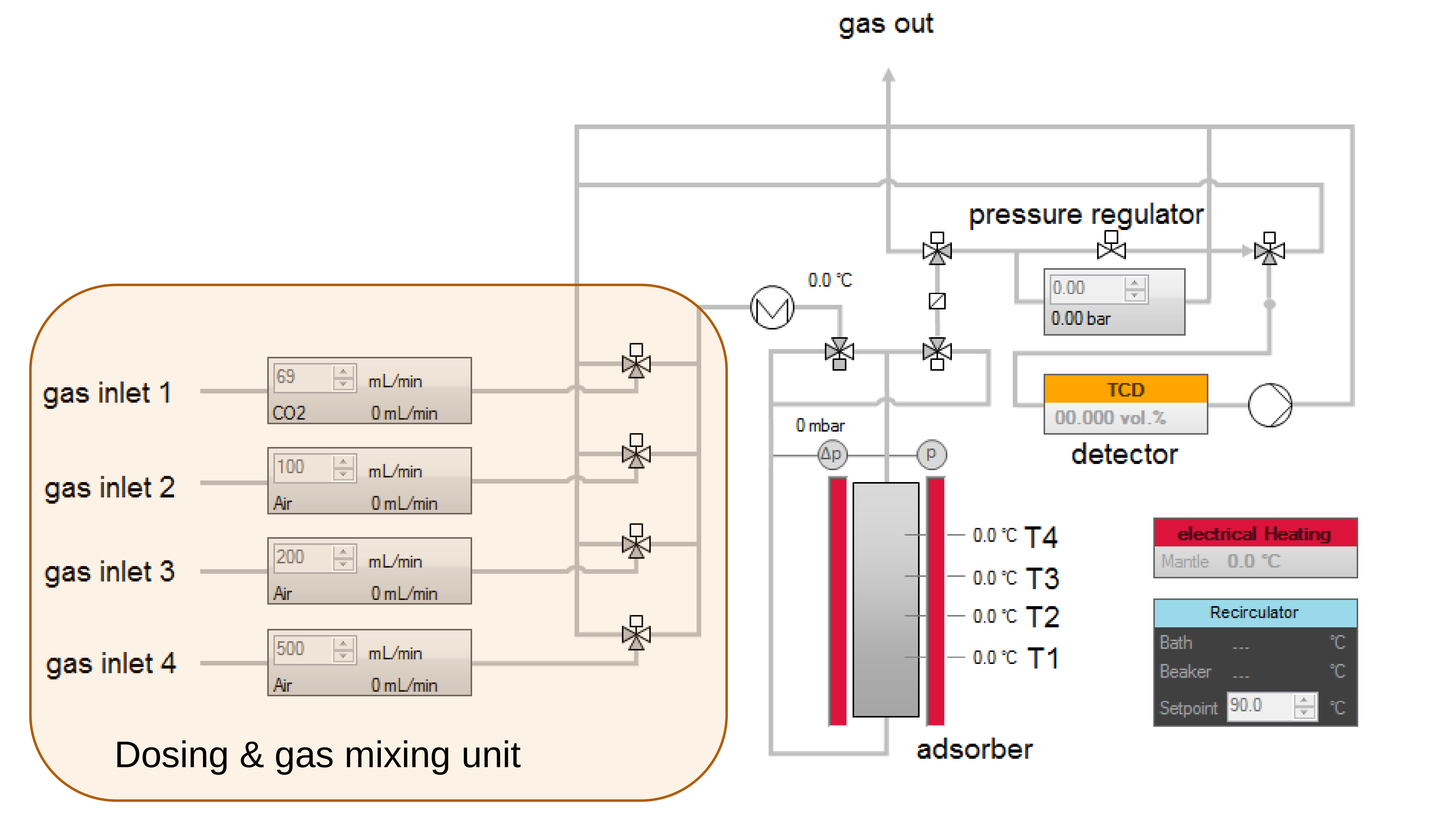
2. Experimental Setup

Flow Chart of the Setup – Dosing Unit



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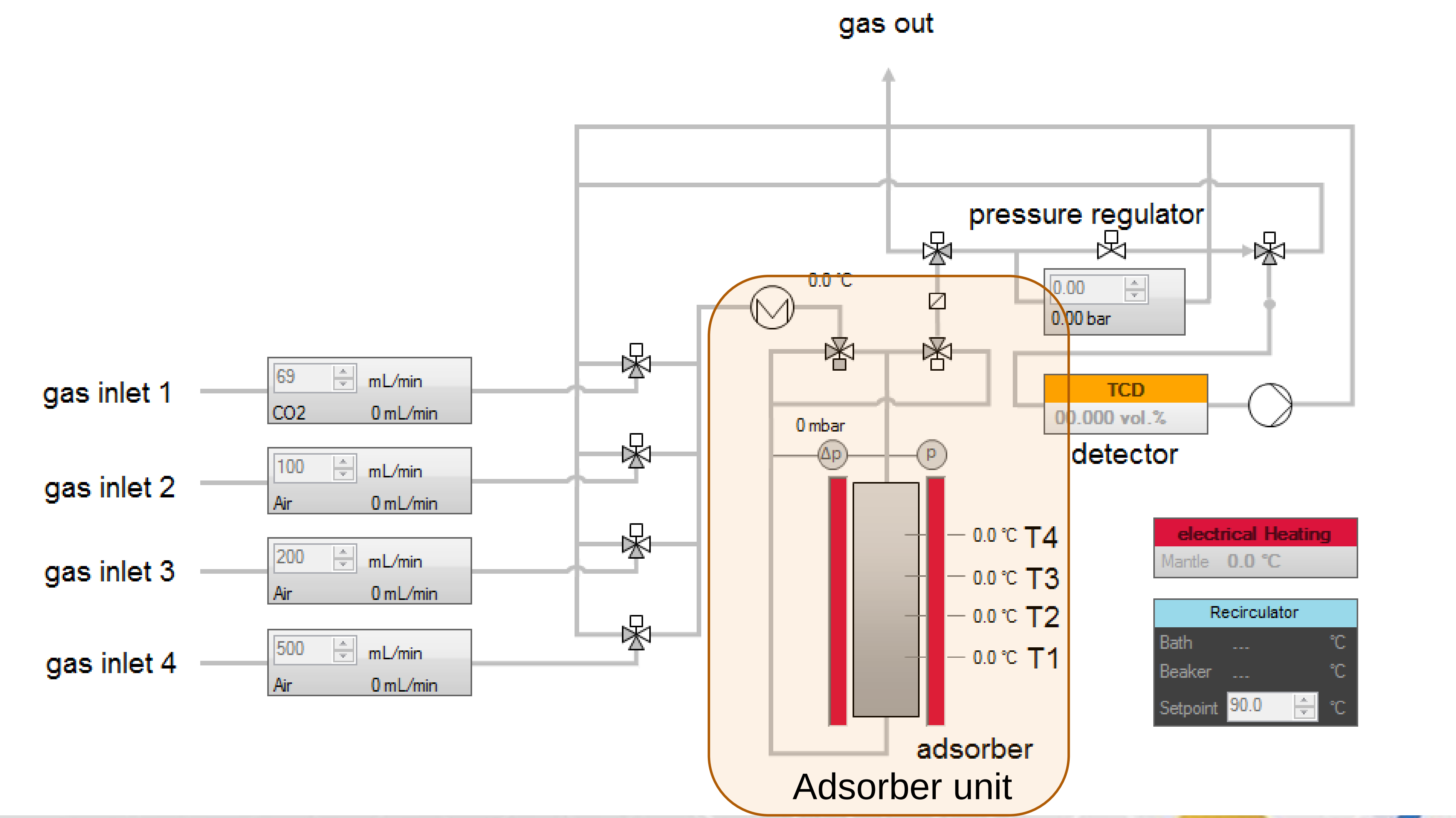
2. Experimental Setup

Flow Chart of the Setup – Adsorber Unit



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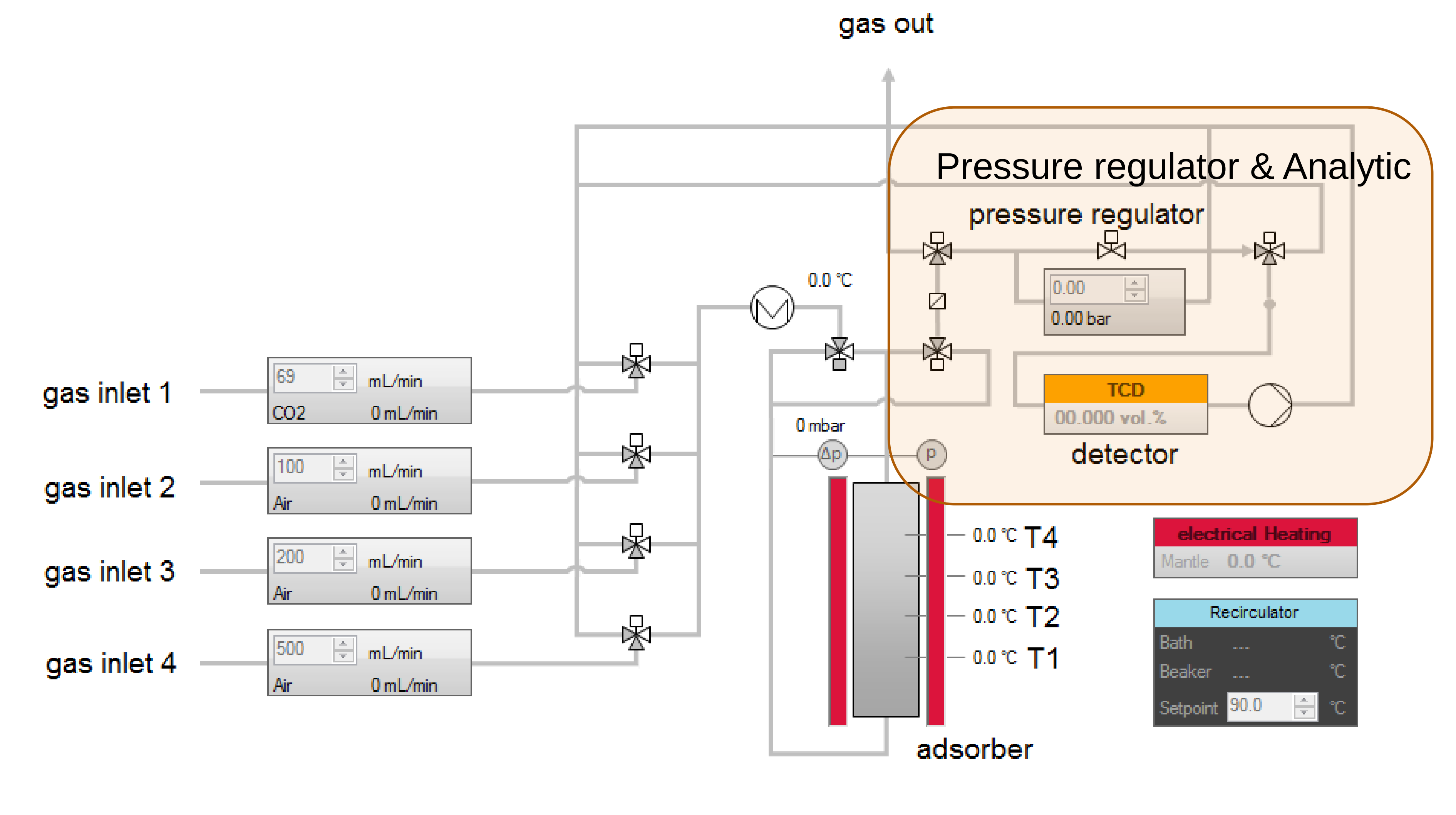
2. Experimental Setup

Flow Chart of the Setup – Pressure regulation and Detector Unit



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3. Specifications & Options

Description

- **Fully automated** control via PC (USB)
- Sequential adsorption and desorption experiments
- Built-in sample preparation station (in situ), **heating up to 400 °C**
- Possibility of fully automated **counter current gas flow**
- Automated regulation of column pressure up to **10 bar** via PC
- Up to **4 high precision mass flow controllers (MFCs)**
- Automated **built-in gas mixing** with high precision mass flow controllers
- Possibility of **bypass-measurements** (measurement of inlet gas composition)
- **Preconditioning** of inlet gas and tempering of adsorber by laboratory circulating bath
- Determination of **heat profiles** in the column with up to four temperature sensors
- Monitoring of **pressure drop** of the column with **differential pressure sensor**
- Monitoring of gas composition by **TCD** at the outlet
- **Optional** gas analysis via interfaced **Mass Spectrometer**
- Safety guard **sensor for flammable gases** for automatic shut down
- Enhanced Safety by **intelligent illuminated workspace**

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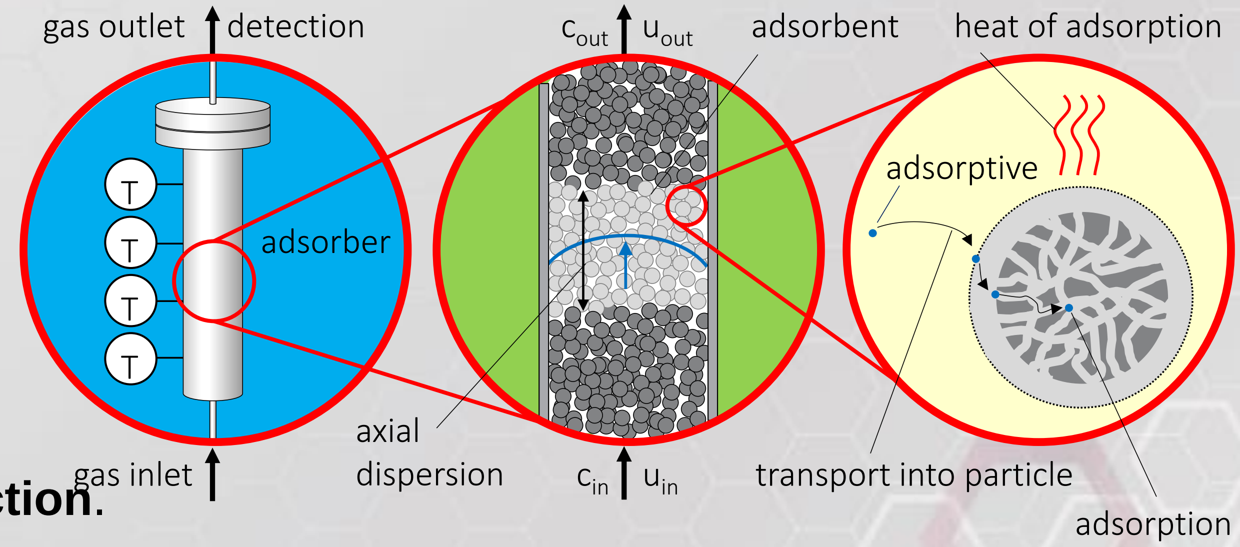
4. Measurement capabilities

Principle of Measurement



- Not all dynamic experiments are breakthrough experiments!
- Requirement**: Fixed Adsorber Bed** → gas must pass the sample.
- Comparable to **gas chromatography** but gas feed has not a pulse function but a **step function**.
- What is the result of a breakthrough experiment?
    - **Time** until 5 %, 50 % ,…, 100 % breakthrough
    - Simplified **Integral** I in min/g (sufficient for production control)
    - Differential **loading** of a gas on the adsorbent in mmol/g (with and without further assumptions)
    - Breakthrough **curve** that can be used in dynaSim for parametric studies and kinetic evaluation

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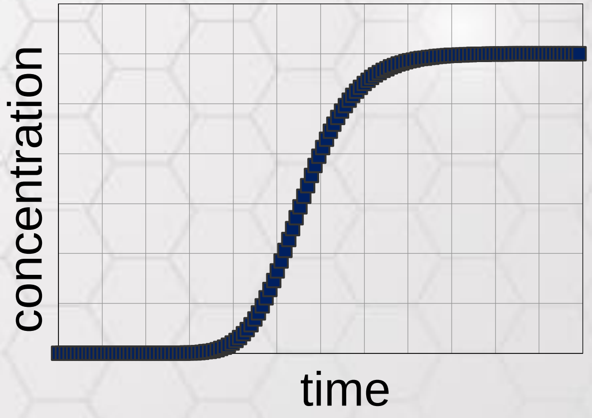
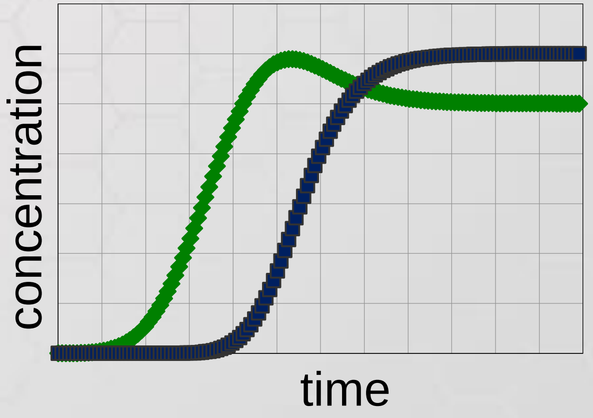
4. Measurement capabilities

Different experiments with dynaSorb BT and their results:

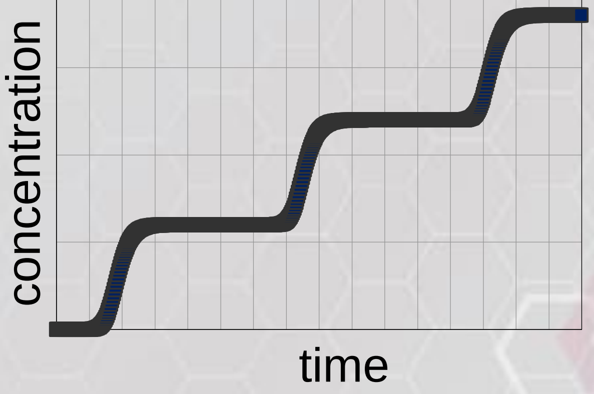
Breakthrough time, Mass Transfer



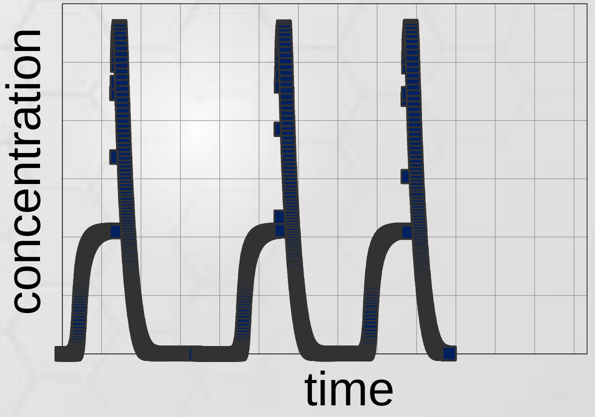
Competitive Adsorption, Displacement



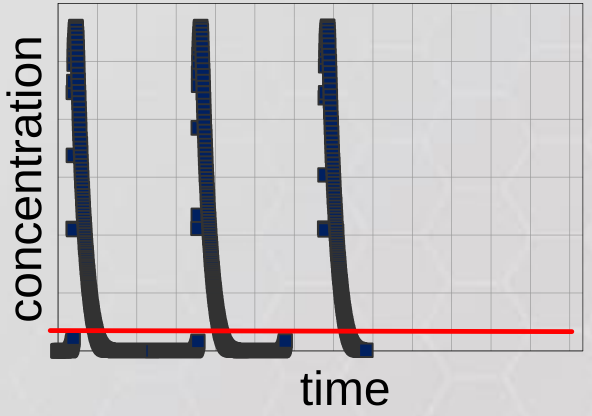
Equilibrium loading, isotherms



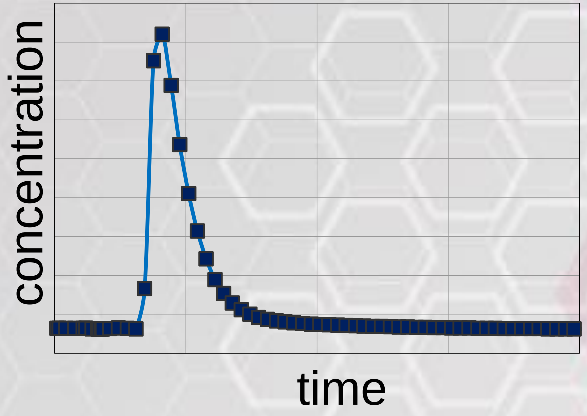
Regenerability, Cycle-Stability



PSA- Process, down scaling



Chromatographic parameter



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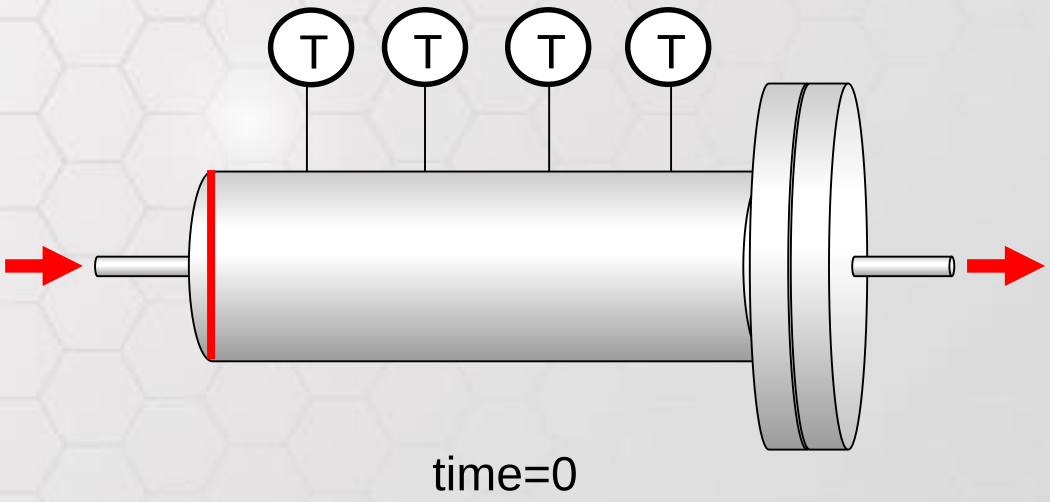
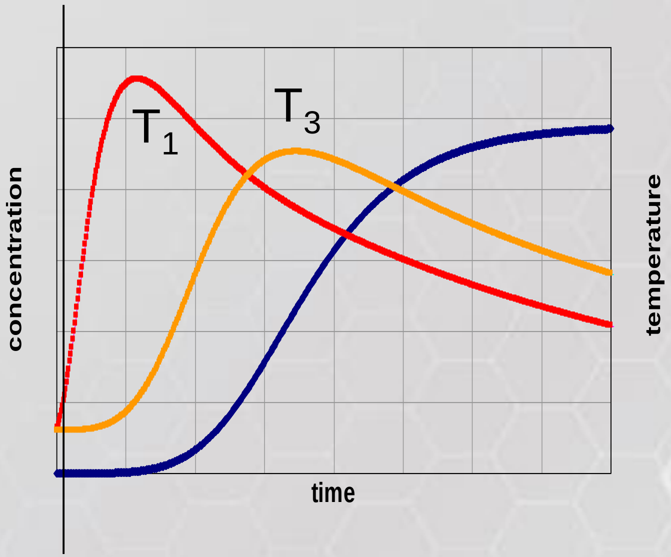
5. Breakthrough Curves - Theory

Determination of Breakthrough Curves





- **Pressurization with auxiliary gas before measurement to desired pressure**
- **Dosing of a well-defined gas mixture as a "step function" at t_{Start}=0**
- **Dosing with constant gas velocity and inlet composition during experiment**
  - Time resolved observation of outlet concentration
  - Time resolved observation of temperature at different locations

→ breakthrough curve reflects the concentration profile in the adsorber column

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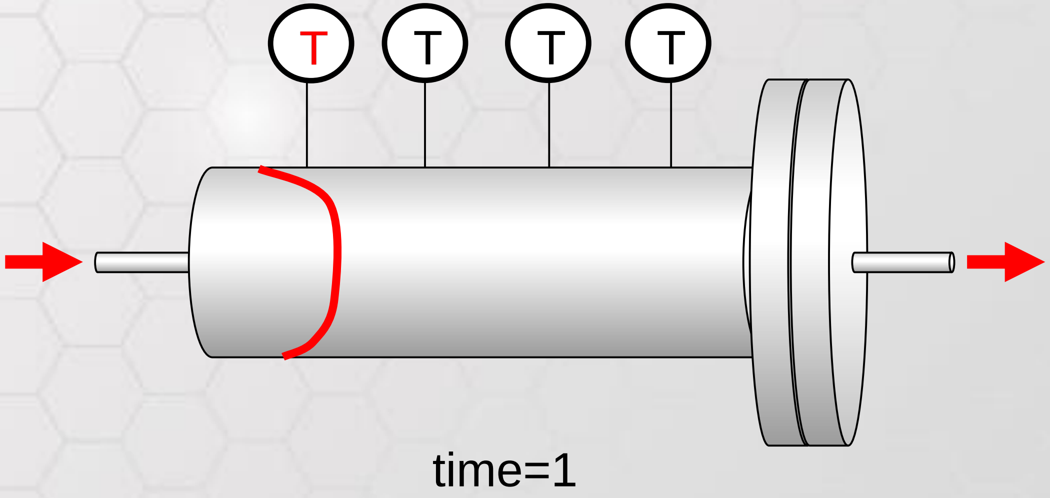

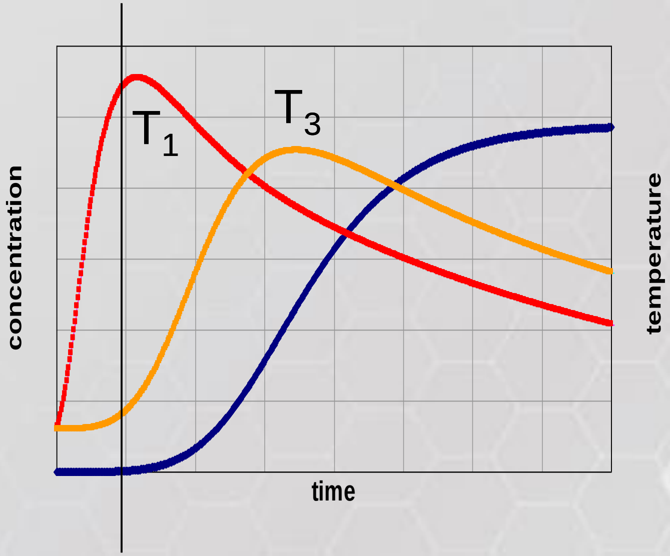

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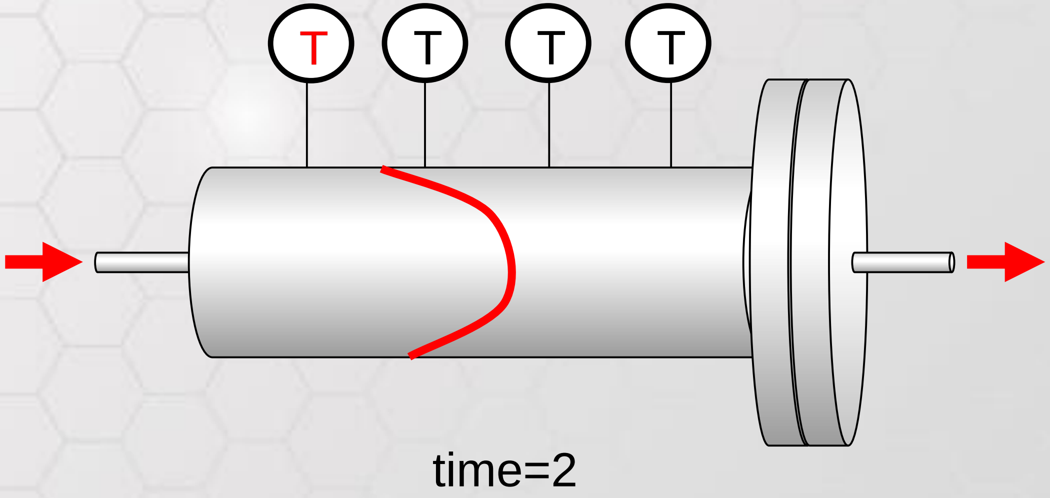

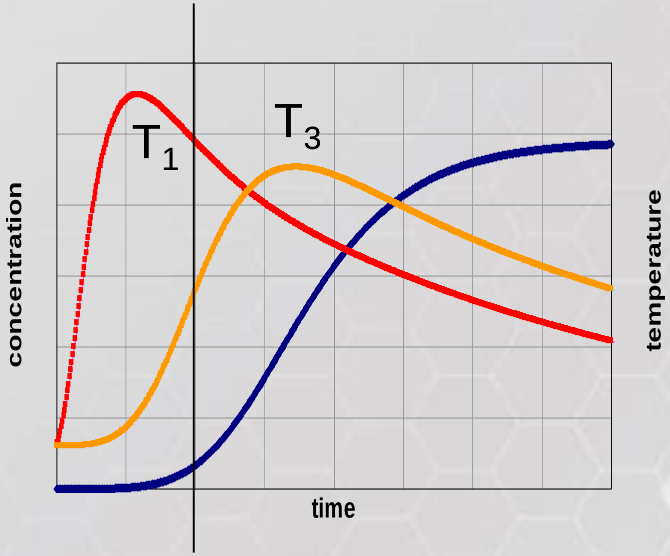

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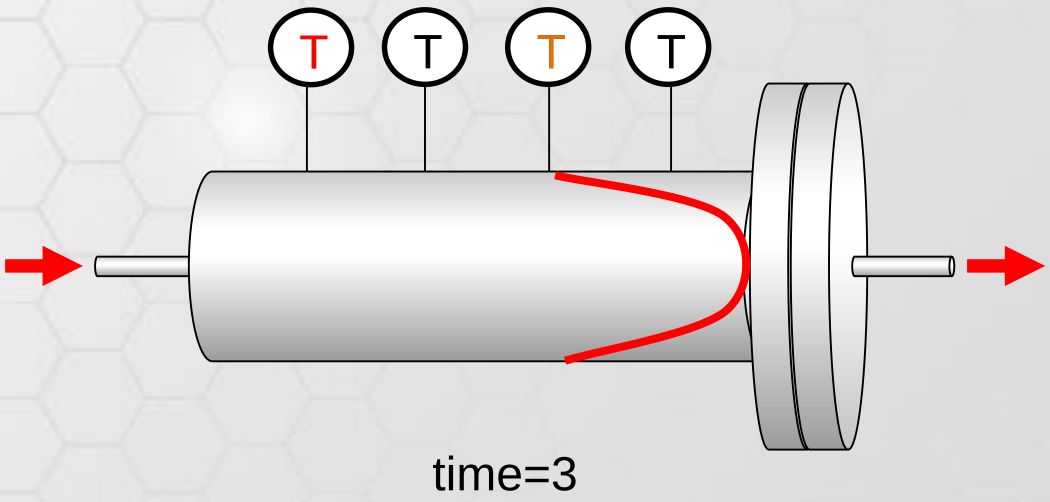

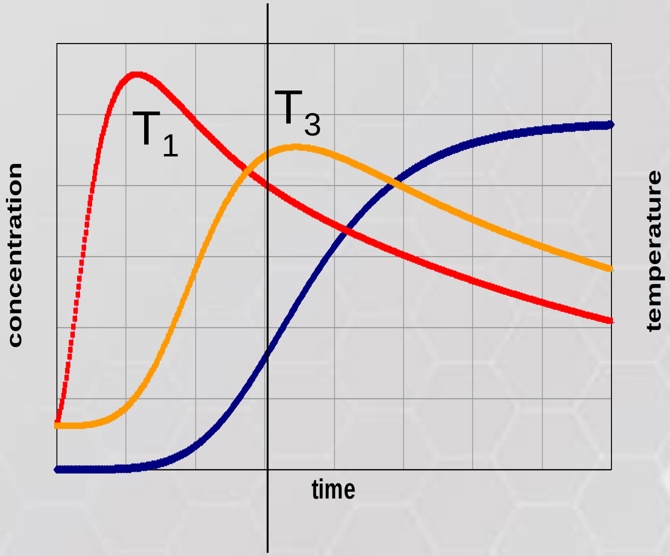

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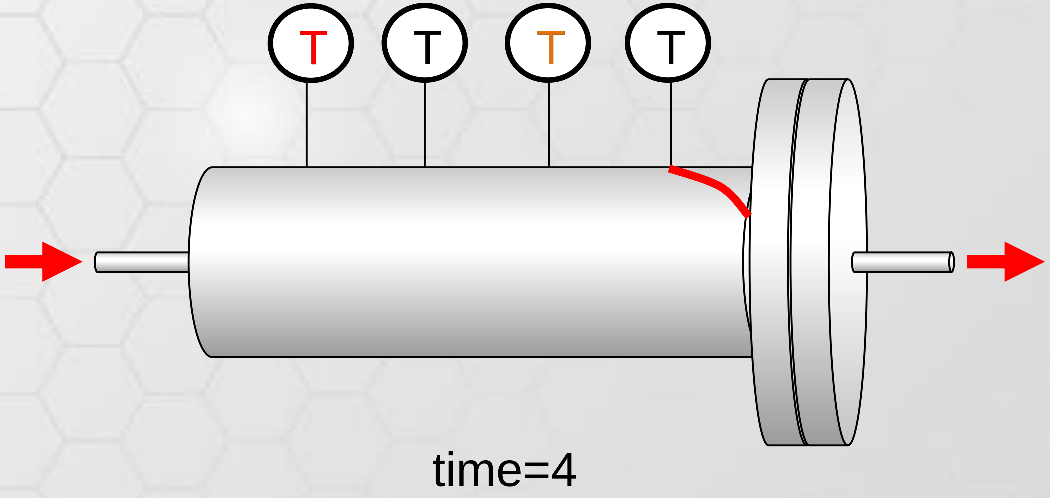

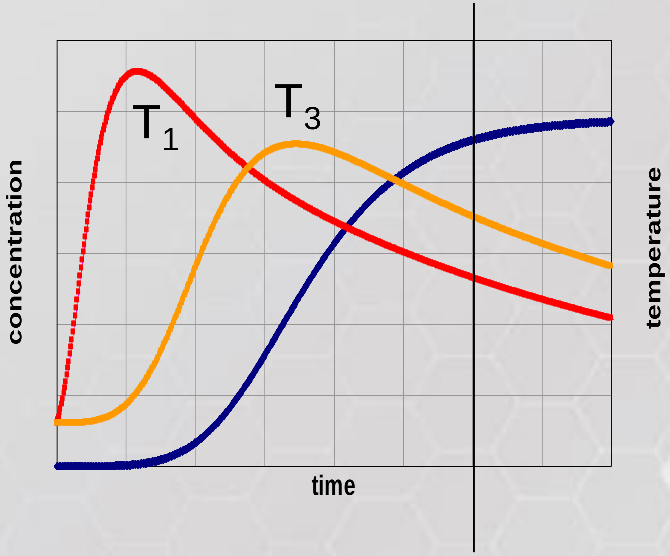

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→ breakthrough curve reflects the concentration profile in the adsorber column

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6. Applications

General Applications

- Technical Adsorbents
- Material Research & Development
- Chemical Engineering

- Energy Storage
- Gas Storage
- Separation Technologies
- Environmental
- Selectivity Studies

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6. Applications

Specific Applications – Pressure Swing Adsorption

PSA-processes were often used in technical plants due to high energy efficiency:

Separation	Adsorptives	Material	Purpose
CO_2 from Air	CO_2	Zeolites	CO_2 -removal before cryogenic air separation
Air	O_2	CMS[1)]	N_2 -production for inerting (food, steel industry …)
Air	N_2, O_2	Zeolites	O_2 -production, enrichment (local supply, medicine…)
H_2 from steam reformer	CH_4, CO, CO_2	AC[2)], Zeolites	H_2 -purification of dry production gas from steam reformer
CO_2 from Biogas	CO_2	CMS[1)]	CO_2 -removal from biogas (upgrading to biomethane)
H_2S from Biogas	H_2S	Impreg. AC[2,3)]	Biogas fine cleaning
Natural Gas	C_xH_Y (x>1)	Silica gel	Decrease of dew point by removal higher hydrocarbons

[1)] CMS Carbon Molecular Sieve
[2)] AC Activated Carbon
[3)] Note: No PSA-Process, material will not regenerate

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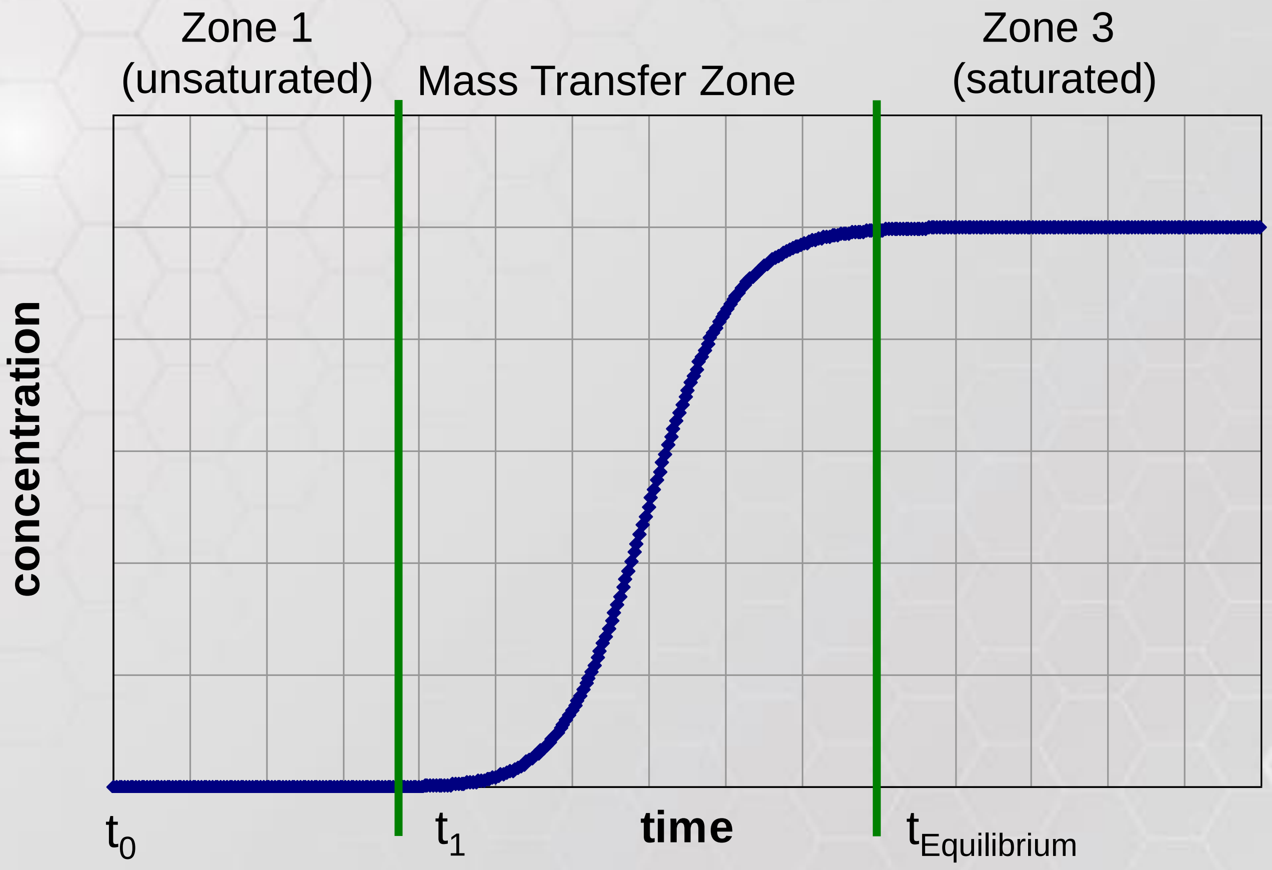
…all these processes can be investigate with dynaSorb BT !

7. Interpretation of Results

Breakthrough Curves- General



- Zone 1 (unsaturated adsorber) → no noticeable breakthrough (production time)
- Mass Transfer Zone → rapid increasing of outlet concentration (should be small)
- Zone 3 (saturated adsorber) → Adsorber is in equilibrium

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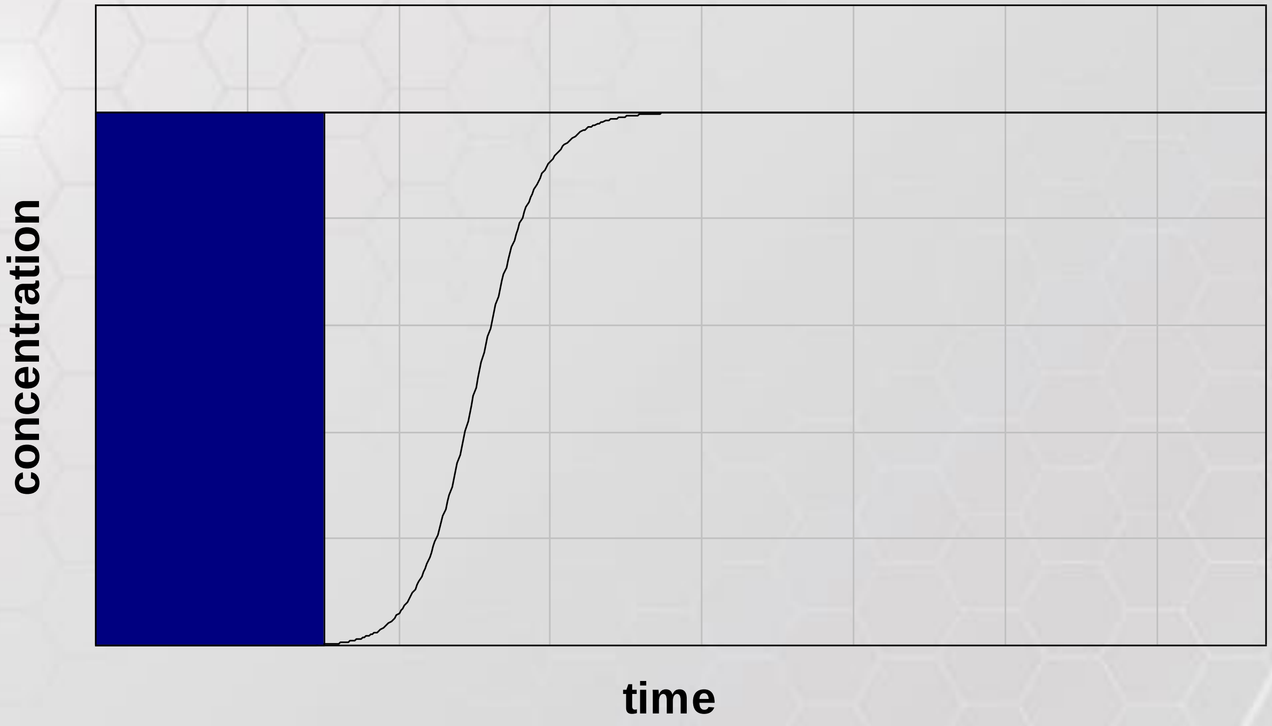
→ breakthrough curve implies sections which can used for different statements

7. Interpretation of Results

Evaluation of Zone 1



- **Area between $t=t_0$ and $t=t_1$ can be used for:**
  - Determination of a technical usable sorption capacity
  - Can be used as benchmark for separation performance of adsorbens
  - **This value gives an indication of the technical usable capacity**
  - **Can only be determined with dynamic method**

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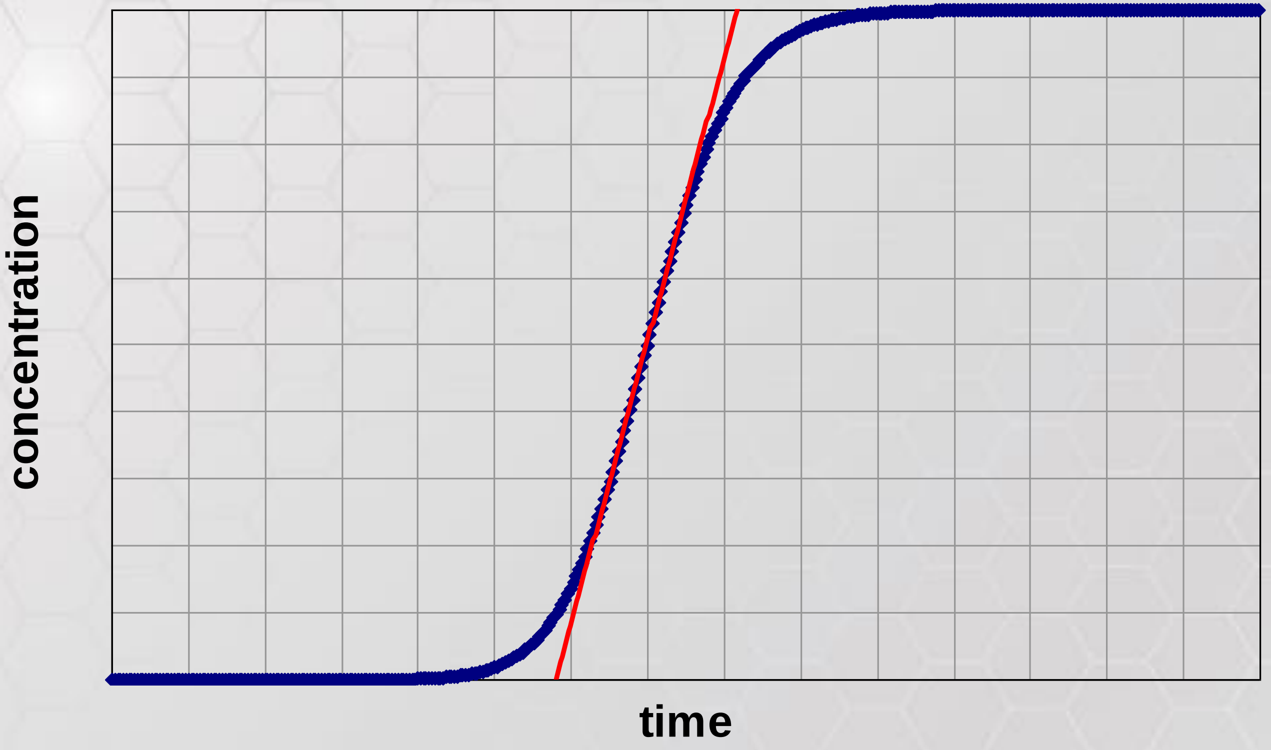
7. Interpretation of Results

Mass Transfer Zone



- **Steepness of breakthrough curve (range t_1 to $t_{Equilibrium}$) depends on:**
  - Mass Transfer coefficient, axial dispersion, shape of isotherm
  - Heat effects, heat dissipation
  - **The time interval of mass transfer zone has to be minimized**
  - **Can only be determined with dynamic method**

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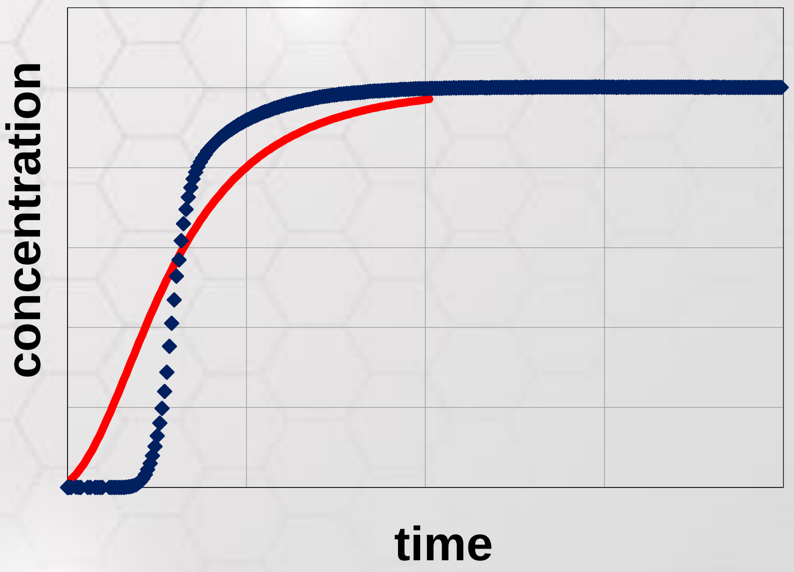
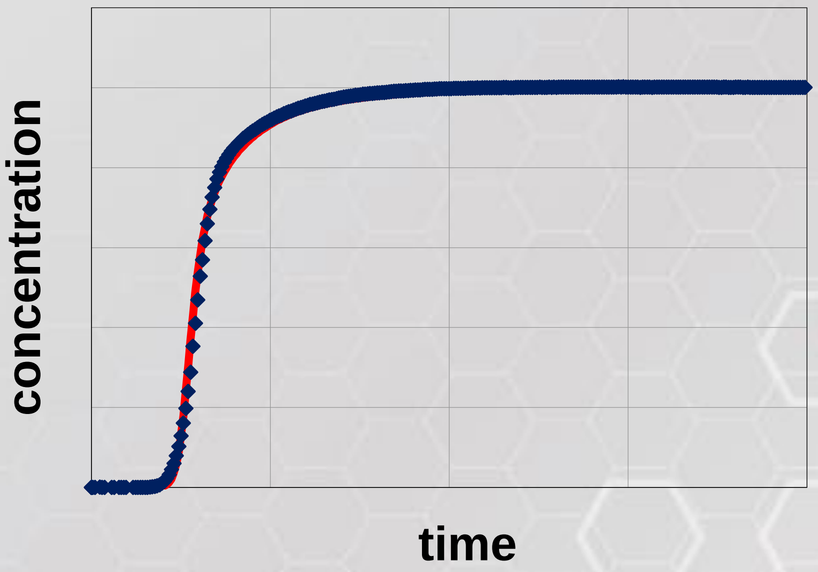
7. Interpretation of Results

Mass Transfer Zone - Investigation of kinetic property (determination of k_{LDF})

Requirement: knowledge of isotherm



Breakthrough curve (experimental blue) and
Simulated data (red) before fitting (**k_{LDF}=1**)



Breakthrough curve (experimental blue) and
Simulated data (red) after fitting (**k_{LDF}=11.7**)

Determination of k_{LDF} by fitting of experimental breakthrough curves with dynaSim

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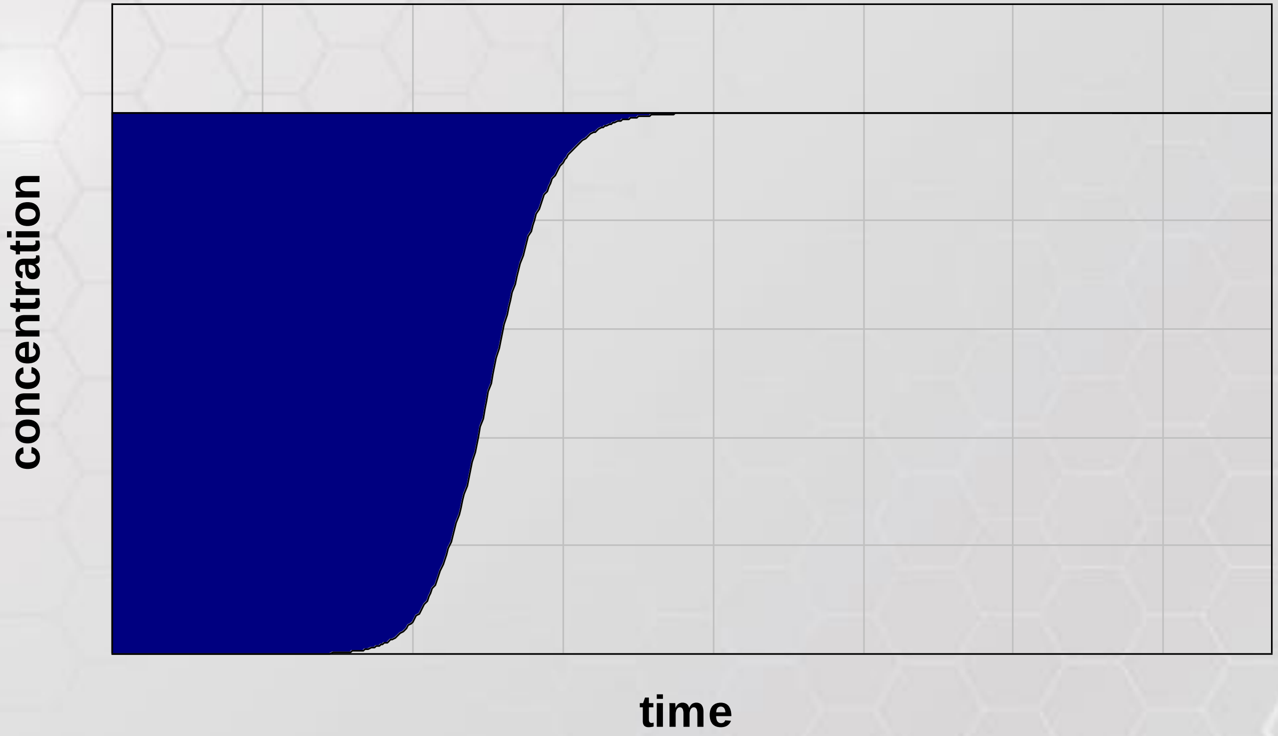
- Comparison for different materials under same testing conditions allowed statements of the kinetic performance

7. Interpretation of Results

Evaluation of Zone 3



- **Area between $t=t_0$ and $t=t_{Equilibrium}$ can be used for:**
  - Determination of saturation capacity
  - By assuming of thermodynamic controlled system
    - Measurement of pure component isotherms and mixtures possible

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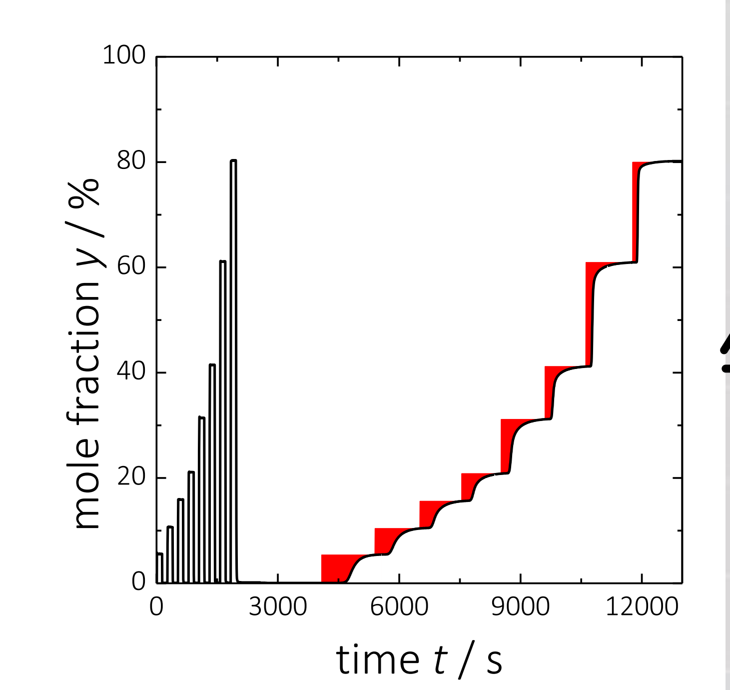
7. Interpretation of Results

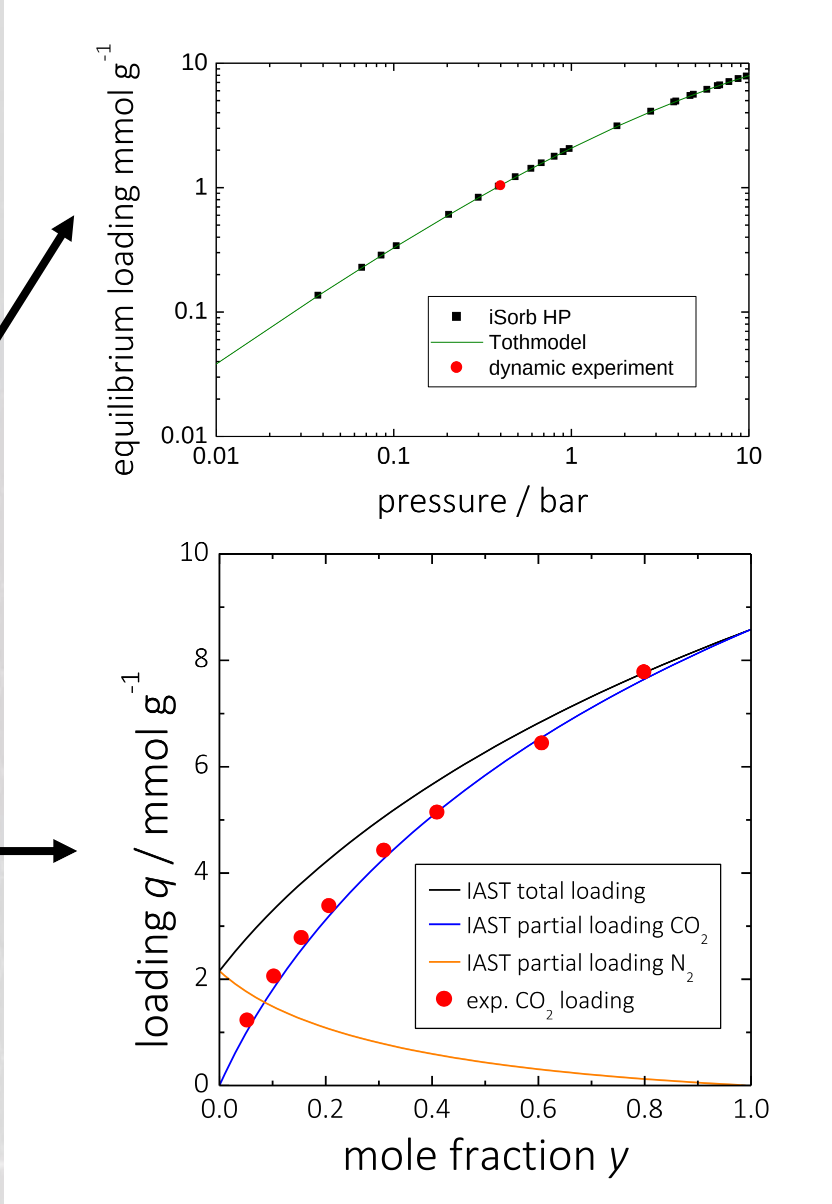
Determination of pure component and mixture isotherms

- **Dynamic Methods work with mixtures:**
- Using Helium as one component and assuming that it is not adsorbed allows measurement of pure component isotherms (Flowmeter Option is recommended)
- Using other gases than Helium yields in mixture isotherms (Flowmeter Option is recommended)



CO$_2$/He

CO$_2$/N$_2$



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7. Interpretation of Results

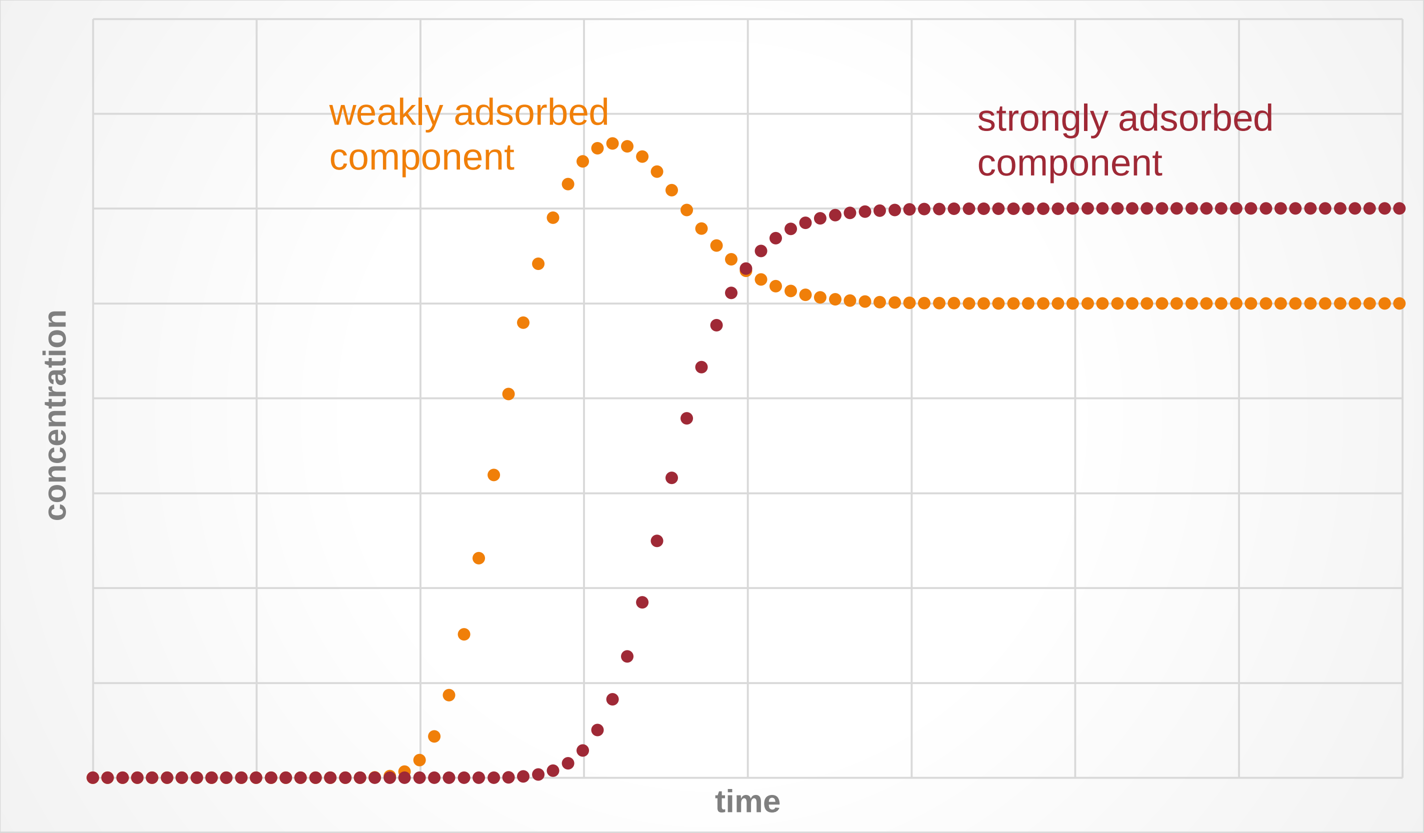
Investigation of co-adsorption and displacement phenomena (I)

Example:

- 3 component mixture: $CO_2/CH_4/He$
- Different breakthrough times
- Weakly adsorbed component (CH_4) is displaced by stronger adsorbed component (CO_2)

→ **partial desorption**

→ **role up effect**



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7. Breakthrough Curves - Theory

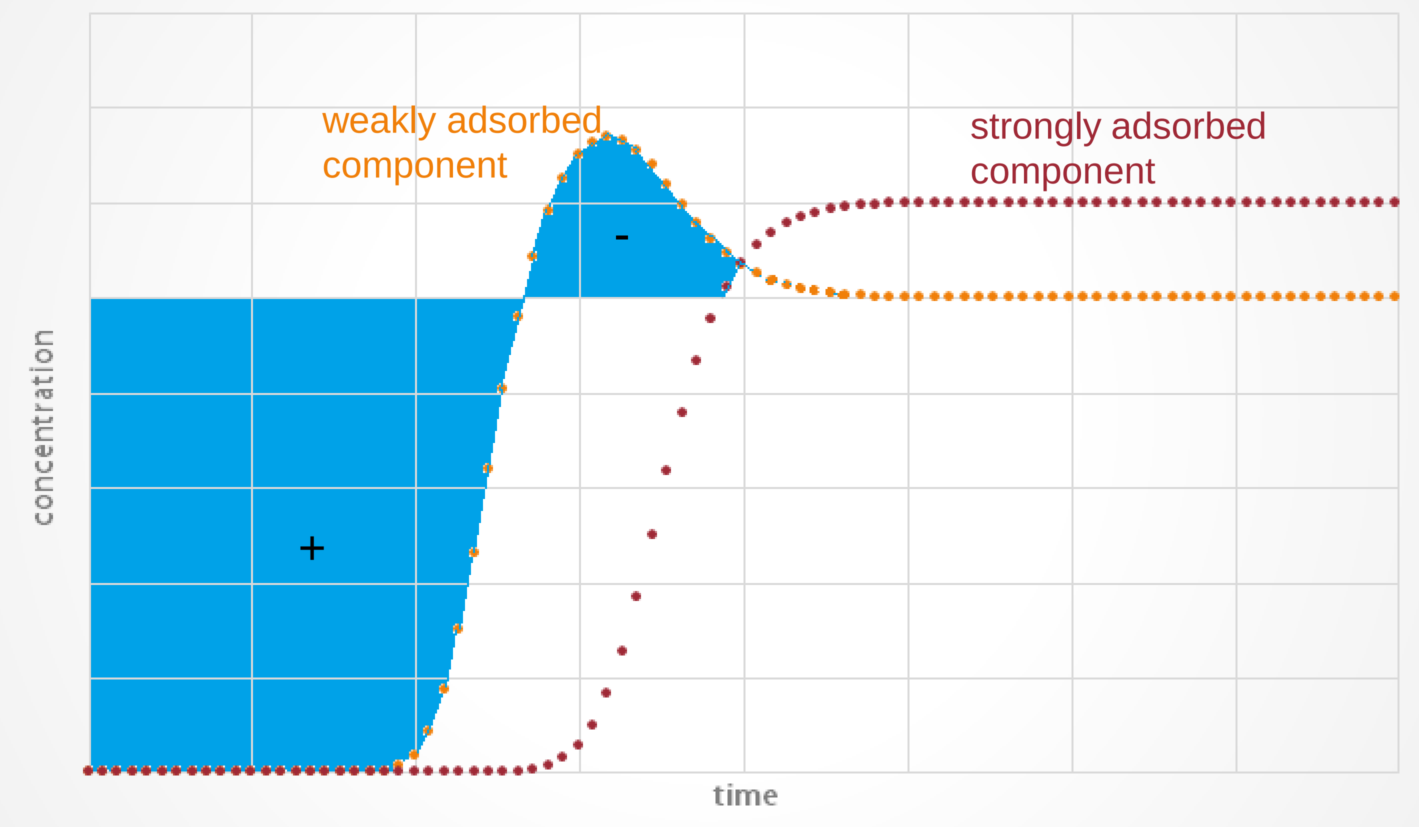
Investigation of co-adsorption and displacement phenomena (II)

Example:

- 3 component mixture: $CO_2/CH_4/He$
- Different breakthrough times
- Weakly adsorbed component (CH_4) is displaced by stronger adsorbed component (CO_2)

→ **partial desorption**

→ **role up effect**

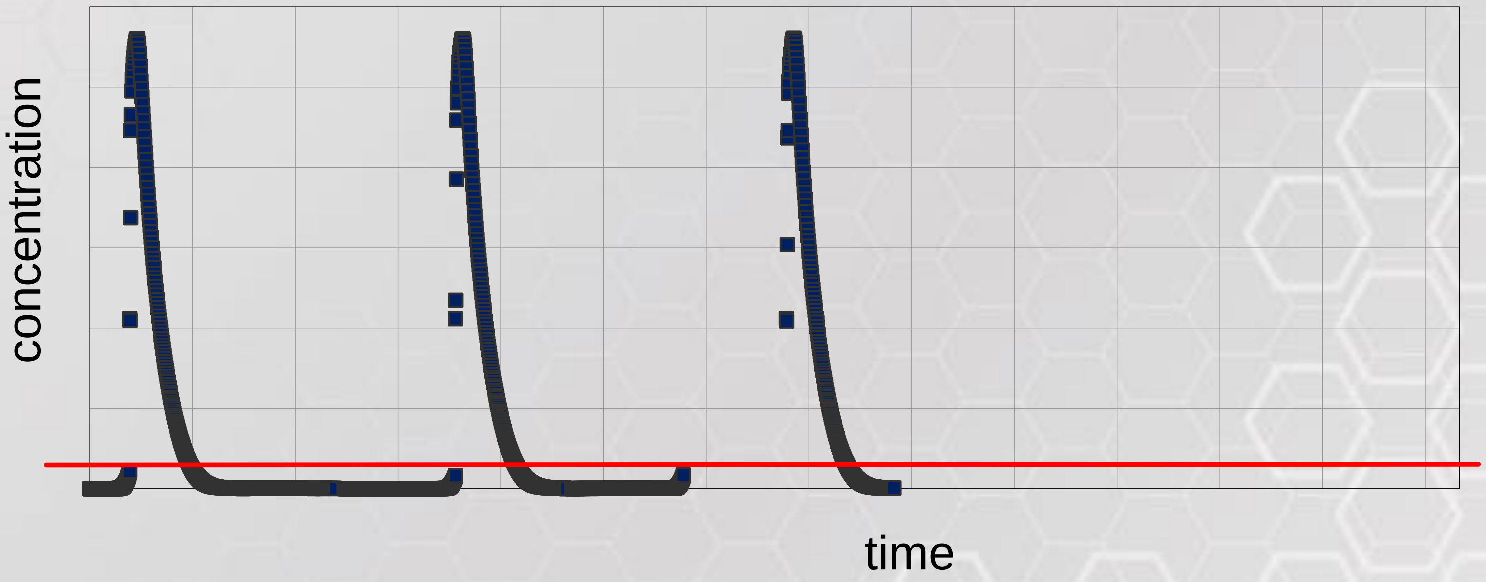


7. Interpretation of Results

Emulation of PSA-processes

dynaSorb BT can emulate PSA processes with one Adsorber by applying Sequences

1. Pressurize Adsorber with inert gas (or product gas) to *e.g.* 3 bar
2. Apply Feed gas and pressurize to 5 bar.
3. Automatically stop adsorption at *e.g.* 5 % breakthrough
4. Depressurize to 1 bar and purge with inert (or product) gas.



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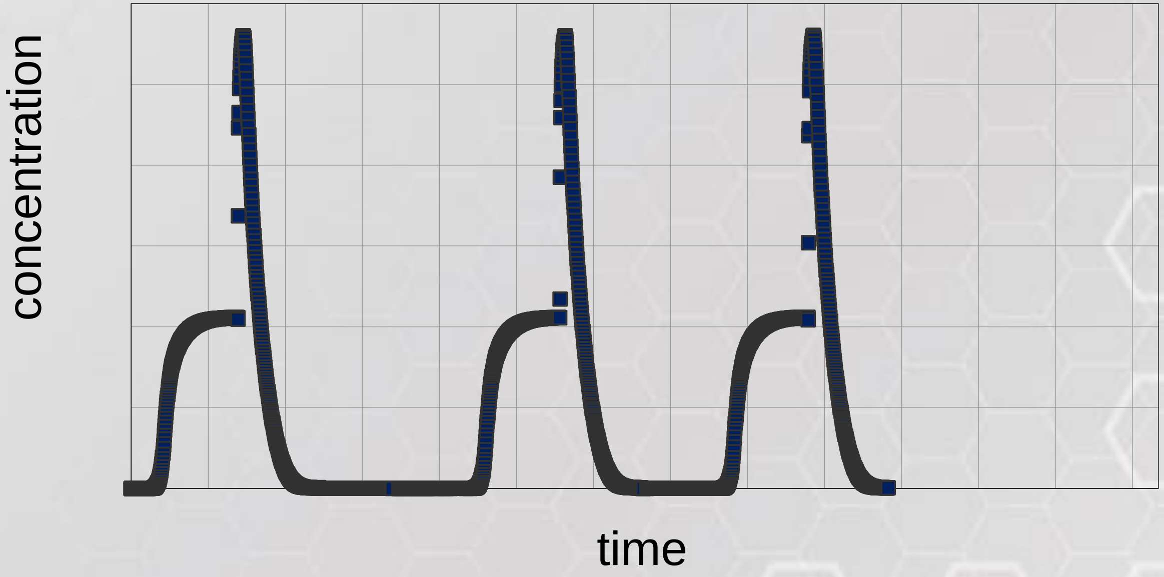
7. Interpretation of Results

Investigation of cycle stability of new materials

Similar to PSA process, but

- Wait for stationary conditions at 100 % Breakthrough (i.e. at 5 bar)
- Regeneration/Desorption at elevated or atmospheric pressure.
- Integration will give adsorbed and desorbed amount



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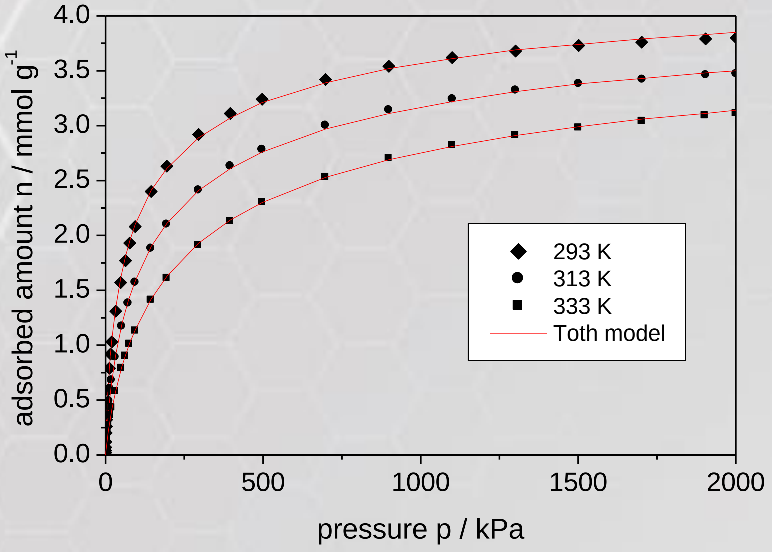
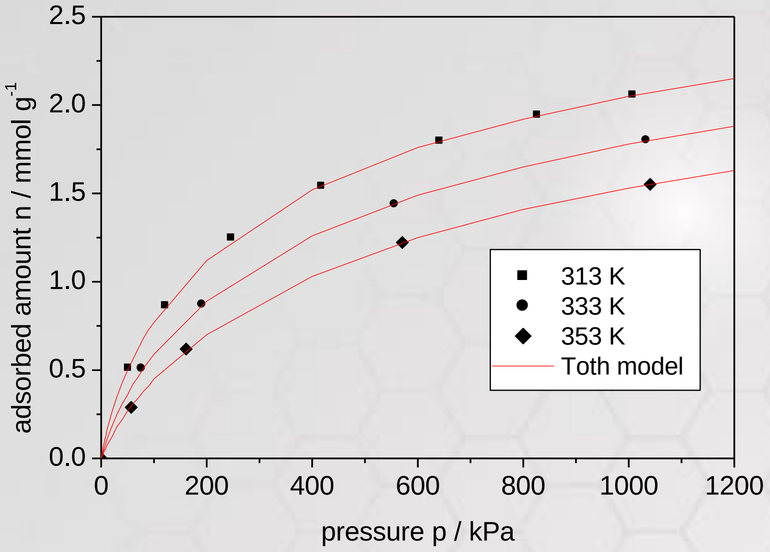
8. Examples for breakthrough experiments

CO_2-removal from CH_4 rich gas mixtures (biogas)

- Utilization of kinetic-steric separation effect on Carbon Molecular Sieves (CMS)
- Thermodynamic selectivity and comparison of BET surfaces of such materials without kinetic information leads to significant misinterpretation



CO_2-isotherms on CMS



CH_4-isotherms on CMS

- **Thermodynamic selectivity in range of 3** for CO_2 (calc. with IAST and Toth-equation)

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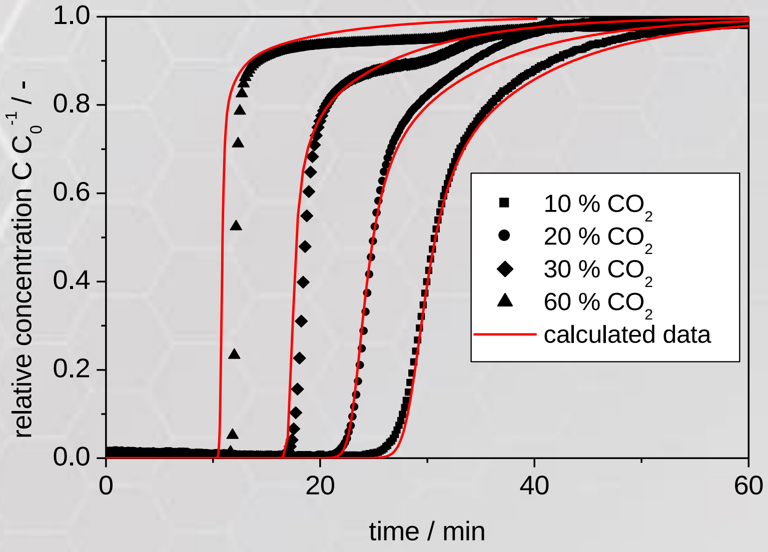
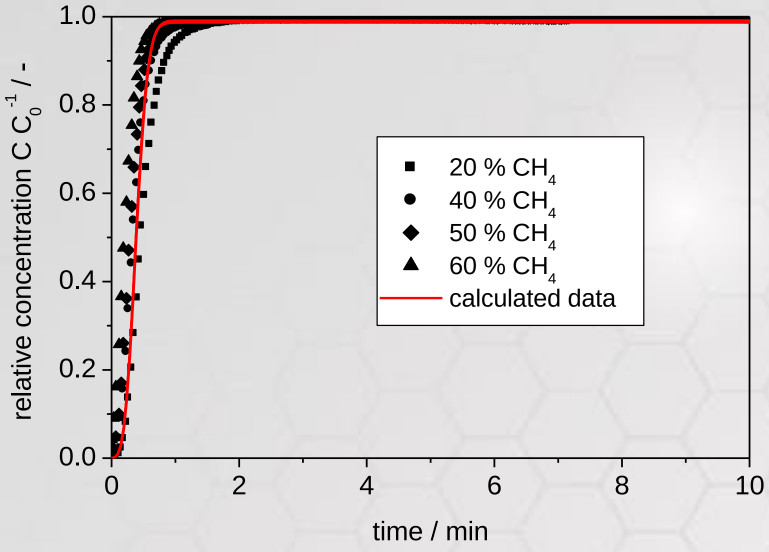
8. Examples for breakthrough experiments

CO_2-removal from CH_4 rich gas mixtures (biogas)

- Spontaneous breakthrough for CH_4, **system is not under thermodynamic control for CH_4**, for CO_2 breakthrough is determined by sorption capacity



Breakthrough curves of CO_2 on CMS



Spontaneous breakthrough of CH_4 on CMS

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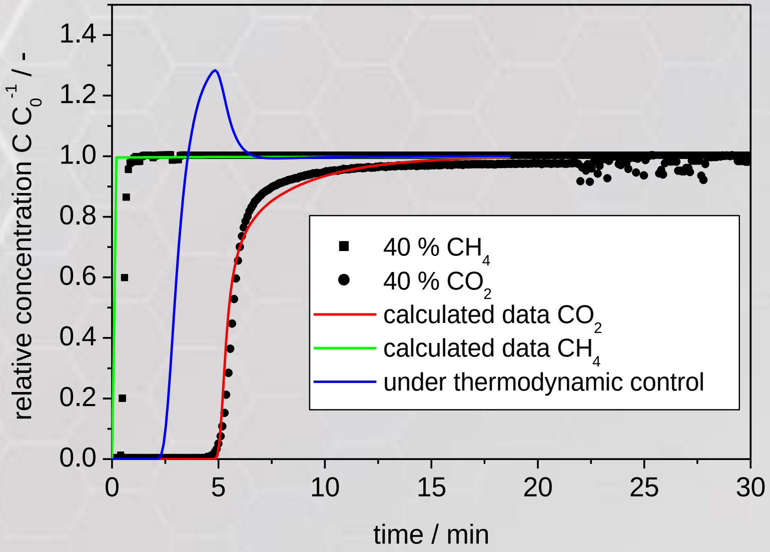
- Conditions: 1000 ml/min total flow at 4 bar total pressure
- calculated effective selectivity: > 30
  - Input values: k_{LDF}-values for CO_2 (1.2 min^{-1}) and CH_4 (0,00115 min^{-1}), sorption capacities of CO_2 and CH_4

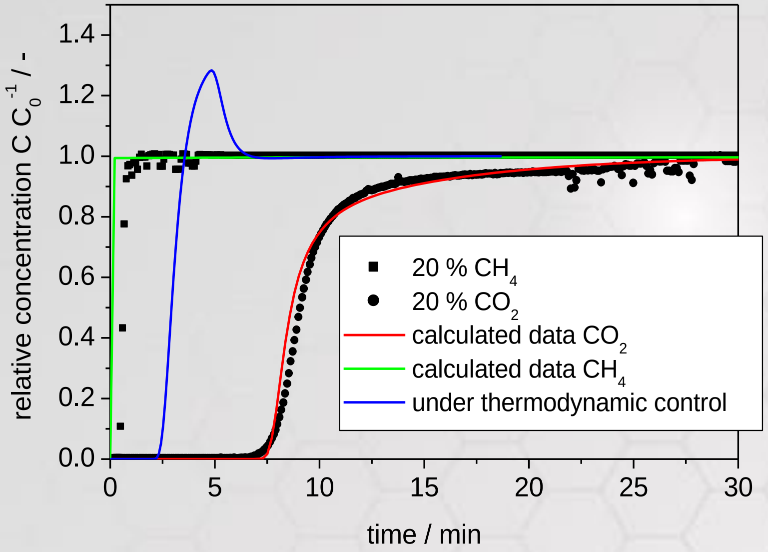
8. Examples for breakthrough measurements

CO_2-removal from CH_4 rich gas mixtures (biogas)

- breakthrough behavior for complete thermodynamic controlled system (blue and red curve) and kinetic controlled breakthrough for CH_4 (green and red curve), measured data (black curves)



Breakthrough curve of CO_2 /CH_4 mixture in He on CMS



Breakthrough curve of CO_2 /CH_4 mixture in He on CMS

- Consideration of BET-surfaces and isotherms is **not enough** for interpretation of separation efficiency under process near conditions.
- Dynamic measurements are very helpful for overcome such problems!

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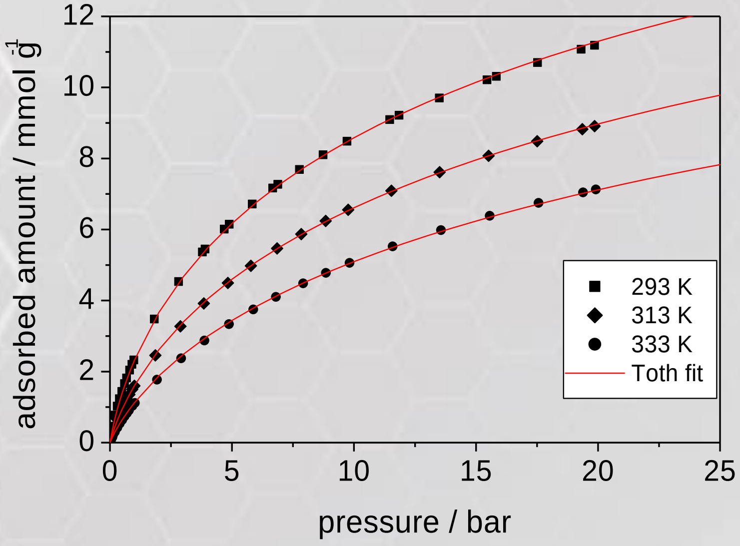
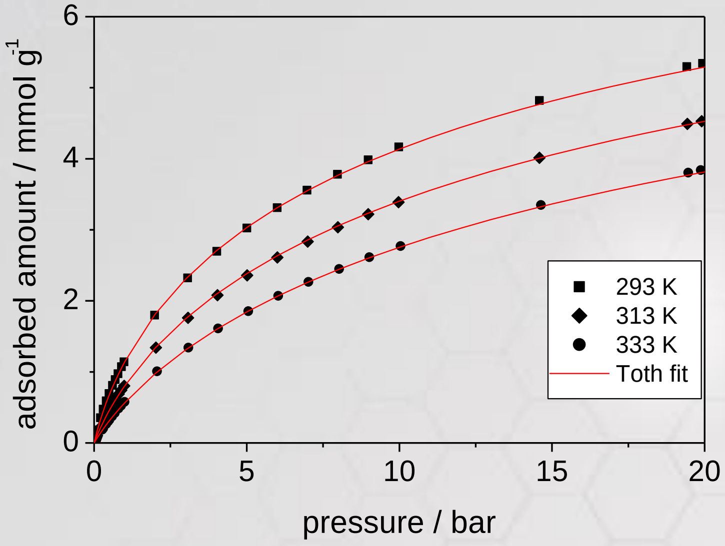
8. Examples for breakthrough experiments

CO_2-removal from CH_4 rich gas mixtures

- Investigation of separation performance of classical Activated Carbon



CO_2-isotherms on AC



CH_4-isotherms on AC

- **Thermodynamic selectivity in range of 5** for CO_2 (calc. with IAST and Toth-equation)

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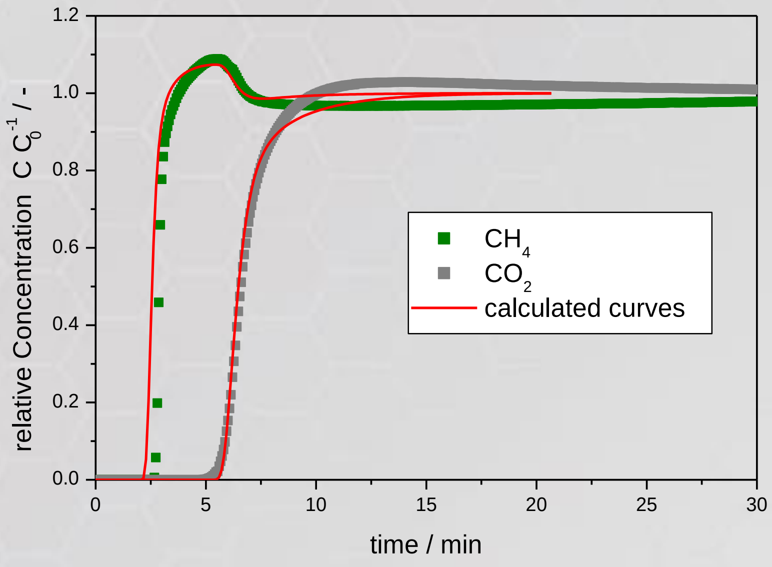
8. Examples for breakthrough experiments

CO_2-removal from CH_4 rich gas mixtures

- breakthrough for CH_4 and CO_2 according their sorption capacities, whole system is under thermodynamic control



Breakthrough curves of CH_4/CO_2 mixture in He on AC (15 % CH_4, 5 % CO_2)

- Conditions: 2500 ml/min total flow at 5 bar total pressure

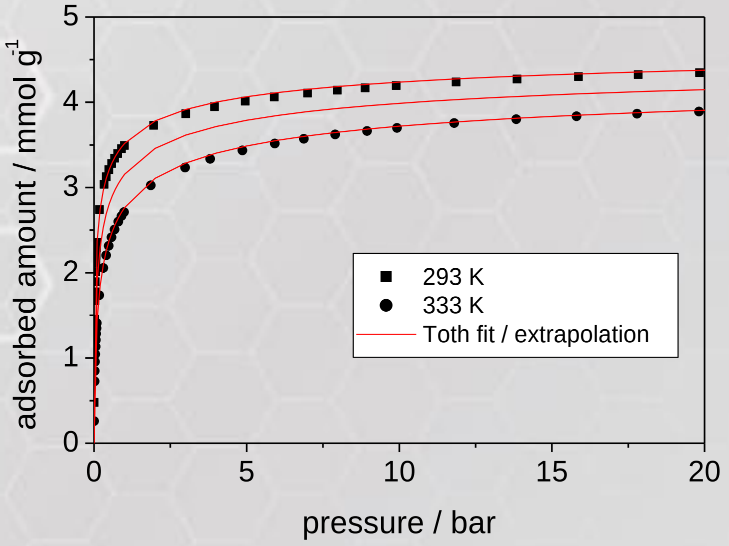
➢ Classical AC not increasing of separation performance by kinetics

  ➢ Selectivity not high enough for economic separation !

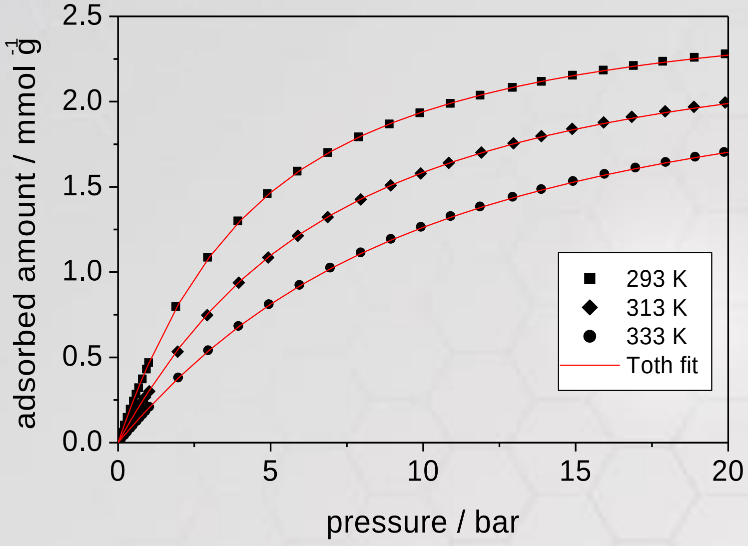
8. Examples for breakthrough experiments

CO_2-removal from CH_4 rich gas mixtures

- Investigation of separation performance of Zeolite 13 X



CO_2-isotherms on 13X



CH_4-isotherms on 13X

- **Thermodynamic selectivity in range of 300** for CO_2 (calc. with IAST and Toth-equation)
  - ➢ High thermodynamic selectivity due to strong CO_2-interaction (steep isotherms)

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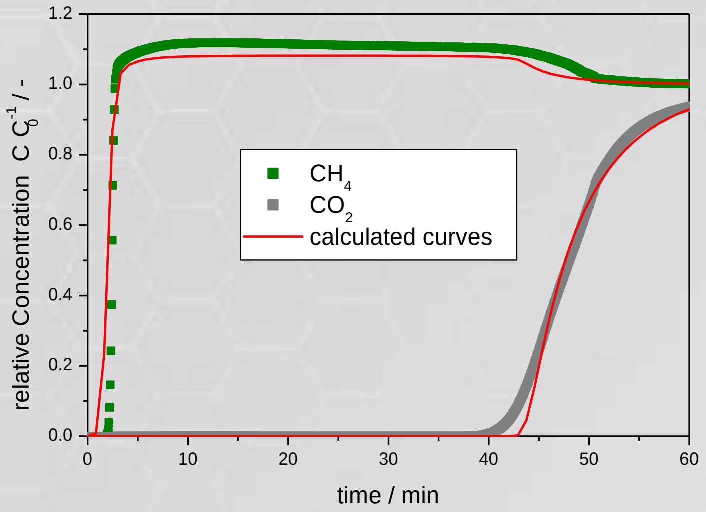
8. Examples for breakthrough experiments

CO_2-removal from CH_4 rich gas mixtures

- Breakthrough curves for CH_4 and CO_2 reflect the high thermodynamic selectivity



Breakthrough curves of CH_4/CO_2 mixture in He on Zeolite 13X (15 % CH_4, 5 % CO_2)

- Conditions: 2500 ml/min total flow at 5 bar total pressure

➢ Zeolite 13X show a very high separation performance
  - ➢ Very high selectivity enables applications for fine cleaning of such gas mixtures
  - ➢ Material should use only with dry gas flows due to high affinity to water

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8. Examples for breakthrough measurements

CO_2-removal from CH_4 – results from dynamic experiments

Material	Separation Effect	Separation Performance	Possible Application
Carbon Molecular Sieve (CMS)	Kinetic-Steric	Good separation, advantage of easy regeneration, insensible regarding water	Biogas refining
Activated carbon (AC)	thermodynamic	Ineffective separation	No application for CO_2 removal from CH_4
Zeolite 13X	thermodynamic	Very good separation, regeneration more difficult compared to CMS, sensible regarding Water	Fine purification of dry gas flows, production of high purity gases

Dynamic measurements allows direct comparison of separation performance without knowledge of isotherms!

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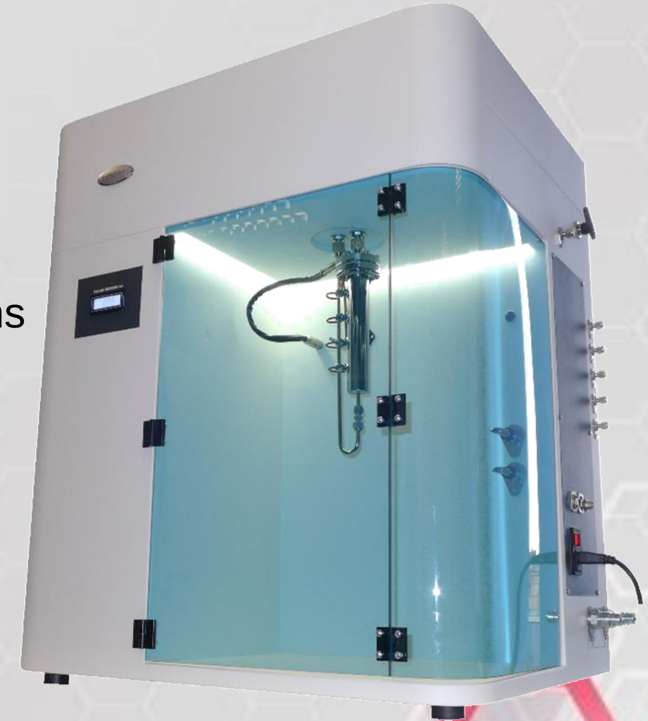
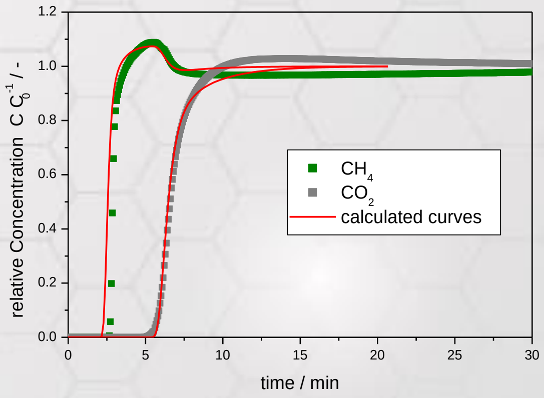
9. Summary

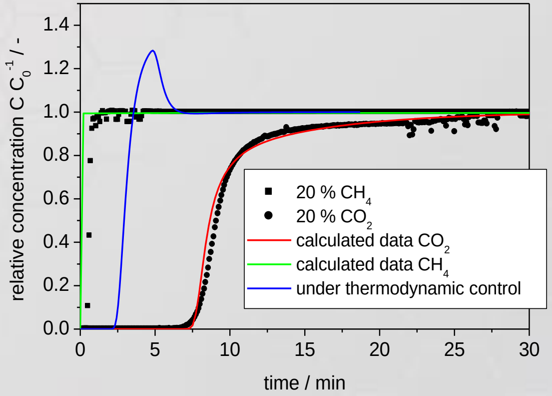
The **dynaSorb BT** is an unique setup which allows:

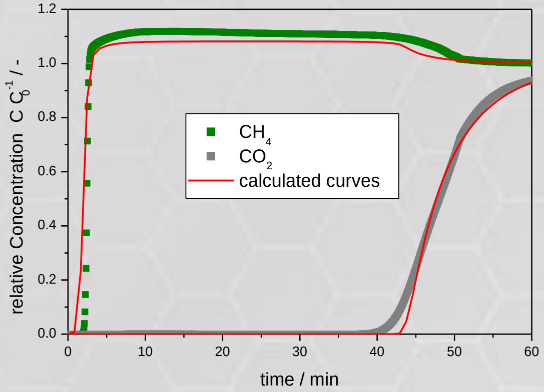
- Dynamic fully automatic flow adsorption, desorption experiments
- Determination and evaluation of breakthrough curves under process relevant conditions
- Investigation of selectivity performance of materials up to 10 bar
- Downscaling of technical separation processes



Experiments with **dynaSorb BT** serve the evaluation of technical adsorbents,







… can generate valuable information for the design of tailor-made materials …

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… are useful for investigations to improve gas separation processes and can help for parametric and feasibility studies.

Thank you for your attention!

Literature:

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[2] M. Bastos-Neto, A. Möller, R. Staudt, J. Böhm, R. Gläser, *Separation and Purification Technology* **2011**, *77,* 251

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