3P Instruments GmbH & Co. KG

Analysis of Breakthrough Curves – Sorption Equilibria and Kinetics

Andreas Möller

Characterization of
particles · powders · pores

Schedule

- **Introduction**
- **Sorption Equilibria**
  - Theory
  - Basics of dynamic experiments
  - Information from breakthrough curves
  - Planning an experiment
  - Examples
  - Summary Part I – Mixture Equilibria
- **Kinetics**
  - Influence shape of isotherms and heat effects on kinetics
  - Model for calculation of transport parameter
  - Examples for evaluation of breakthrough curves
  - Application of a well-calibrated model
  - Summary Part II – Kinetics

Application of Porous Materials as Adsorbents

Fine cleaning of gases (i.e. purification of H_2, natural gas, bio methane…)

Waste air treatment, respiratory protection, solvent recovery, removal of pollutants…)

Gas separation (i.e. Air separation…)

Modern and effective materials should have high sorption capacities, high selectivities , and a good kinetic performance.

➡ For such applications, one must consider gas mixtures and their sorption properties in any case.

Introduction – Characterization of Adsorbents

Number of Samples

Application Progress

Synthesis and First Characterization	Determination of Thermodynamic Data	Basic Process Design, Granulation of Adsorbents	Detailed Process Design, Application

Chemists

3P surface

- BET
- Pore Volume
- Pore Size Distribution

Chemists, Physicists

3P meso

- Isotherms
- Heat of Adsorption

Chemical Engineers

mixSorb L

- Techn. Useable Sorption Capacity
- Gas Mixtures
- Selectivities
- Kinetics
- Cycle Stability

Engineers

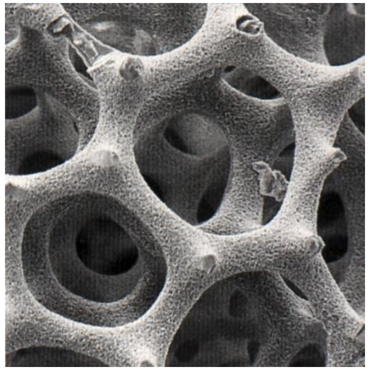
Bench scale, Pilot plants, Industrial Plant

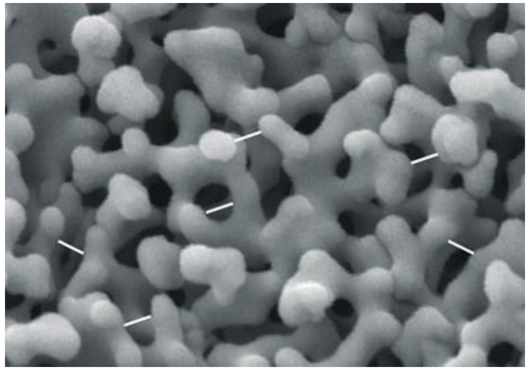
- Process Optimization
- Production

Introduction – Why are Textural Properties not enough…?

Textural Properties of Adsorbents:

- BET-Surface
- Pore Size Distribution
- Micropore Volume





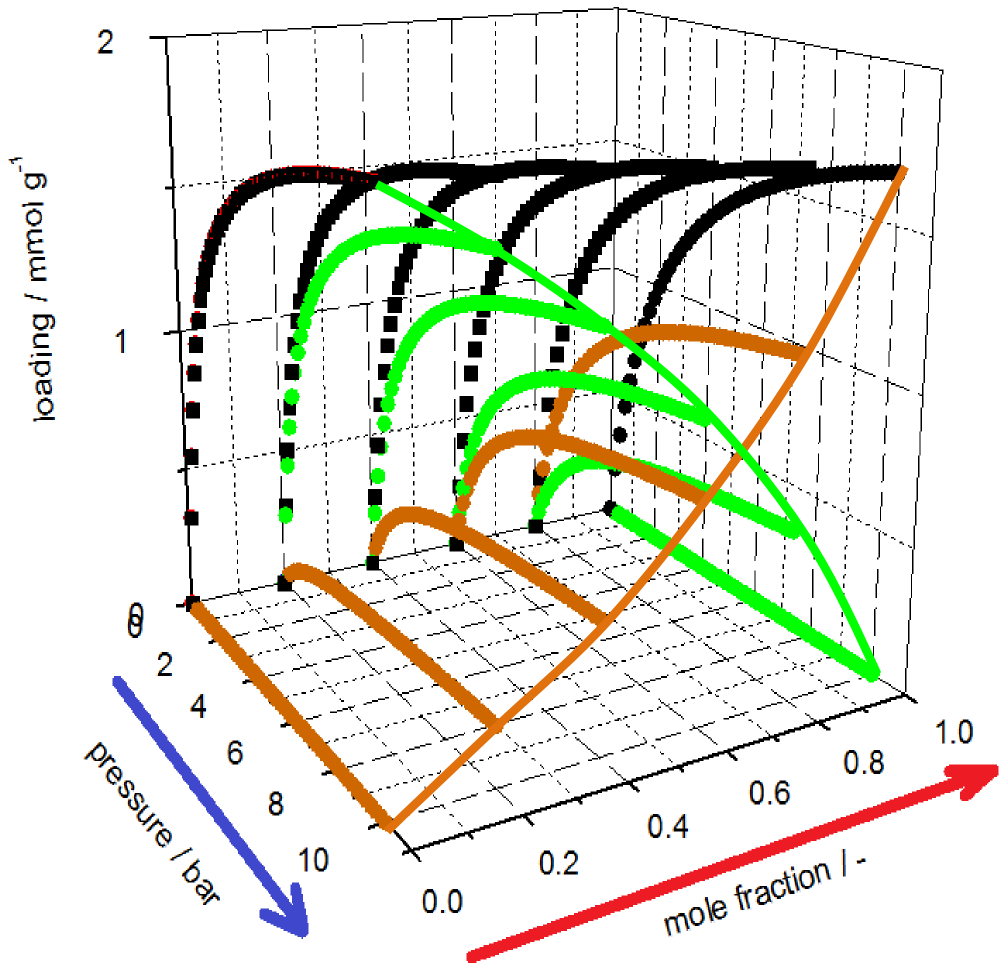
→ Textural properties allow only limited qualitative statements regarding:

- expected saturation capacity (i.e. from micropore volume)
- rough assessment of general sorption properties from pore size distribution

→ Textural properties do not allow quantitative statements regarding:

- sorption affinity
- selectivity
- No information of kinetics

Dependence of partial and total adsorption amounts



- - partial loadings, - total loading

General:

$$n_{CO_2,CH_4,total} = FKT\left(Y_{CO_2}, Y_{CH_4}, p\right)$$

Investigation along:

THE READ LINE – Case A

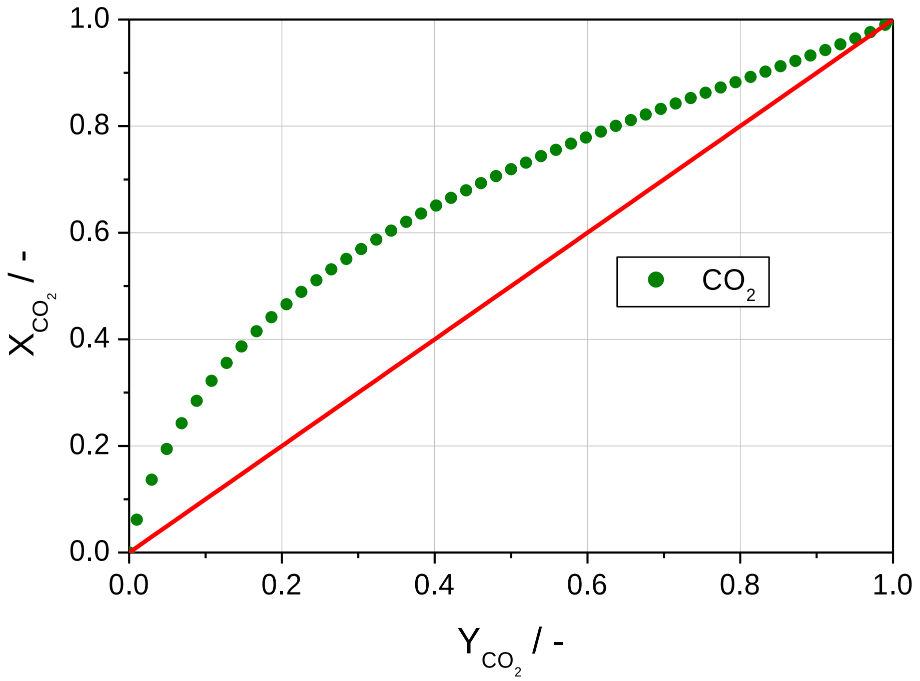
$$n_{CO_2,CH_4,total}\left(p = const.\right) = FKT\left(Y_{CO_2}, Y_{CH_4}\right)$$

THE BLUE LINE – Case B

$$n_{CO_2,CH_4,total}\left(Y_{CO_2}, Y_{CH_4} = const.\right) = FKT\left(p\right)$$

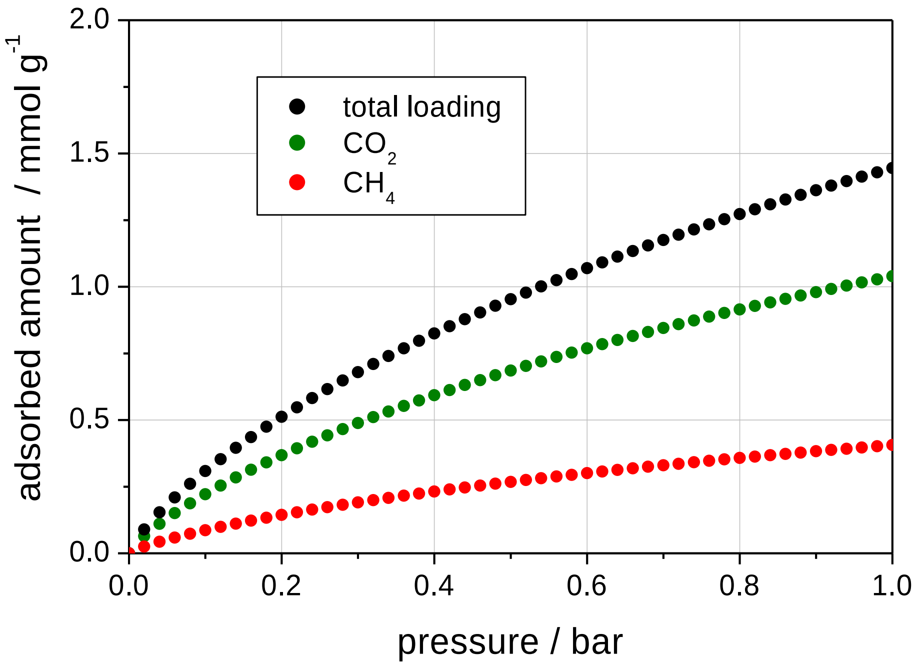
Typical presentation of sorption capacities for binary mixtures

Case A – variable gas composition



p=const. (1 bar), CO_2,CH_4 on D55-1.5 (calc.)

Case B – variable pressure



Y=const. (50:50), CO_2,CH_4 on D55-1.5 (calc.)

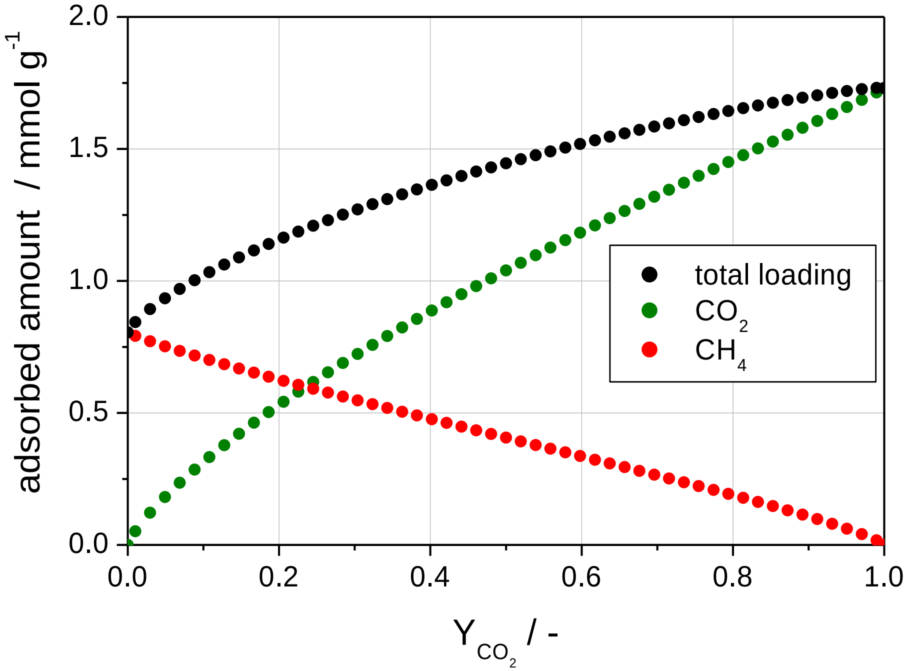
X-Y-Plot with statement to the composition of adsorbed phase at constant pressure

N-p-Plot with statement to the adsorbed amount at constant gas phase composition

Basics – Mixture Equilibria (Theory)

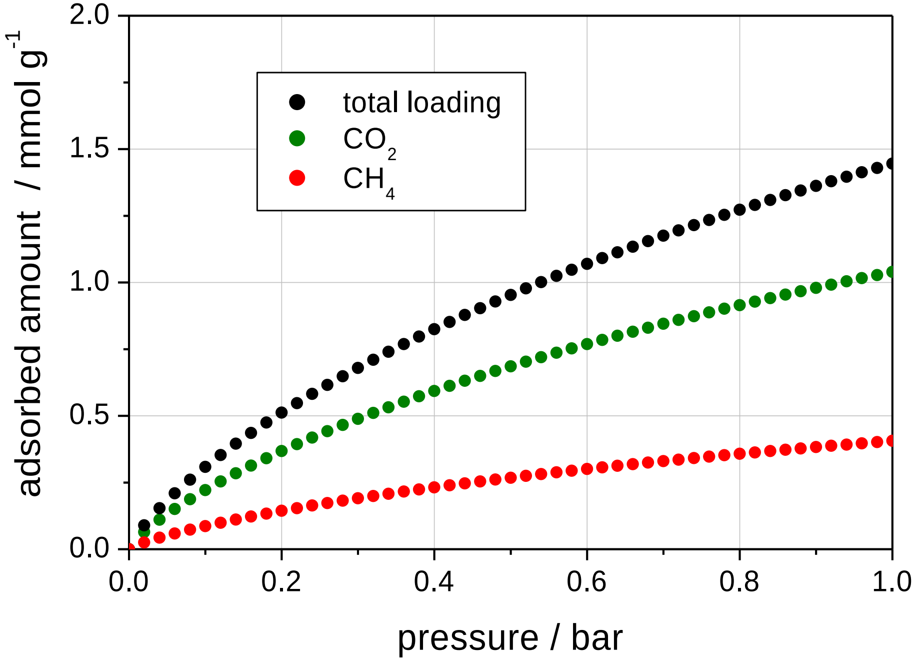
Typical presentation of sorption capacities for binary mixtures

Case A – variable gas composition



p=const. (1 bar), CO_2,CH_4 on D55-1.5 (calc.)

Case B – variable pressure



Y=const. (50:50), CO_2,CH_4 on D55-1.5 (calc.)

- N-Y-Plot with statement to the partial loadings at constant pressure
- N-p-Plot with statement to the adsorbed amount at constant gas phase composition

Basics – Mixture Equilibria (Theory)

Models for mixture data

- Extended langmuir-like equations
- IAS-Theory
- VS-Model

Requirements:

- Knowledge of pure component isotherms

Extended langmuir-like equations

- Multi Component-Langmuir (MCLAI)
- Multi Component-Sips (MCSIPS)
- Multi Component-DSLAI (MCDSLAI)

$$q_i = q_{m,i} \frac{(b_i p_i)^{x_i}}{1 + \sum (b_j p_j)^{x_j}}$$

MCSIPS

IAS-Theory

- IAST with Langmuir
- IAST with Toth
- IAST with DSLAI, DSLAISIPS
- IAST with UNILAN

$$\frac{A \cdot \pi}{RT} = \int_0^{p_{i0}} \frac{n}{p} dp = const.$$

$$n = Isotherm(p_{io})$$

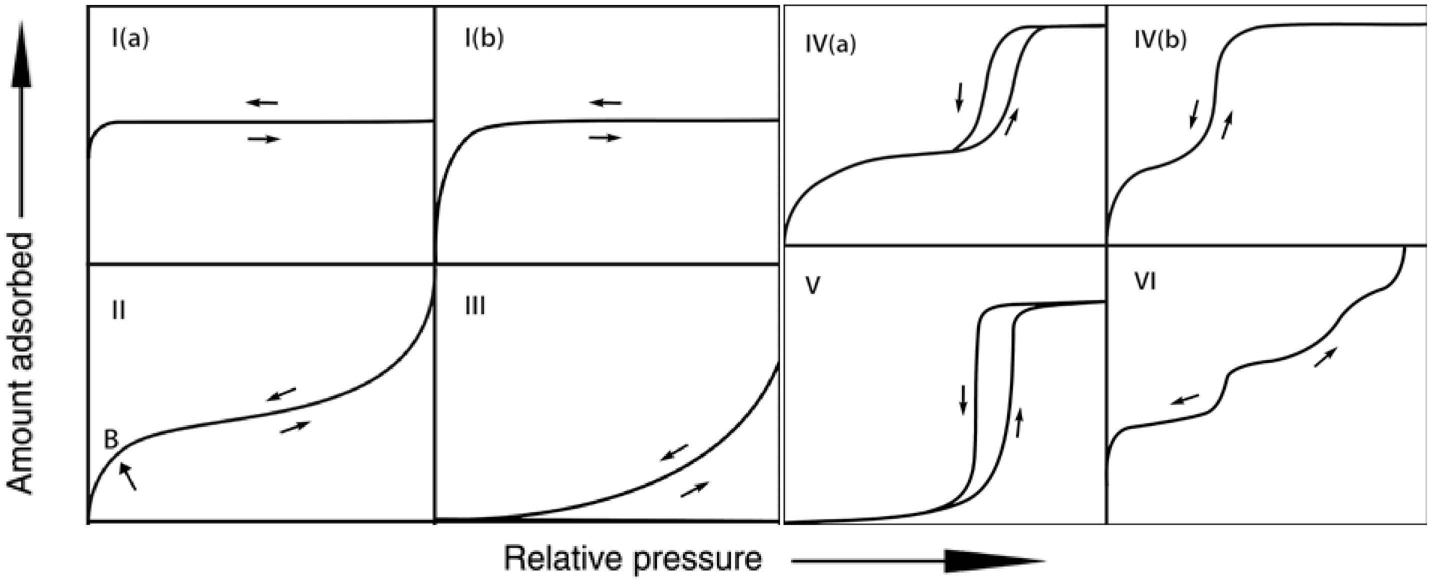
VS-Model

- VS-Model with Wilson

predictive calculations with **3P sim** possible

Calculations of mixture data with **3P sim** – Recommendations for pure components

1. Fitting of pure component data at **same temperature for all components**
2. All data as table - **pressure / bar** (mbar) and **adsorbed amount / mmol g^{-1}**
3. **All components** must be fitted with **same isotherm model**



TYP I: Langmuir, SIPS, Toth, DSLangmuir, DSLangmuirSIPS, UNILAN

Typ II: (Freundlich)

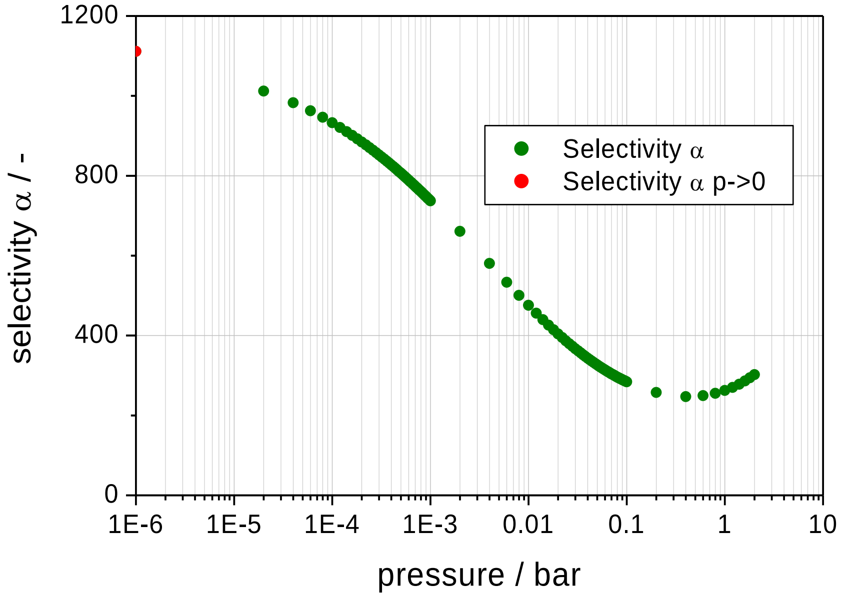
Typ IV, V: DSLangmuirSIPS, (DSLangmuir), (SIPS)

Relationship between loading – mole fraction – selectivity

1. Calculation of **mole fractions of adsorbed phase** from partial loading
2. Calculation of **mole fraction of gas phase** from partial pressures
3. Calculation of **selectivity**
4. Check **plausibility with** help of **limit for selectivity** (for IAST-Calculations)

$$X_{CO_2} = \frac{n_{CO_2}}{n_{CO_2} + n_{CH_4}} \qquad Y_{CO_2} = \frac{p_{CO_2}}{p_{CO_2} + p_{CH_4}}$$

$$\alpha_{CO_2,CH_4} = \frac{Y_{CH_4}}{Y_{CO_2}} \frac{X_{CO_2}}{X_{CH_4}} \qquad \alpha_{CO_2,CH_4}(p \rightarrow 0) = \frac{H_{CO_2}}{H_{CH_4}}$$

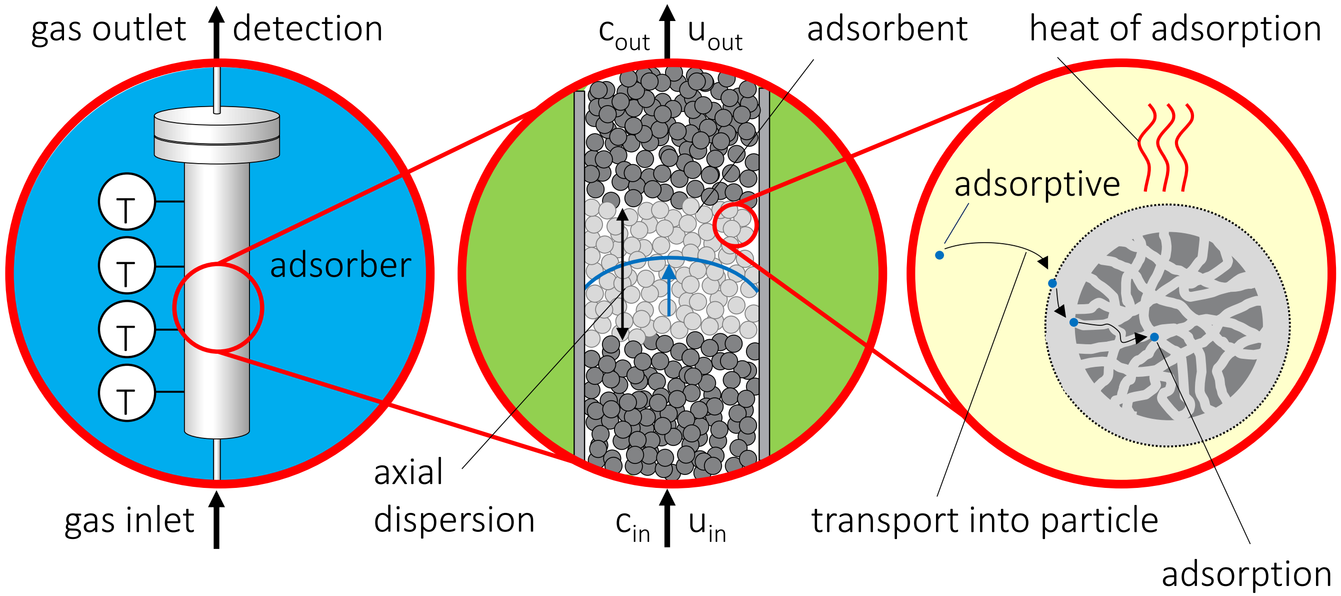


50% CO_2,50% CH_4 on NaMSX, IAST with Toth

Limit of selectivity can be used to check the results **of IAST-Calculations or other models** (only for models with Henry range)

Often **Limit of selectivity** do not reflect the **selectivity** for the real separation process, therefore a **single consideration is not enough**

Basics – Dynamic Gas Sorption a multi-scale Process

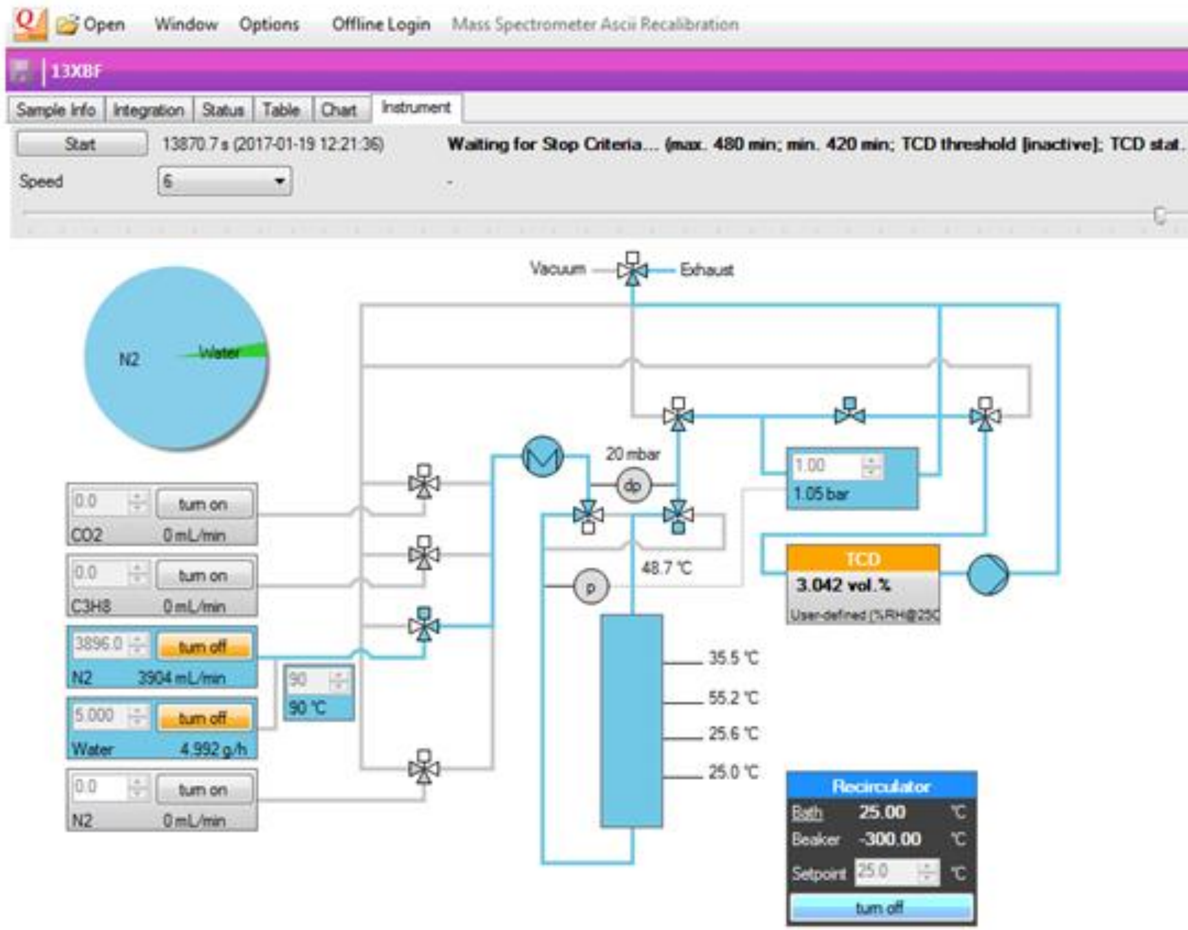


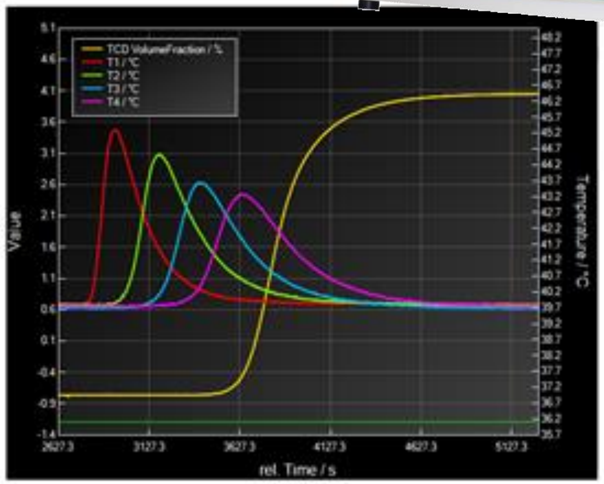
- Size of Adsorber
- Shape of Adsorber

- Nature of the Fixed Bed
- Bed Porosity
- Shape of Particles

- Textural Properties
- Surface Characteristics
- Accessibility

Basics – Flow Plot of a Setup for Dynamic Measurements



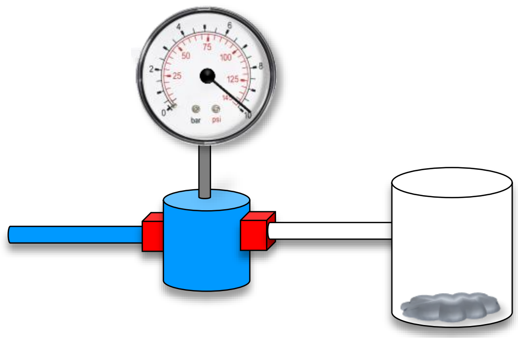


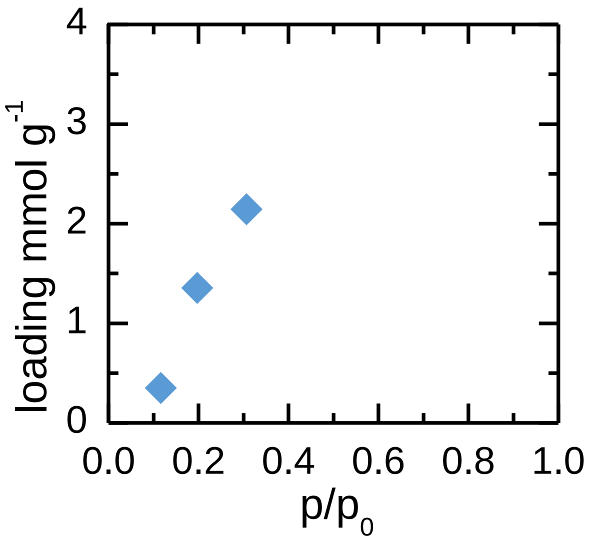
- Flow through the regenerated sample with a predefined gas mixture
- Measurement of data at **a specified pressure and gas mixture**

Basics – Comparison of static and dynamic methods

Static Volumetric Measurements

- Sorption takes place in enclosed chamber
- Pressure is recorded over time
- **Pure gases only**





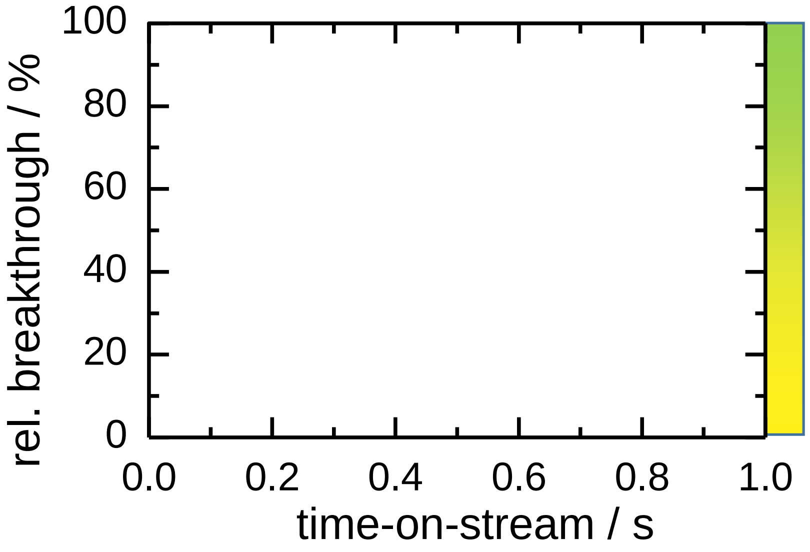
$$n_{\text{ads},i} = n_{\text{dosed},i} - n_{\text{free},i}$$

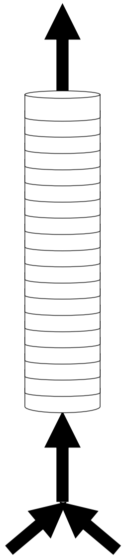
$$n_{\text{dosed},i} = \frac{p_{\text{Dose},i}\, V_{\text{Dose}}}{RT}$$

$$n_{\text{free},i} = \frac{p_{\text{Cell},i}\,(V_{\text{Dose}} + V_{\text{Cell}})}{RT} \qquad n_{\text{ads}} = \sum_{0}^{i} n_{\text{ads},i}$$

Breakthrough Experiments

- Sorption takes place in open system
- **Gas mixtures only**, constant pressure
- Outlet composition is recorded over time



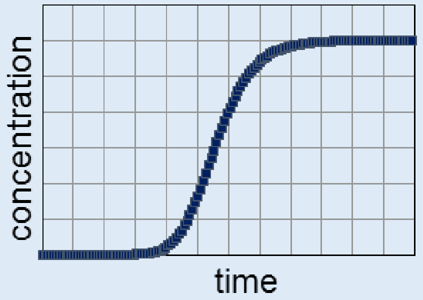


$$n_{\text{adsorbed}} = \int \dot{n}_{\text{in}}(t)\text{d}t - \int \dot{n}_{\text{out}}(t)\text{d}t$$

$$n_{\text{adsorbed}} = \int \dot{V}_{\text{in}}(t)\frac{y_{\text{in}}(t)}{V_{\text{m}}}\text{d}t - \int \dot{V}_{\text{out}}(t)\frac{y_{\text{out}}(t)}{V_{\text{m}}}\text{d}t$$

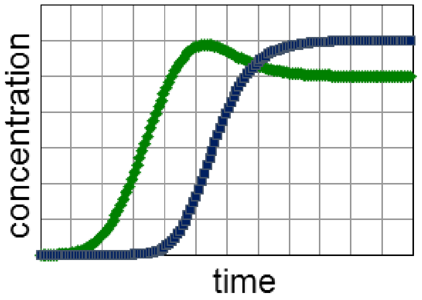
Basics – Experimental Possibilities of dynamic Method

Simple Breakthrough Curves



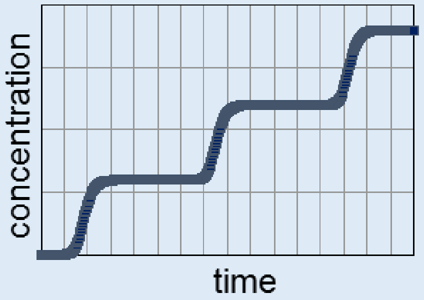
- Breakthrough time
- Mass transfer
- Technically usable sorption capacity
- Modelling

Multicomponent Adsorption



- Competitive adsorption
- Displacement

Isotherms



- Saturation capacity
- Isotherms (single or mixture)

Cycle stability testing

- Regenerability
- Cycle-Stability

PSA-Emulation

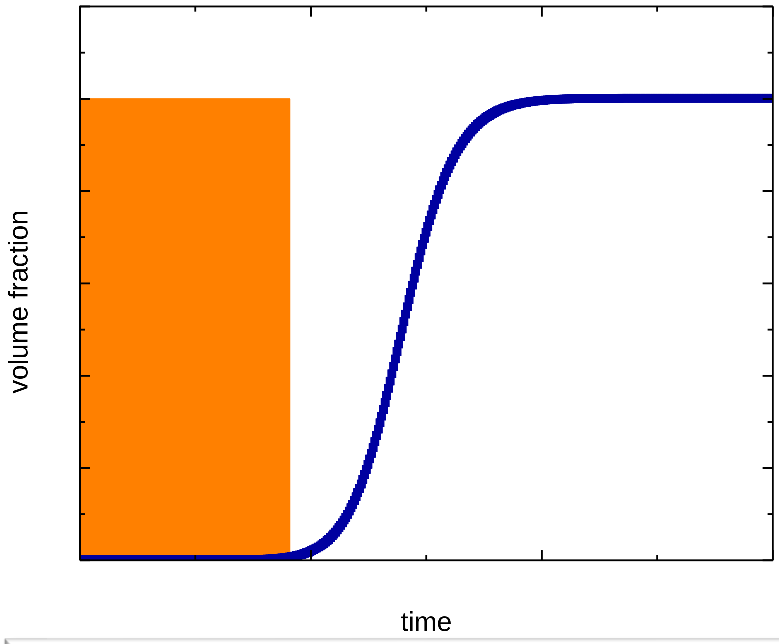
- Emulation of PSA
- Down-Scaling

Chromatography

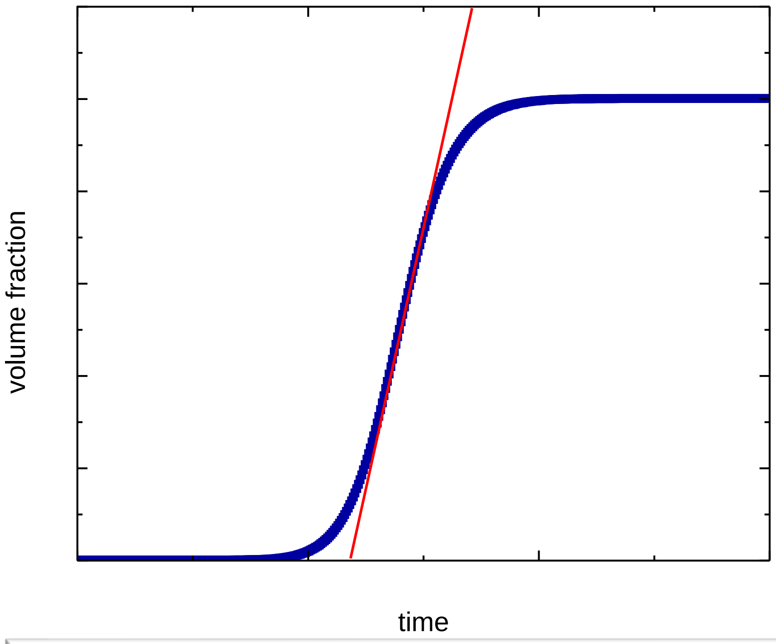
- Chromatographic parameters

Basics -Different segments of a Breakthrough Curve

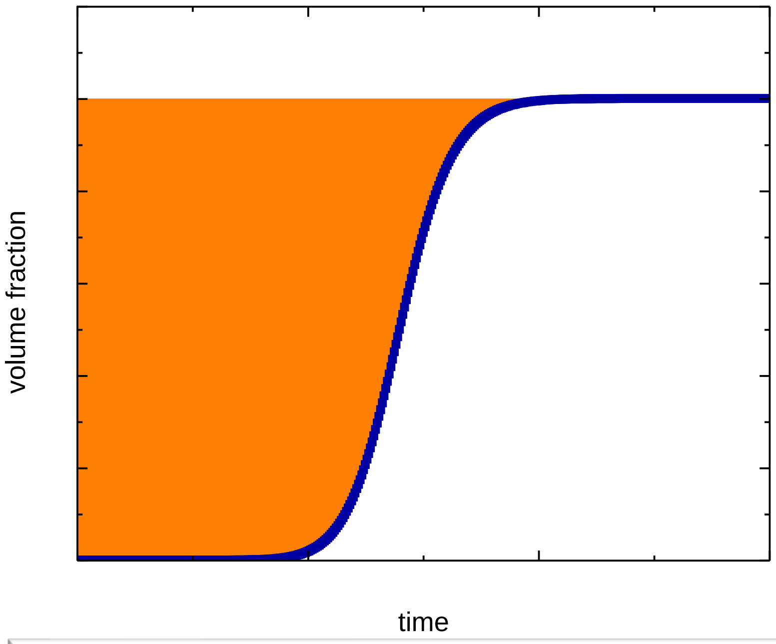
Unsaturated Zone



Mass Transfer Zone



Saturated Zone

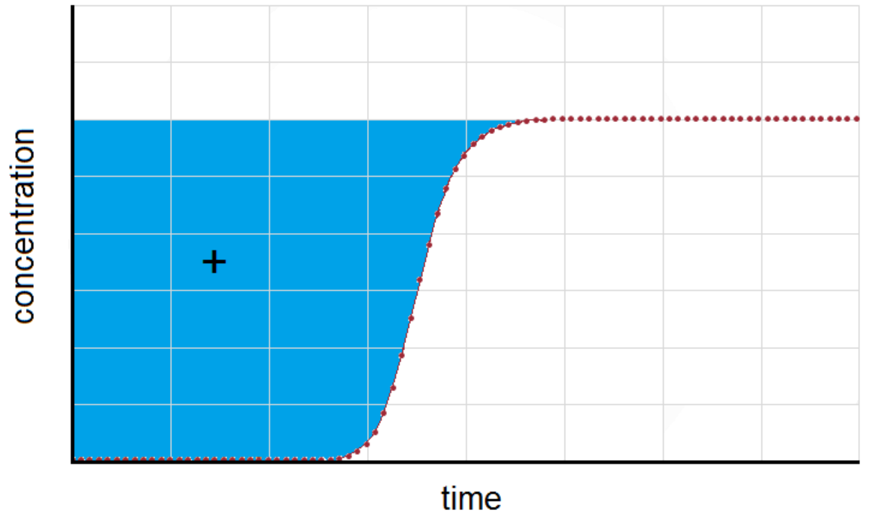


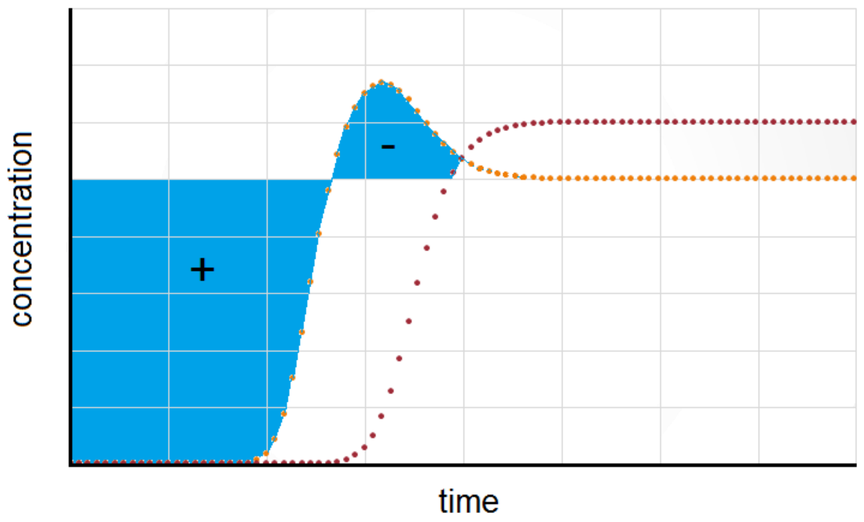
- Determination of technical usable sorption capacity
- Can be used as benchmark for separation performance of adsorbents

- Mass transfer coefficient, axial dispersion, shape of isotherm
- Heat effects, heat dissipation
- The time interval of mass transfer zone has to be minimized

- Determination of saturation capacity
- By assuming of thermodynamic controlled system → Measurement of isotherms possible

Basics – Mixture Equilibria





- binary mixture:

  CO_2/He (non-adsorbable carrier gas)

  → Pure component equilibria

  CO_2/CH_4 (adsorbable carrier gas)

  → Preloading of sample with pure CH_4

  → Incomplete determination of the system (evaluation mostly simple)

  → Partial loading for CO_2 (mixture sorption data)

- ternary mixture:

  CO_2/CH_4/He (non-adsorbable carrier gas)

  Displacement of less adsorbed component

  → Partial desorption, role-up effects

  → Complete determination (evaluation complex)

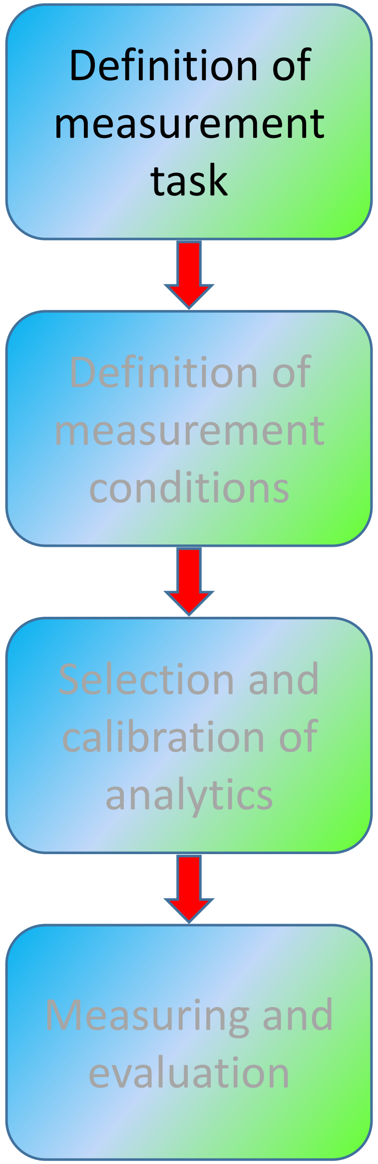
  CO_2/CH_4/N_2 (adsorbable carrier gas)

  → Preloading of sample with pure N2

  → Incomplete ternary mixture data (CO_2, CH_4)

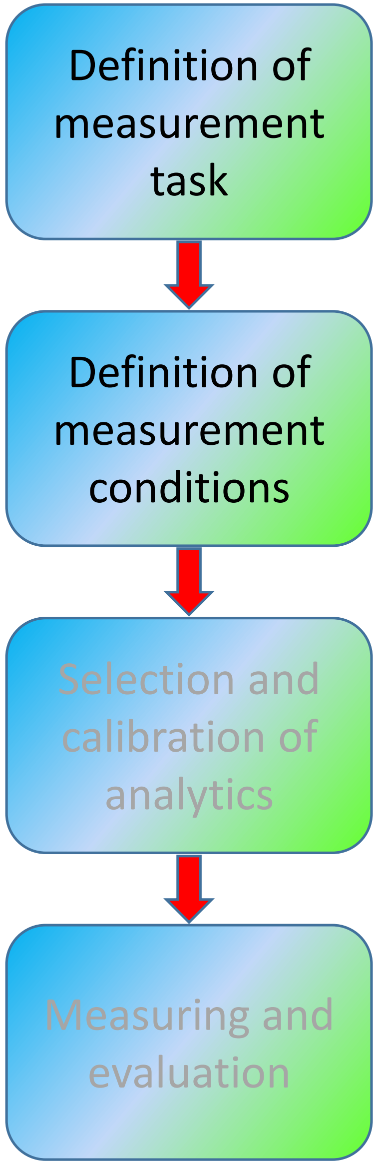
Basics – Schedule of a Mixed Gas Experiment

- **Predictive calculation of mixture data** desired (**Y**/N)?
  → Pure component isotherms necessary
- Is a **complete determination of the system** desired?
  → **determination of all partial loadings**, diluting with Helium-carrier gas (**Y**/N)
- Definition of total flow, concentration, measurement temperature etc.
  → **Sample must be under „thermodynamic control"** (always)
- Depending on **concentration range** one should consider:
  → Calibration of suitable analytic technique (always)
- Sample preparation and definition of preparation conditions
  → Temperature, carrier gas (always)
- Build up of a measurement routine
  → pressurization, Helium or adsorptive 1 (**Helium for complete determination**)
- Evaluation of the experiment



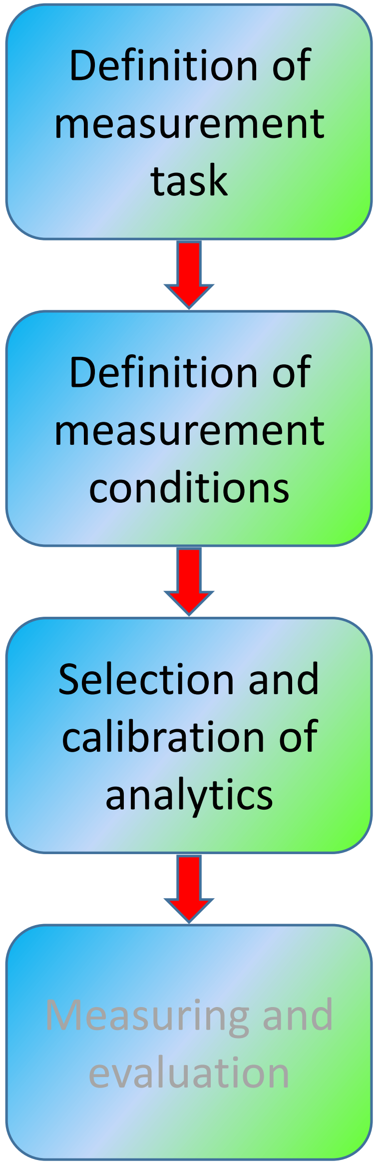
Basics – Schedule of a Mixed Gas Experiment

- **Predictive calculation of mixture data** desired (**Y**/N)?
  - → Pure component isotherms necessary
- Is a **complete determination of the system** desired?
  - → **determination of all partial loadings**, diluting with Helium-carrier gas (**Y**/N)
- Definition of total flow, concentration, measurement temperature etc.
  - → **Sample must be under „thermodynamic control“** (always)
- Depending on **concentration range** one should consider:
  - → Calibration of suitable analytic technique (always)
- Sample preparation and definition of preparation conditions
  - → Temperature, carrier gas (always)
- Build up of a measurement routine
  - → pressurization, Helium or Adsorptive 1 (**Helium for complete determination**)
- Evaluation of the experiment



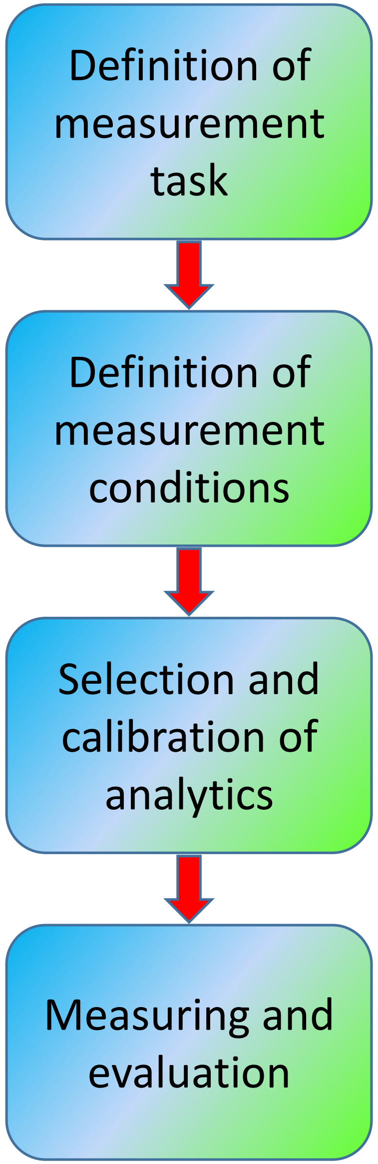
Basics – Schedule of a Mixed Gas Experiment

- **Predictive calculation of mixture data** desired (**Y**/N)?
  - → Pure component isotherms necessary
- Is a **complete determination of the system** desired?
  - → **determination of all partial loadings**, diluting with Helium-carrier gas (**Y**/N)
- Definition of total flow, concentration, measurement temperature etc.
  - → **Sample must be under „thermodynamic control“** (always)
- Depending on **concentration range** one should consider:
  - → Calibration of suitable analytic technique (always)
- Sample preparation and definition of preparation conditions
  - → Temperature, carrier gas (always)
- Build up of a measurement routine
  - → pressurization, Helium or Adsorptive 1 (**Helium for complete determination**)
- Evaluation of the experiment



Basics – Schedule of a Mixed Gas Experiment

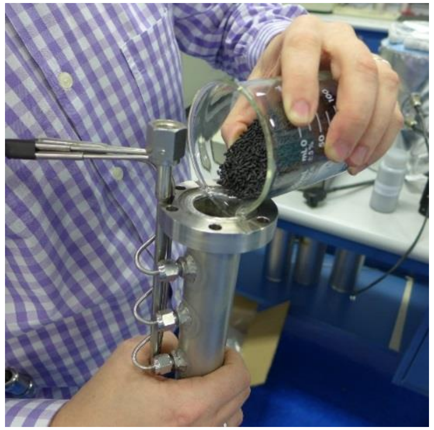
- **Predictive calculation of mixture data** desired (**Y**/N)?
  - → Pure component isotherms necessary
- Is a **complete determination of the system** desired?
  - → **determination of all partial loadings**, diluting with Helium-carrier gas (**Y**/N)
- Definition of total flow, concentration, measurement temperature etc.
  - → **Sample must be under „thermodynamic control“** (always)
- Depending on **concentration range** one should consider:
  - → Calibration of suitable analytic technique (always)
- Sample preparation and definition of preparation conditions
  - → Temperature, carrier gas (always)
- Build up of a measurement routine
  - → pressurization, Helium or Adsorptive 1 (**Helium for complete determination**)
- Evaluation of the experiment

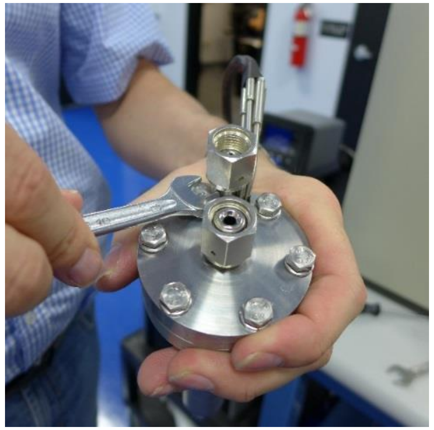


Task: Investigation of a binary system

Activated Carbon, CO_2 (25%), CH_4 (75%), complete determination at 5 bar

1. **Weighting the sample and sample preparation** at 120°C, He-flow 200 ml min^{-1} (STP)
2. **Definition of partial pressures:** 1.25 bar CO_2; 3.75 bar CH_4; 5 bar He; Σ10 bar
3. **Gas flows:** 0.25 l min^{-1} (STP) CO_2, 0.75 l min^{-1} (STP) CH_4, 1l min^{-1} (STP) He
4. **Pressurization with Helium up to 10 bar**
5. Start of measurement by **simultaneous dosing of CO_2 and CH_4** in Helium
6. Recording of effluent **gas composition via MS** (all components!)
7. After breakthrough, regeneration of sample for **determination of activated mass**

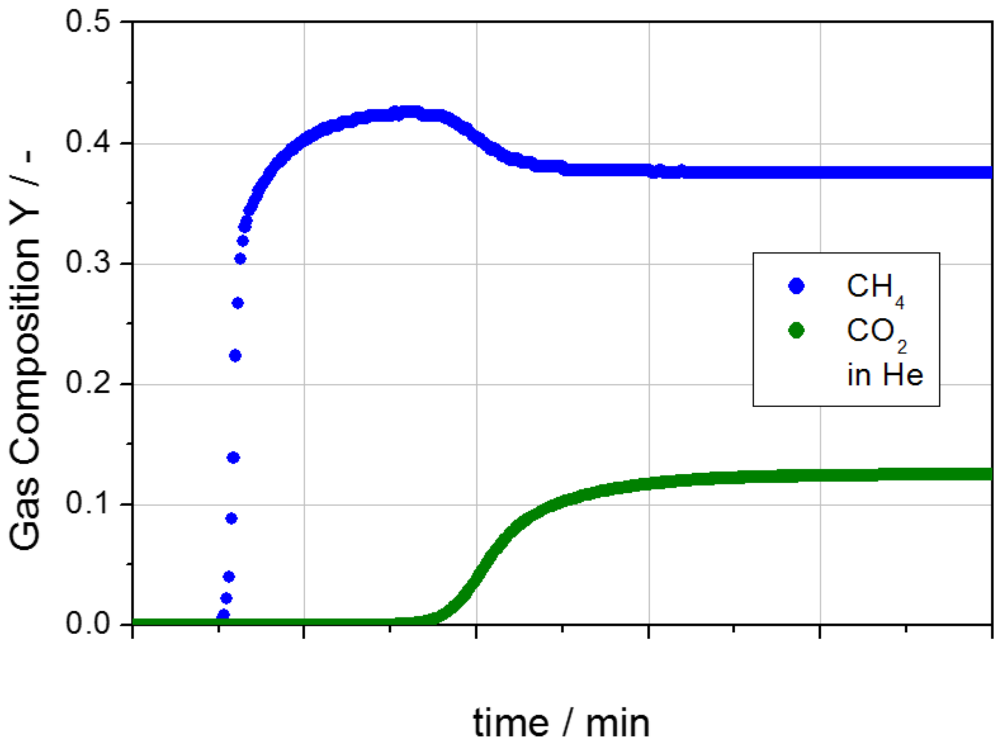




Basics – Example of a Mixed Gas Experiment

Task: Investigation of a binary system

Activated carbon, CO_2 (25%), CH_4 (75%), complete determination at 5 bar



Result of experiment:

Breakthrough curve with "role-up" effect

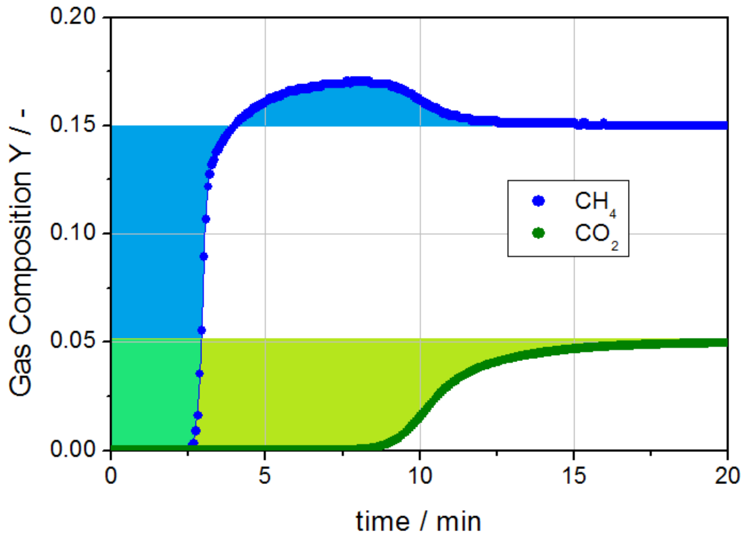
- Includes all partial loadings
- Reference on p_{CO2}=1.25 bar and P_{CH4}=3.75 bar
- Mole fraction: y_{CO2}=0.25; y_{CH4}=0.75
- **Helium will not be considered!**

Integration of areas:

- $n(CO_2)$; $n(CH_4)$; n(total); α

Mixture Equilibria – Examples of a Mixed Gas Experiment

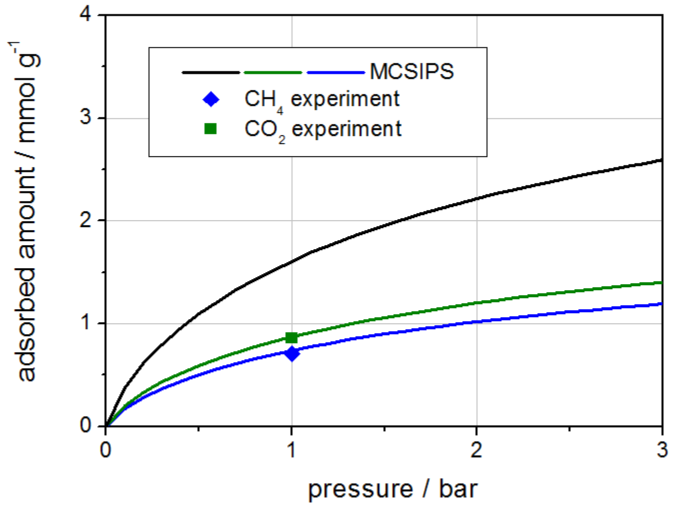
5% CO_2 15% CH_4 in He at 20°C, 5 bar, 2500 ml min^{-1} (STP) on D 55/1.5



Dynamic experiment (determination of **all partial loadings**)

n_{CO2}= 0.86 mmol g^{-1}
n_{CH4}=0.71 mmol g^{-1}

$\alpha_{Experiment}$=3.63

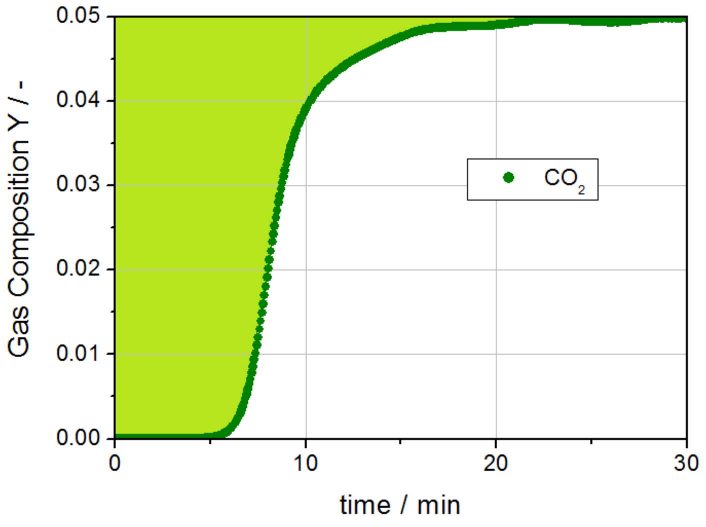


➡ System is complete determined, all partial loadings were measured (points).

➡ Data can be used to confirm predictive models for mixture sorption (lines).

Mixture Equilibria – Examples of a Mixed Gas Experiment

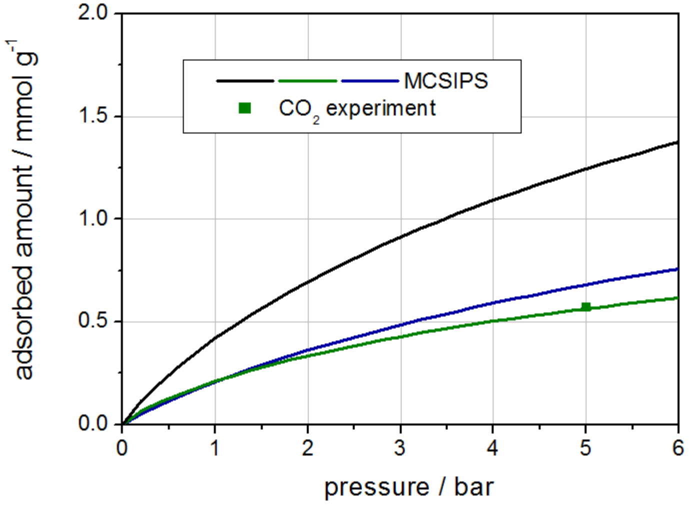
5% CO_2 in N_2 at 20°C, 5 bar, 2500 ml min^{-1} (STP) on D 55/1.5



Dynamic experiment (determination **only** of **CO_2 loading**)

n_{CO2}= 0.57 mmol g^{-1}
n_{N2}= not determined

$\alpha_{Experiment}$= not determined



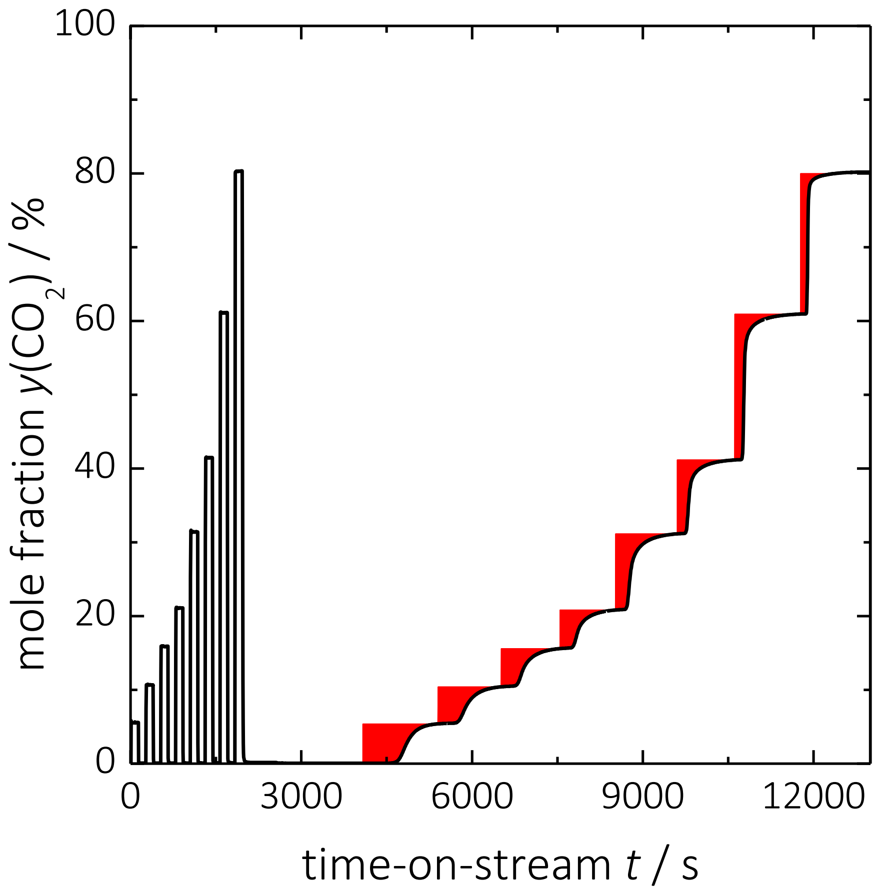
System is incomplete determined.

A thermodynamic model is necessary to get all data!

This simple technique is widely used in practice (i.e. only the separation of a harmful component is of interest)

Mixture Equilibria – Examples of a Mixed Gas Experiment

Sequence of several breakthrough curves on activated carbon D 55-1.5



Conditions:

- 20°C, 2 L min^{-1}
- 10 bar (pressurization with N_2)
- Concentrations: 5% CO_2 - 80% CO_2 in N_2

Procedure:

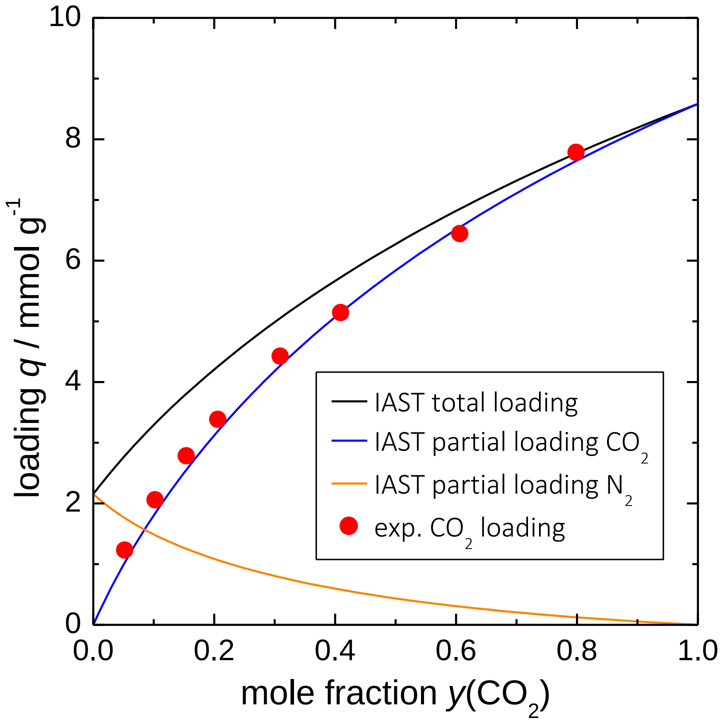
- Start further breakthroughs after equilibrium before
- **Integration** and **summation** results in partial loading data of CO_2
- Volume ratio and total pressure defines the partial pressure of CO_2

→ Mixed isotherm data of CO_2 in N_2

→ Always less adsorbed component as carrier (here: N_2)

Mixture Equilibria – Examples of a Mixed Gas Experiment

Measured partial loading data for CO_2 on activated carbon D 55-1.5 at 10 bar



- Dynamic measured data (**red**)
- IAST-Model (**I**deal **A**dsorbed **S**olution **T**heory) based on pure component isotherms (lines)
- Mixture of CO_2 and N_2 shows **ideal** behavior on AC

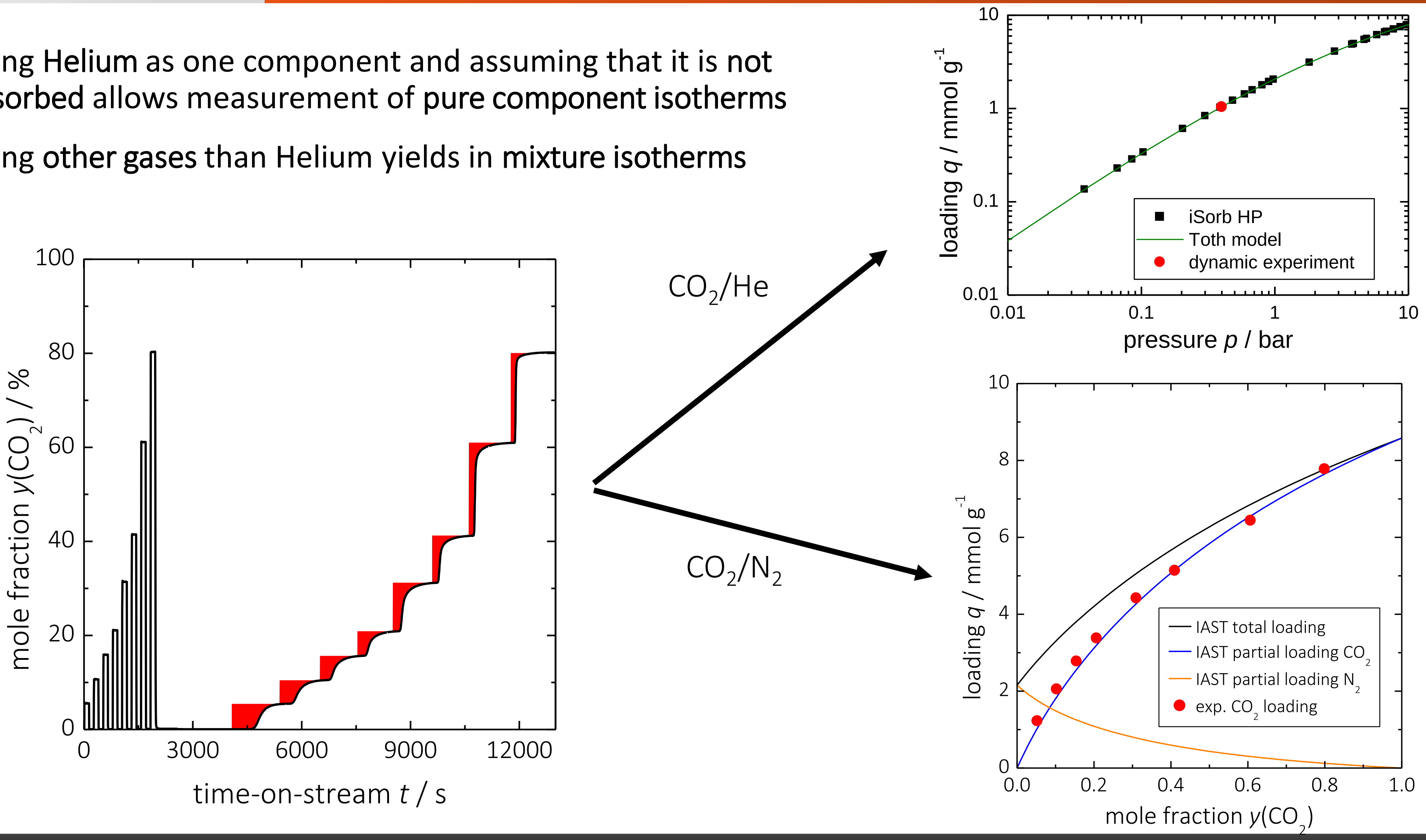
➡ A thermodynamic model is necessary to get all data!

➡ Determination of partial loading data of CO_2 on AC D 55-1.5 by performing sequentially experiments **along constant total pressure**.

$$n_{CO_2,N_2,total}(p = const.) = FKT(Y_{CO_2}, Y_{N_2})$$

Mixture Equilibria – Examples of Pure and Mixed Gas Isotherms

- Using **Helium** as one component and assuming that it is **not adsorbed** allows measurement of **pure component isotherms**
- Using **other gases** than Helium yields in **mixture isotherms**

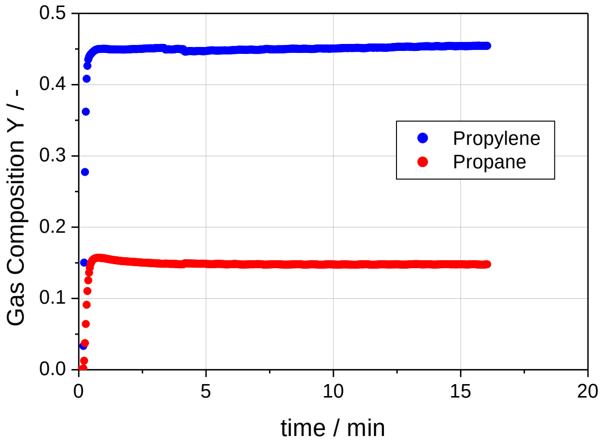


Pure component isotherm

Isotherm of a mixture (only one component)

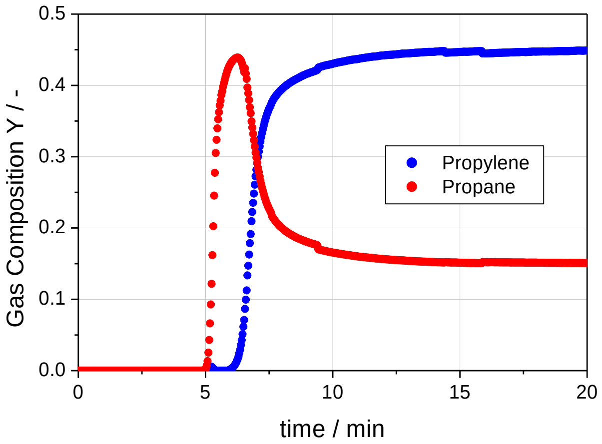
Breakthrough Experiments - Comparison

15% Propane 45% Propylene in He at 25°C, 5 bar, 1000 ml/min on AC1, AC2, AC3



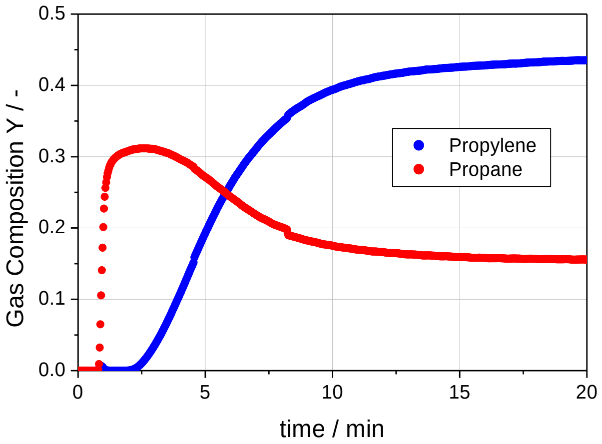
Sample: AC1
$Y_{Propane}$= 0.25
$Y_{Propylene}$= 0.75
$n_{Propane}$= 0.03 mmol g^{-1}
$n_{Propylene}$= 0.06 mmol g^{-1}

$\alpha_{Propylene}$= 0.67



Sample: AC2
$Y_{Propane}$= 0.25
$Y_{Propylene}$= 0.75
$n_{Propane}$= 0.2 mmol g^{-1}
$n_{Propylene}$= 1.7 mmol g^{-1}

$\alpha_{Propylene}$= 2.83



Sample: AC3
$Y_{Propane}$= 0.25
$Y_{Propylene}$= 0.75
$n_{Propane}$= ca. 0 mmol g^{-1}
$n_{Propylene}$= 2.1 mmol g^{-1}

$\alpha_{Propylene}$= not determined (>20)

Selectivity

- Statements on selectivity also possible without thermodynamic models
- Determination of sorption capacities and selectivities, recording of kinetic

Summary Part I - Mixture Equilibria

- With **breakthrough experiments mixture sorption data** with He also pure component are **accessible**.
- By assumption of a non-adsorbable carrier (i.e. He) a complete determination of mixture system is possible (adsorptive 1+adsorptive 2+He).
  - Investigation of **role up effects**
  - Determination of **all partial loadings** and calculation of thermodynamic **selectivity** α

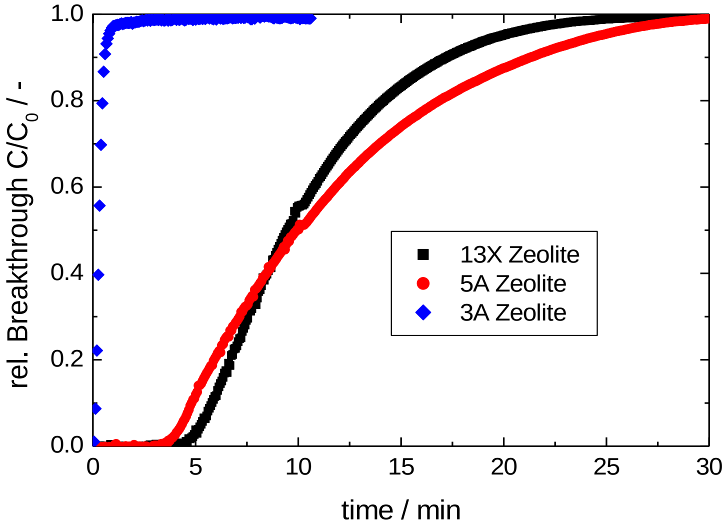
For the investigation of role up effects and α → selective analytical devices necessary (Mass Spec)

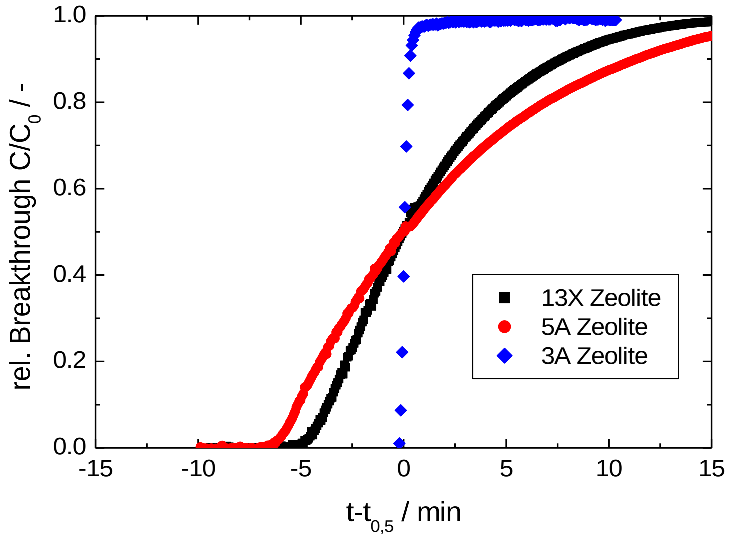
- Simple breakthrough data can also contain mixture equilibria (i.e. for carrier gas as second adsorptive)
  - **No role up effect** can be observed, thermodynamic model necessary for whole description
  - **No** experimental determination of **selectivity** α possible
  - Carrier gas should be the less adsorbed component

Unselective analytical devices are enough for binary systems (i.e. TCD)

Kinetics from Breakthrough Experiments

Breakthrough curves of 5% CO_2 in N_2 on zeolites 13X, 5A, 3A (1 bar, 5 l/min (STP), 20°C)





Qualitative observation of Mass Transfer Zone:

- Zeolite 3A have a spontaneous breakthrough due too narrow pores (kinetic-steric exclusion)
- Zeolite 5A exhibits a broad mass transfer zone
  → indicates lower kinetic for 5A as 13X
- Both zeolites, 5A and 13X have quite unsymmetrical breakthrough curves
  → indicate a **big influence of temperature effects** and shape of isotherms

Kinetics from Breakthrough Experiments

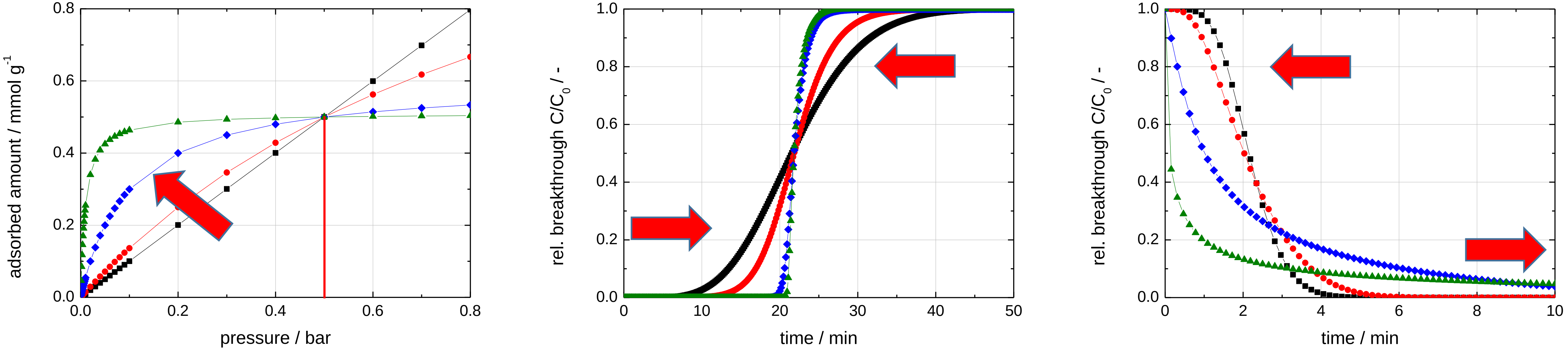
Question:

- Is it possible to get reliable kinetic data from such experiments?
- How is the influence of the isotherm shape and temperature effects?

Answer:

- Yes, but associated with high effort (model of mass- and energy balances is necessary)
  → Simple comparison of slope can be erroneous
- For quantification of temperature effects also a model must be used!
  → I.e. in some cases heat effects can be control nearly the whole curve

Parametric study - Influence of isotherm shape (favored isotherm)



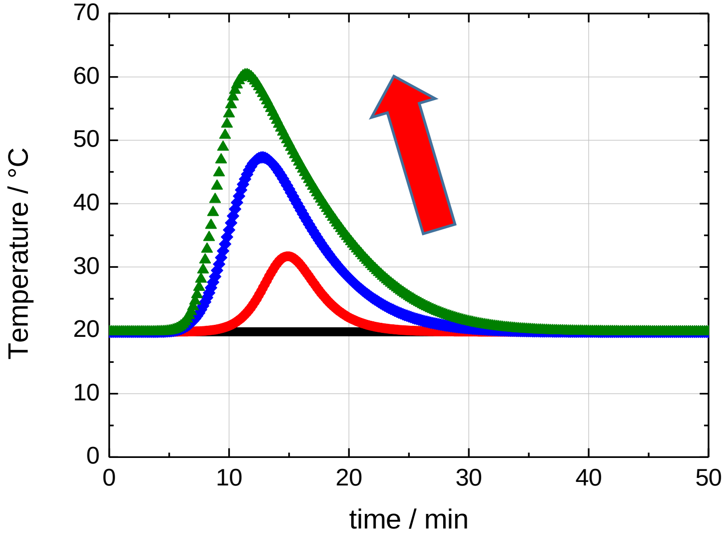
Increasing of curvature | Sharpening with curved isotherm | Flattening with curved isotherm

Calculation of breakthrough with same k_{LDF} value and different isotherm shapes

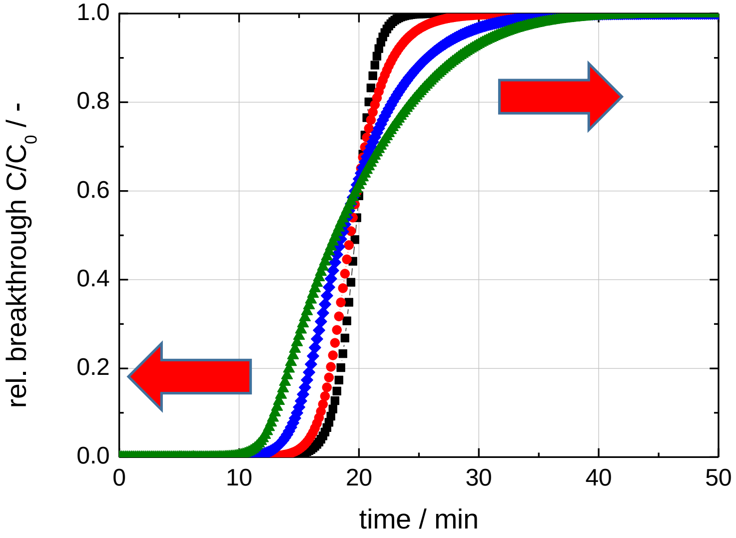
- Slope of breakthrough curves strongly depends on isotherm shape!
  - → simple comparison of slope at $C/C_0=0.5$ only for materials with similar or same isotherm shapes
  - → Shape of isotherms cannot be neglect, view on desorption curves can be helpful

Kinetics from Breakthrough Experiments

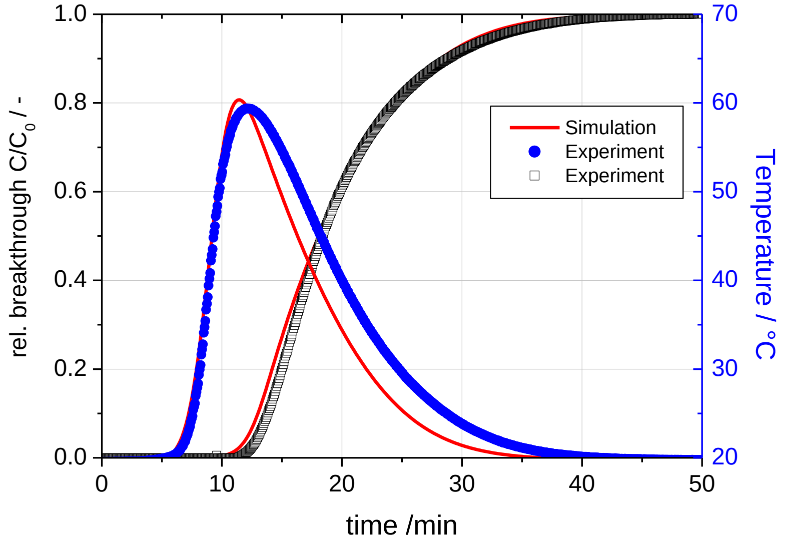
Parametric study - Influence of nonisothermal effects



Increasing of heat effects



Flattening with stronger heat effects



5% CO_2 on NaMSXK (zeolite 13X)

Calculation of breakthrough with same k_{LDF} value and different heat transfer coefficients

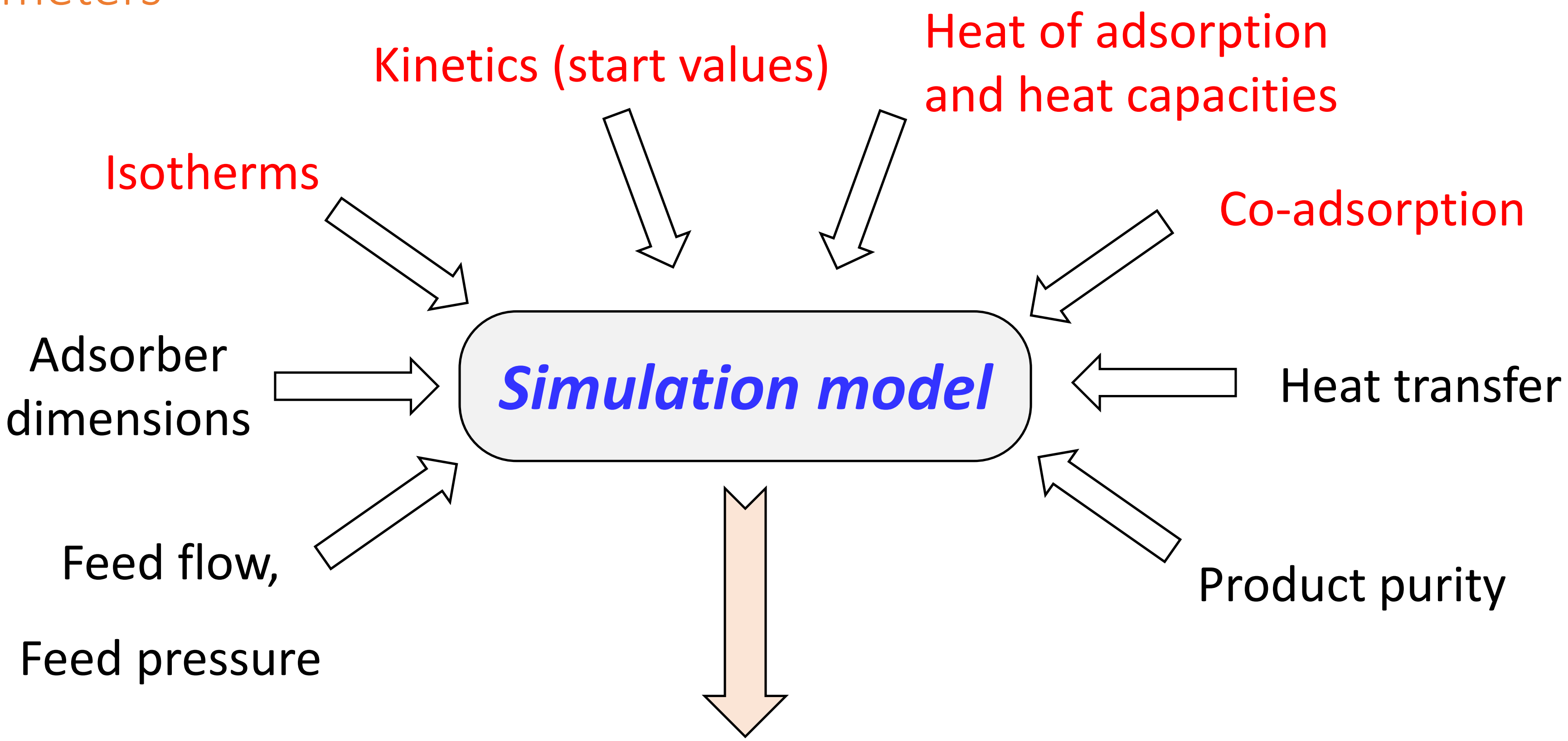
- Slope of breakthrough curves strongly depends on non-isothermal effects!

  → simple evaluation of slope at C/C_0=0.5 leads to wrong interpretation

  → Temperature profiles can't be ignored, lower concentrations and desorption can be helpful

Kinetics from Breakthrough Experiments

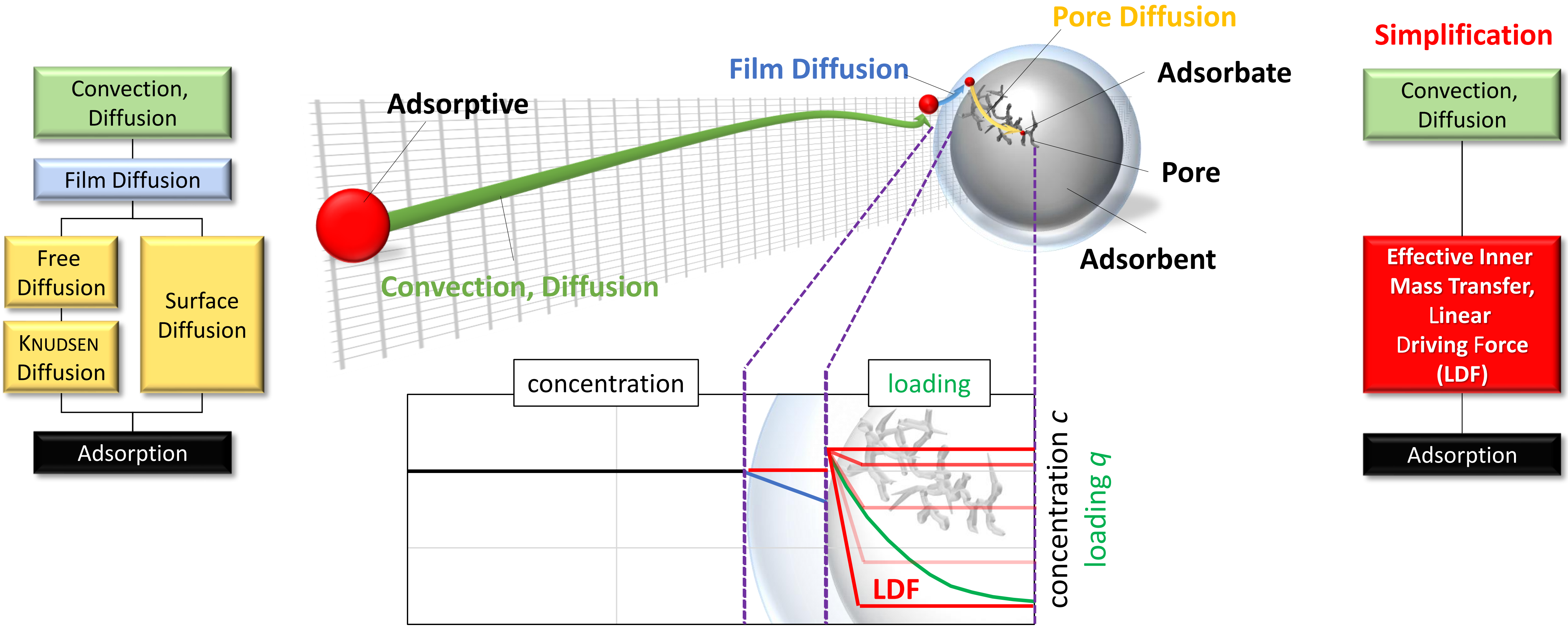
Input Parameters



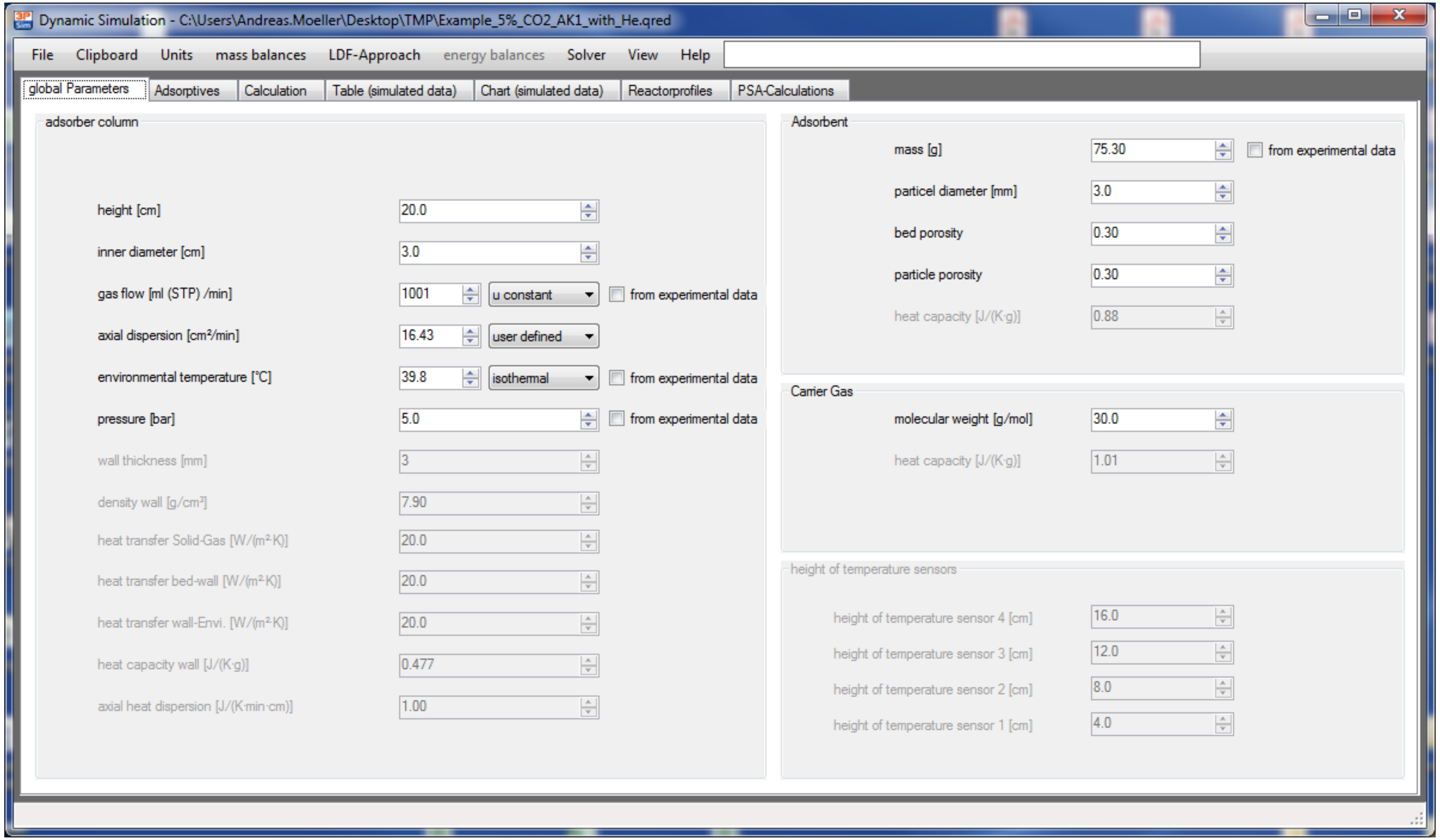
Kinetics, cycle duration, pressure range…

Red: properties of adsorbent/adsorptive system
Black: properties of adsorber and adsorber wall

Kinetic considerations - Mass Transfer coefficient k_{LDF}

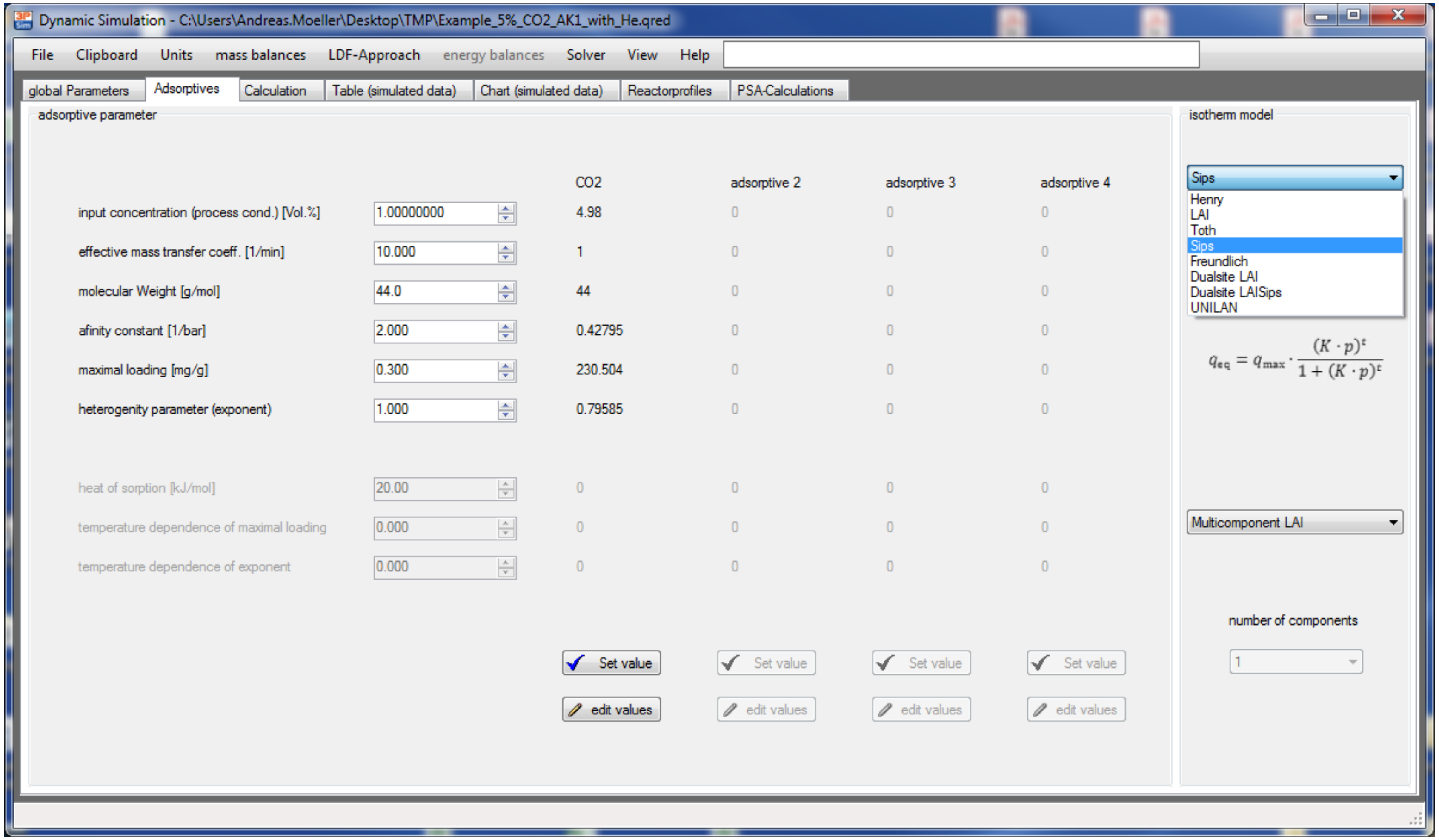


Example breakthrough calculation with isothermal SIPS model



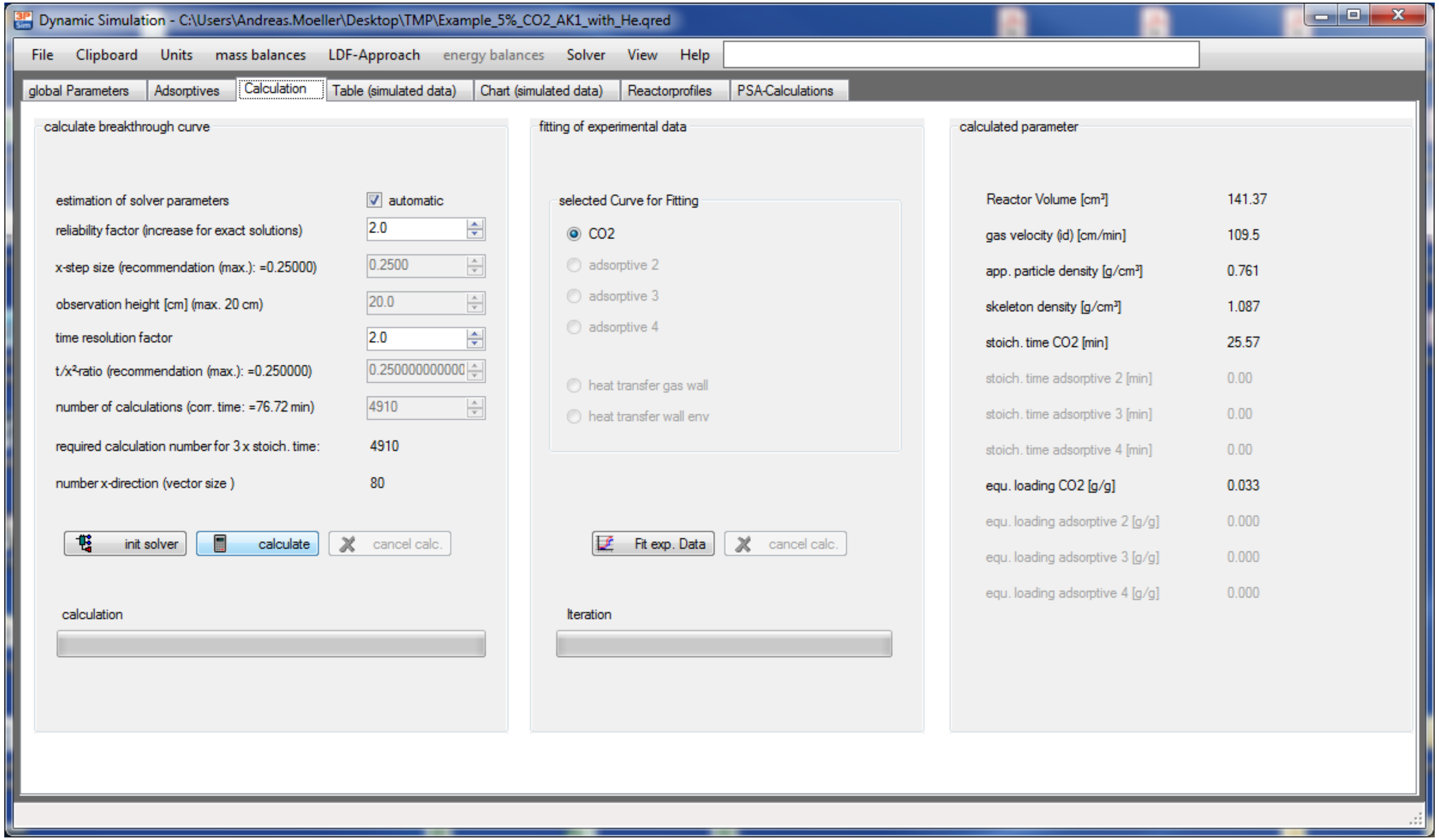
- **No knowledge of script language**
- **Simple input form for parameter**
- Overview of used isotherm model
- No knowledge of solver necessary
- Usage of own Δz, Δt values possible
- Output of stoichiometric values
- Comparison of calculations with Experiment

Example breakthrough calculation with isothermal SIPS model



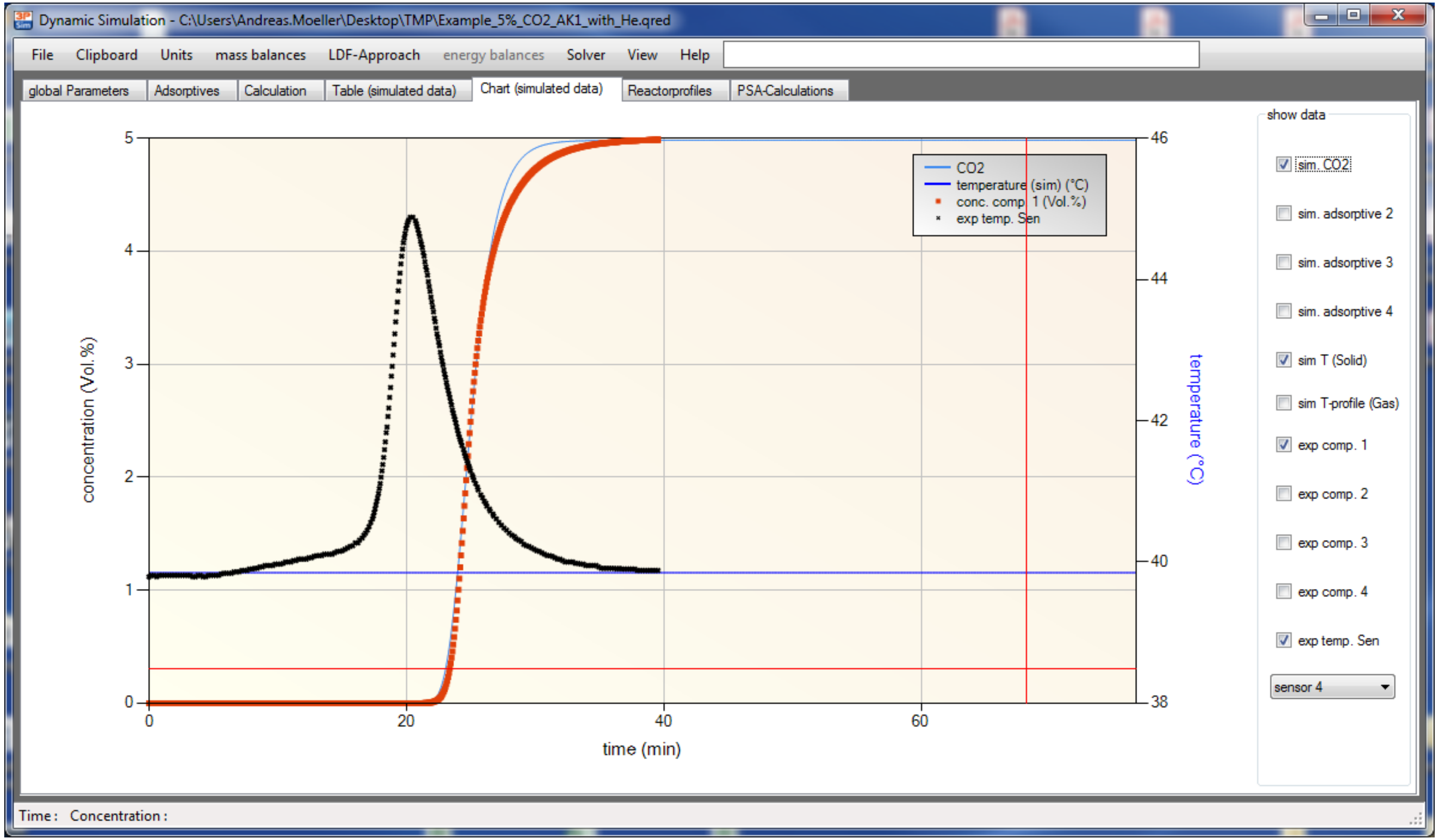
- No knowledge of script language
- Simple input form for parameter
- **Overview of used isotherm model**
- No knowledge of solver necessary
- Usage of own Δz, Δt values possible
- Output of stoichiometric values
- Comparison of calculations with Experiment

Example breakthrough calculation with isothermal SIPS model



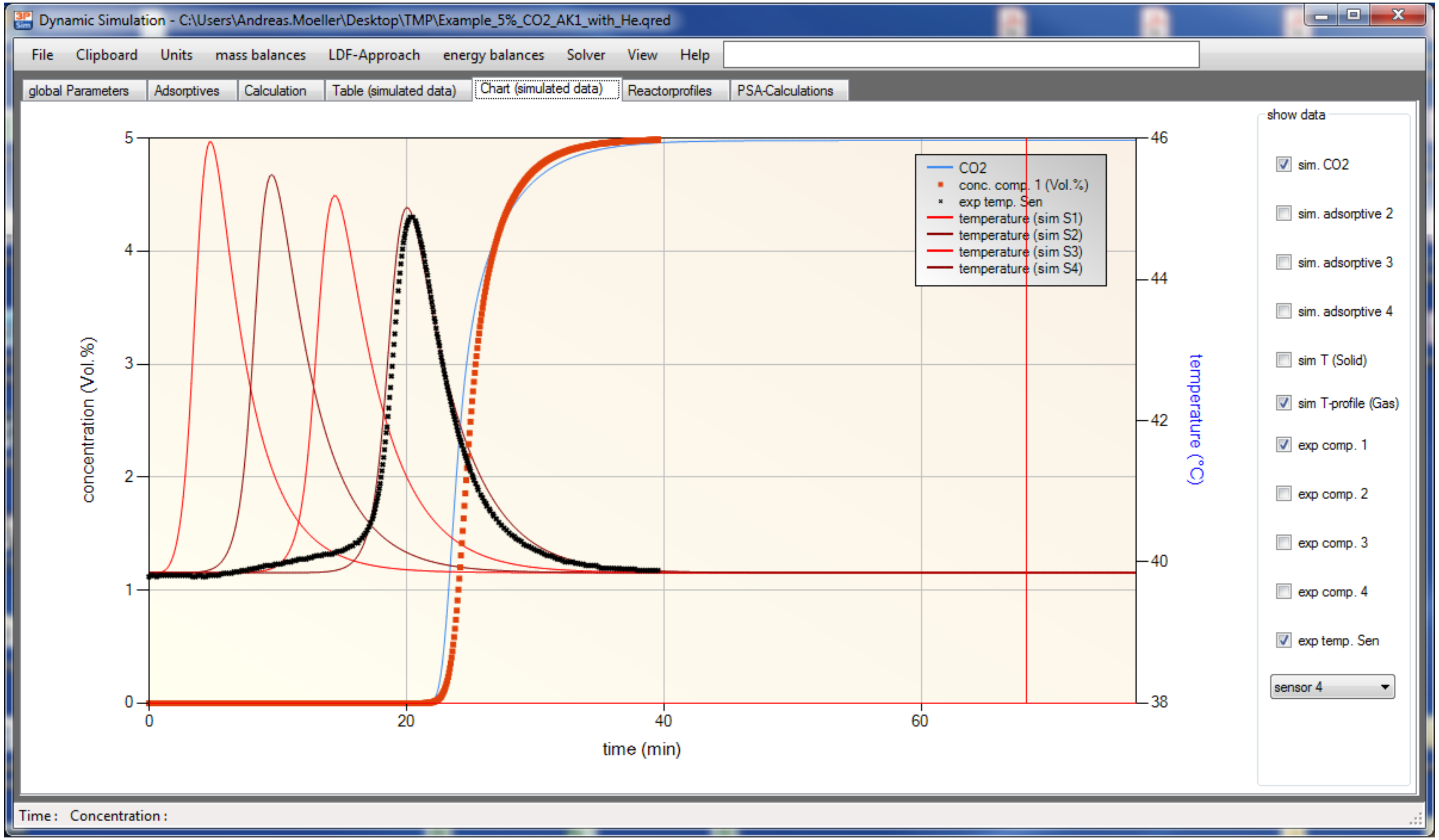
- No knowledge of script language
- Simple input form for parameter
- Overview of used isotherm model
- **No knowledge of solver necessary**
- **Usage of own Δz, Δt values possible**
- **Output of stoichiometric values**
- Comparison of calculations with Experiment

Example breakthrough calculation with isothermal SIPS model



- No knowledge of script language
- Simple input form for parameter
- Overview of used isotherm model
- No knowledge of solver necessary
- Usage of own Dz, Dt values possible
- Output of stoichiometric values
- **Comparison of calculations with Experiment**

Example breakthrough calculation with nonisothermal SIPS model



Observation

- k_{LDF} value (isothermal model)
  → ~ 4 min^{-1}
- k_{LDF} value (nonisothermal model)
  → ~ 13 min^{-1}

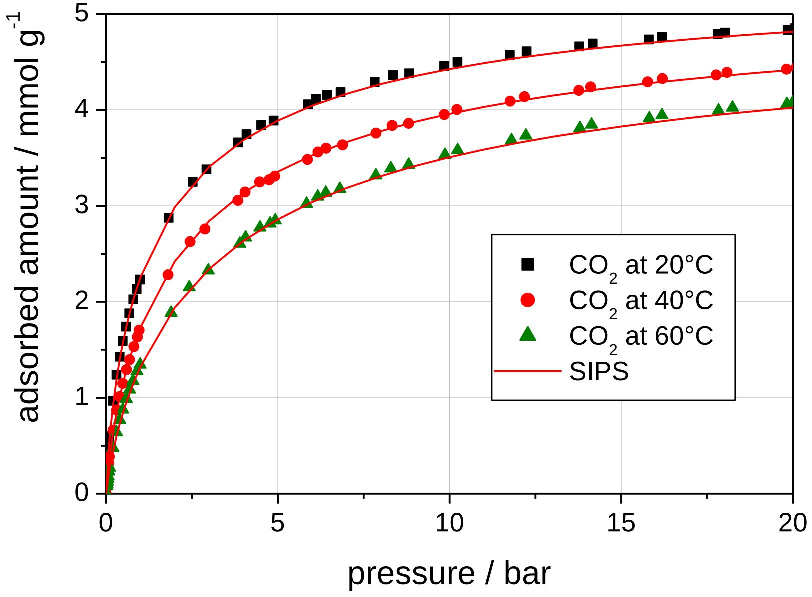
- **approx. 3 times higher**

→ Heat effect should not be neglected

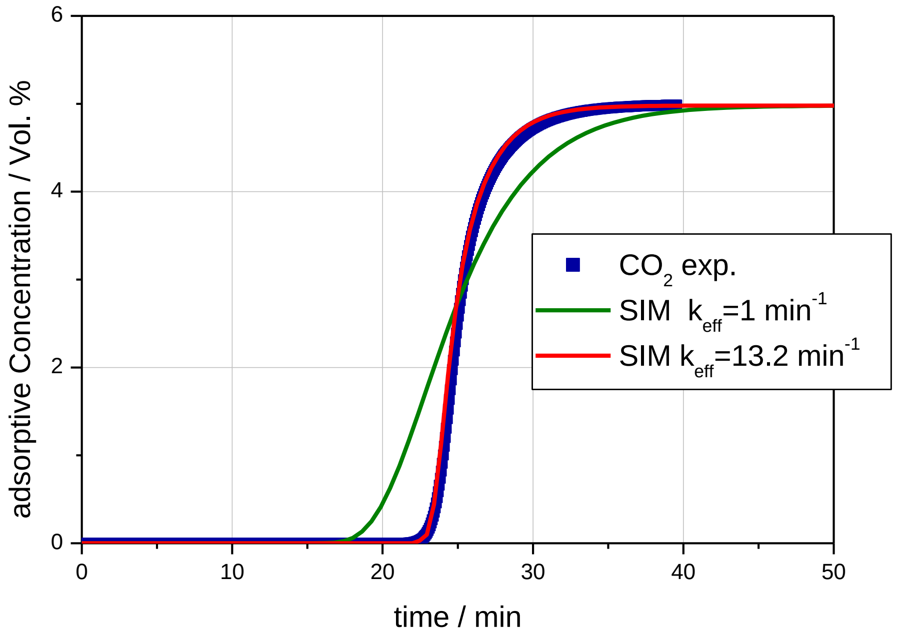
Kinetics from Breakthrough Experiments (one Adsorptive)

Determination of LDF-constant

Input Isotherms



CO_2 isotherms on D 55/1.5



5% CO_2 in He at 40°C, 5 bar, 1000 ml/min on D 55/1.5

Finding of Mass Transfer Coefficient k_{LDF}:

Start value for k_{LDF} 1 min^{-1}

Best fit with k_{LDF} 13 min^{-1}

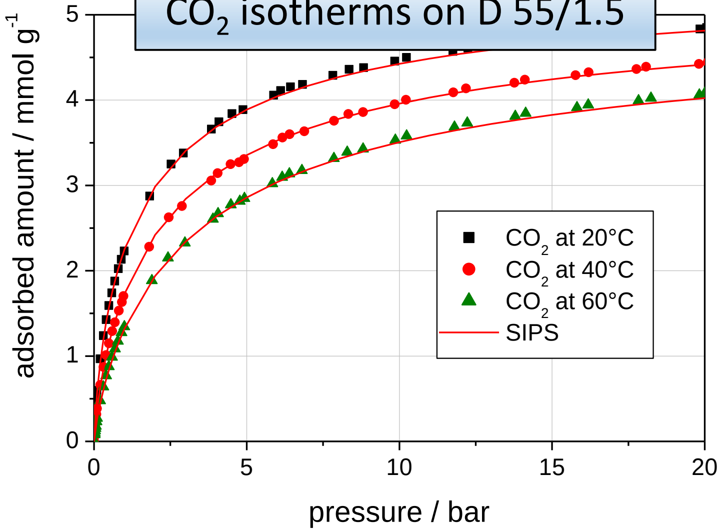
Input Heat Transfer

Bed/Wall ~ 50 W m^{-2} K^{-1})
Wall/Liquid ~ 400 W m^{-2} K^{-1})

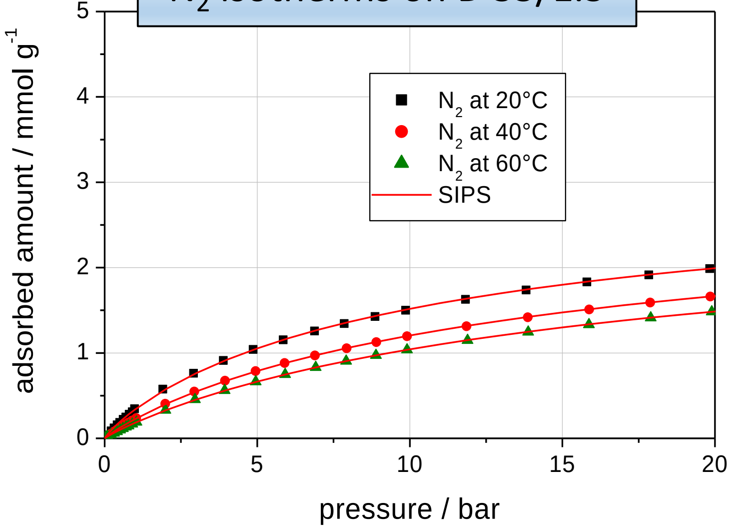
Iterative recalculation !

Kinetics from Breakthrough Experiments (two Adsorptives)

CO_2 isotherms on D 55/1.5



N_2 isotherms on D 55/1.5



Input pure component Isotherms

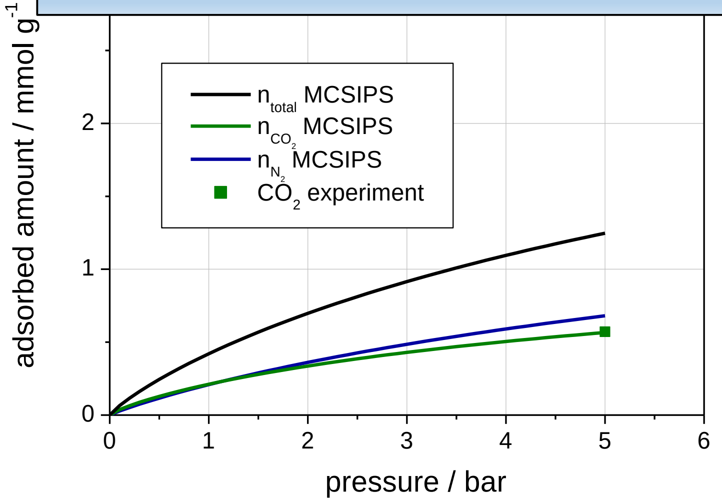
Determination of k_{LDF} only for CO_2

Fitting k_{LDF}

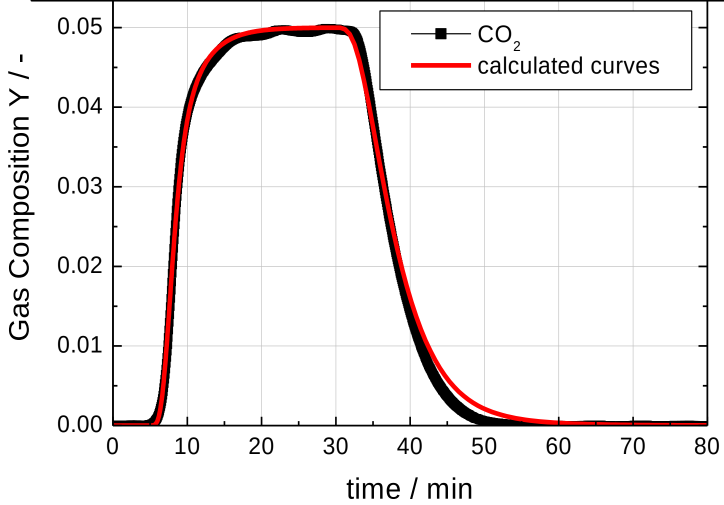
Fitting

Heat Transfer Coeff.

CO_2 /N_2 mixture isotherms on D 55/1.5

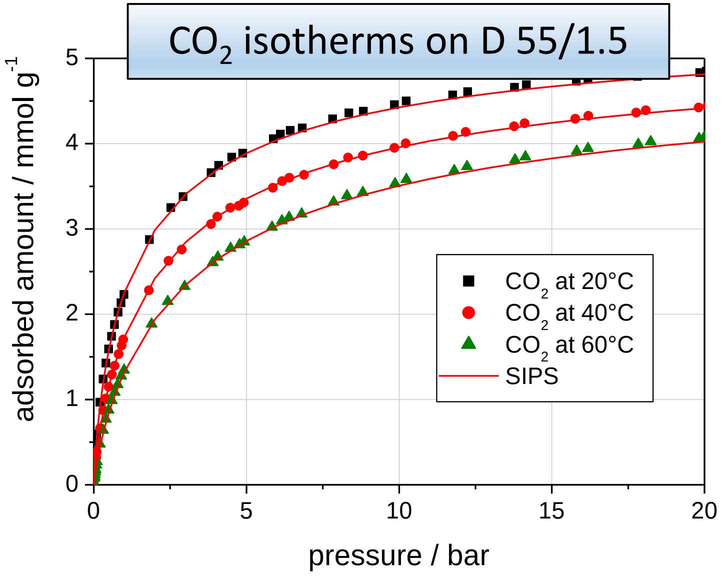


Adsorption and Desorption of CO_2 in N_2

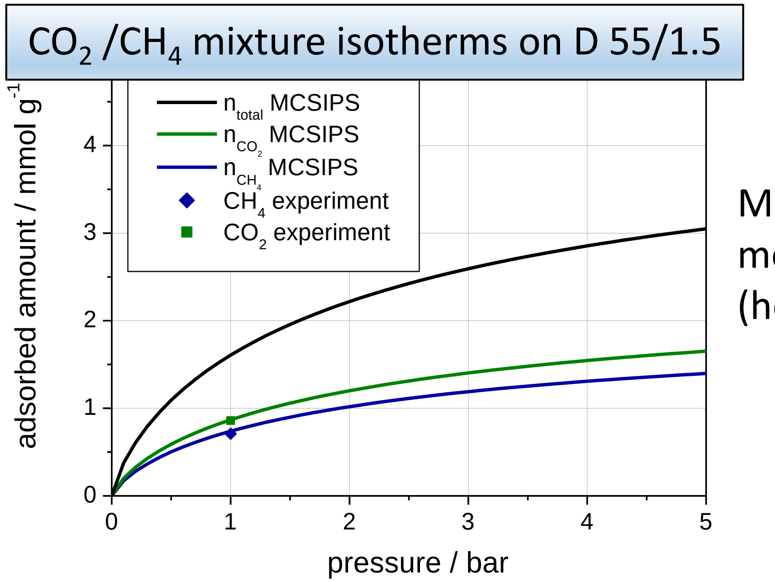


5% CO_2 95% N_2 at 40°C, 5 bar, 2 L/min on D 55/1.5

Kinetics from complex Breakthrough Experiments (two Adsorptives)

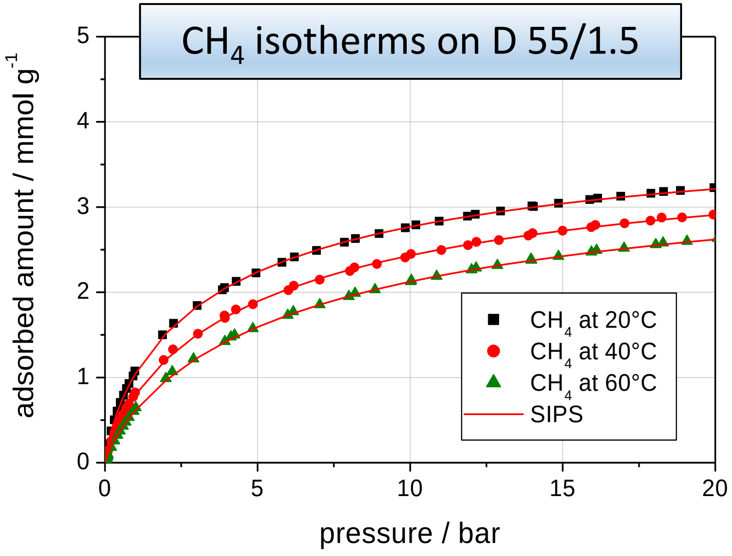


Input pure component Isotherms



Multi component model necessary (here MCSIPS)

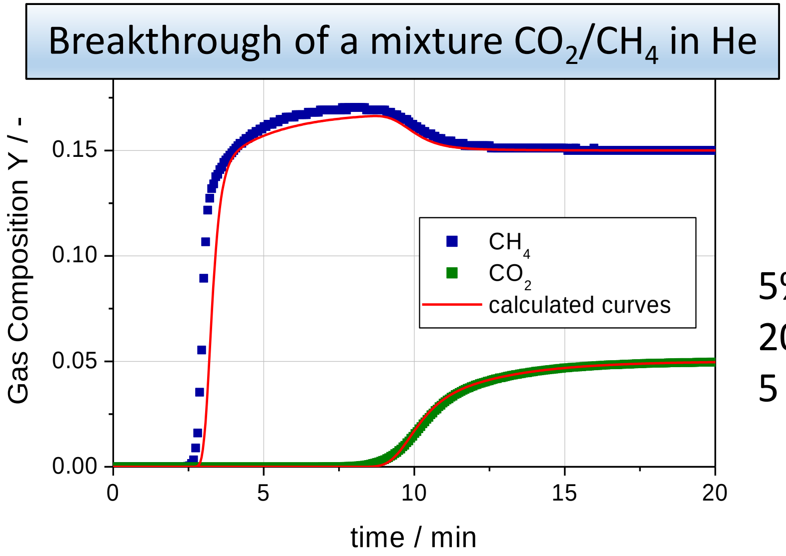
Determination of k_{LDF} for CH_4 and CO_2



Fitting k_{LDF}

Fitting

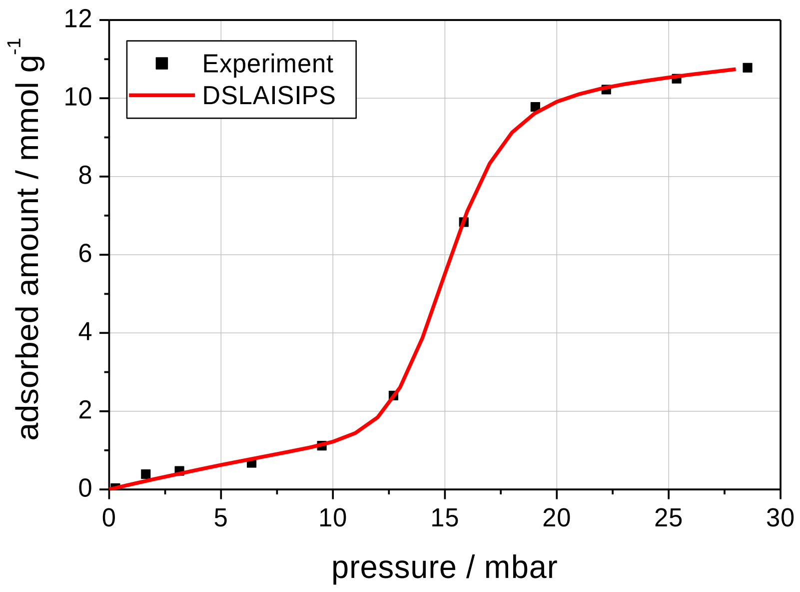
Heat Transfer Coeff.



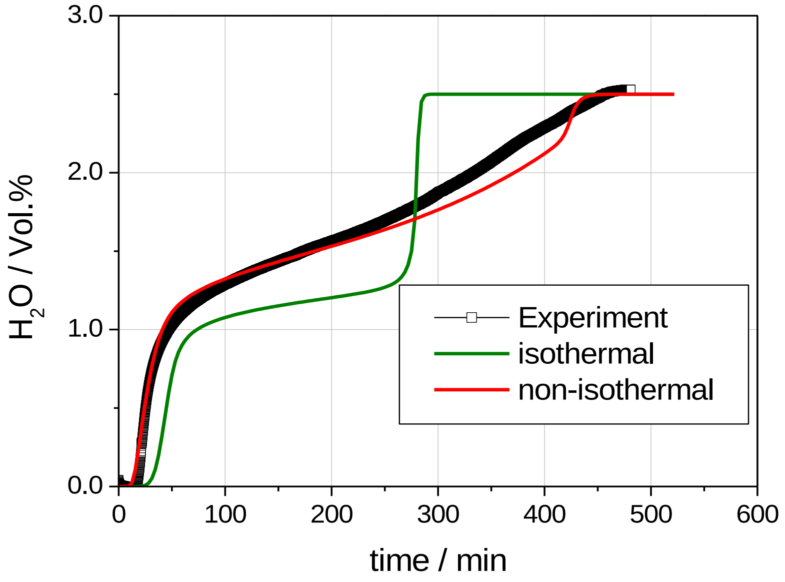
5% CO_2 15% CH_4 in He
20°C, 2500 ml/min,
5 bar on D 55/1.5

Kinetics from Breakthrough Experiments

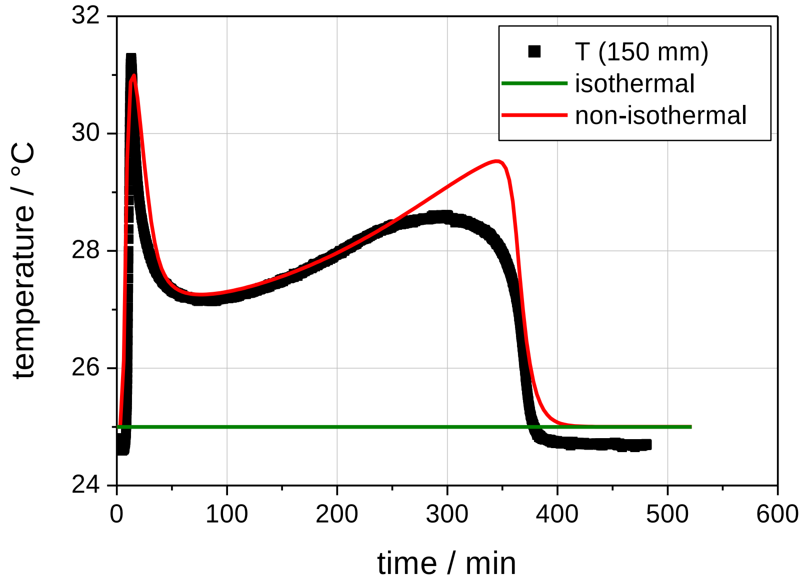
High effort to calculate breakthrough due to shape of isotherm, good isotherm model fit necessary!



H_2O isotherm on D 55/1.5 at 25°C



2.5% H_2O in N_2 at 25°C (RH 80%), 1 bar, 4000 ml min^{-1} on D 55/1.5

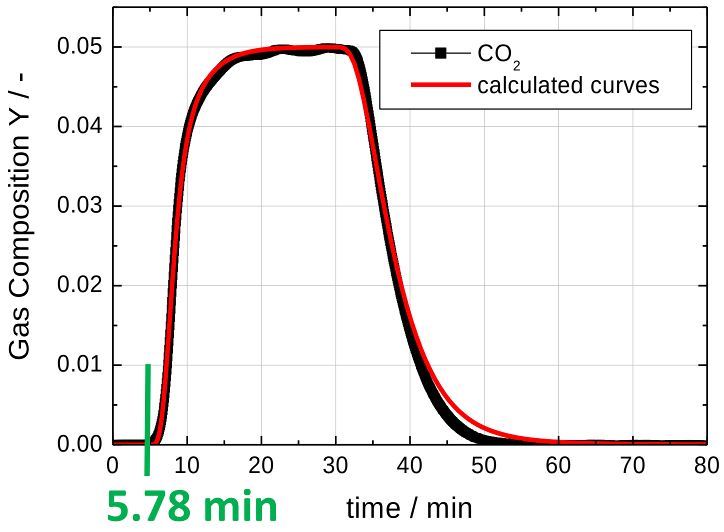


→ k_{LDF} = 1.2 min^{-1}

- Isotherm fit with an empiric dual-site Langmuir-SIPS equation
- Heat of adsorption 60 kJ mol^{-1} assumed
- Heat for condensation 40.8 kJ mol^{-1} (at 100°C)

→ Description of the curve is possible
→ Isothermal calculation failed for this example
→ Stronger deviations for condensation part

Kinetics from Breakthrough Experiments – how to use?



5% CO_2 95% N_2 at 40°C, 5 bar, 2000 ml min^{-1} on D 55/1.5

Known model parameter after fitting

- Isotherms (MCSIPS)
- **Kinetic parameter (k_{LDF})**
- Heat transfer parameter

→ Model can consider slower desorption due to curved isotherm

Parameter from experiment:

- Adsorption time 5.78 min
- Adsorption pressure 5 bar
- Feed flow 2000 ml min^{-1}
- Purge flow 2000 ml min^{-1} pure N_2

General requirements for PSA:

- Purge flow 500 ml min^{-1} pure N_2
- Desorption in counter current flow
- Max. CO_2 content in product 1%

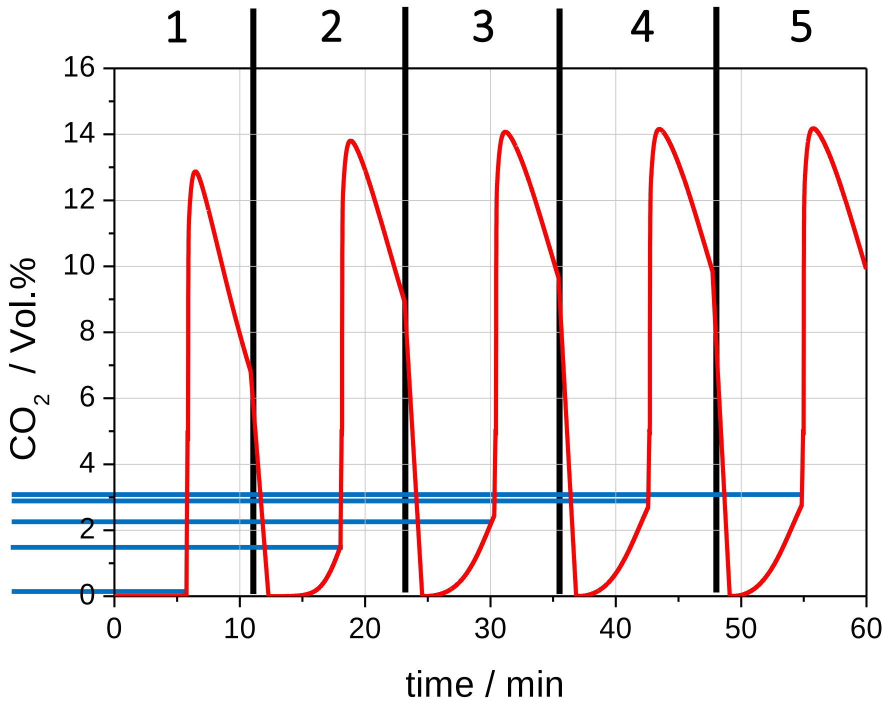
Question concerning:

1) Desorption pressure in Pressure Swing Processes (PSA)?

Kinetics from Breakthrough Experiments – how to use?

Cycle times for modeling:

- Adsorption time 5.78 min
- Desorption time 5.03 min
- Calculating 5 cycles



Cycle times for experiment:

- Adsorption time 5.78 min @ 5 bar
- Blow down time ~ 0.25 min
- Desorption time 4.75 min
- Pressurization to 4.6 bar with N_2
- Pressurization from 4.6 bar to 5 bar with feed
- Measurement of 5 cycles

Calculations with p_{DES}= 1 bar

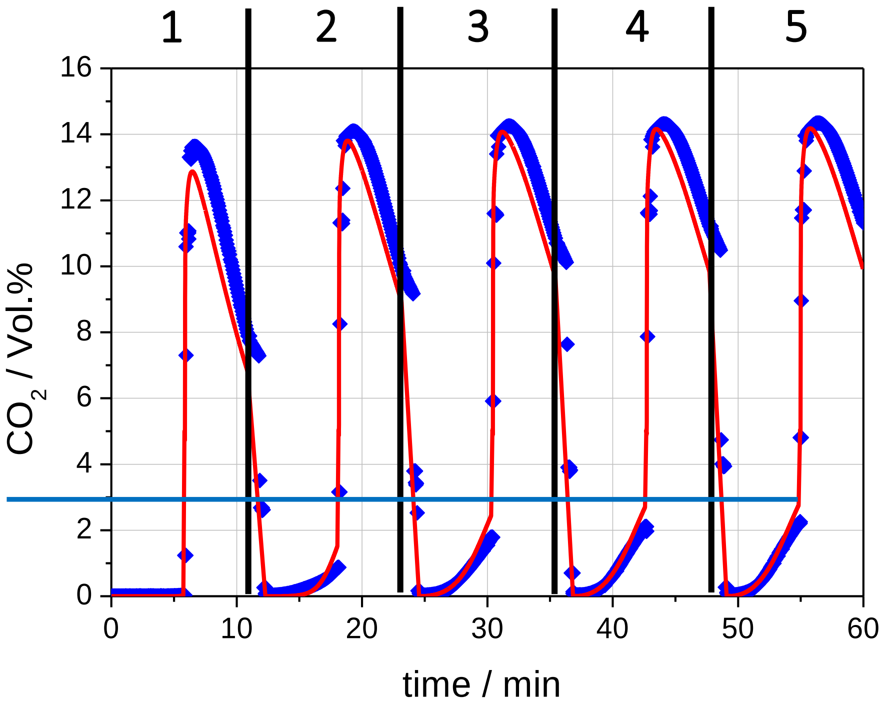
Predictions by modeling:

Regeneration conditions not strong enough
→ CO_2 impurity in effluent flow increases from cycle to cycle to ~ 3 %

Kinetics from Breakthrough Experiments – how to use?

Cycle times for modeling:

- Adsorption time 5.78 min
- Desorption time 5.03 min
- Calculating 5 cycles



Cycle times for experiment:

- Adsorption time 5.78 min @ 5 bar
- Blow down time ~ 0.25 min
- Desorption time 4.75 min
- Pressurization to 4.6 bar with N_2
- Pressurization from 4.6 bar to 5 bar with feed
- Measurement of 5 cycles

Calculations with p_{DES}= 1 bar

Predictions by modeling:

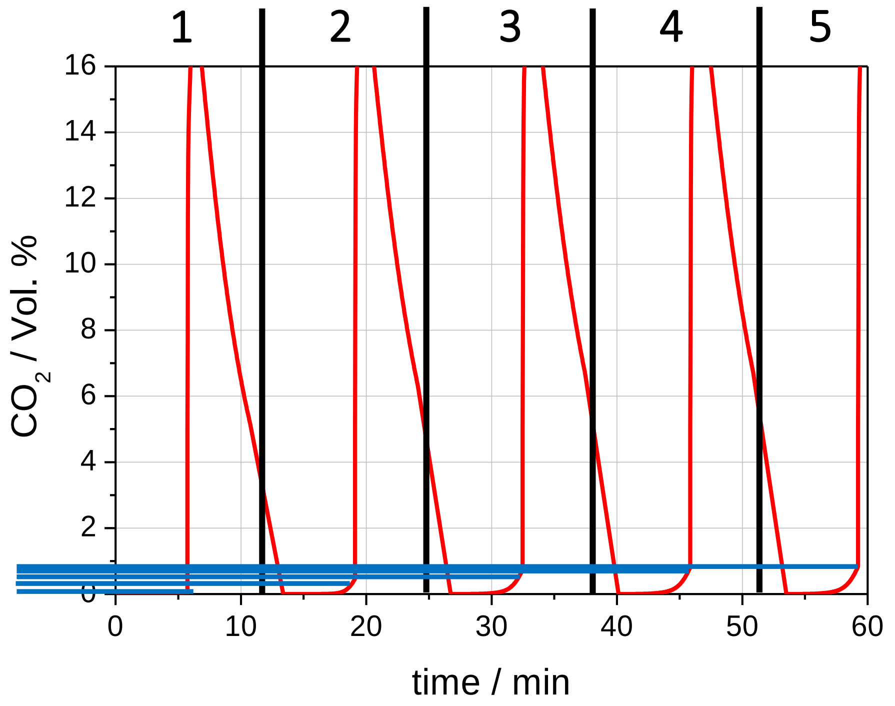
Regeneration conditions not strong enough
→ CO_2 impurity in effluent flow increases from cycle to cycle to ~ 3 %

Predictions were confirmed by experiment

Kinetics from Breakthrough Experiments – how to use?

Cycle times for modeling:

- Adsorption time 5.78 min
- Desorption time 5.03 min
- Calculating 5 cycles



Cycle times for Experiment:

- Adsorption time 5.78 min @ 5 bar
- Blow down time ~ 0.25 min
- Desorption time 4.75 min
- Pressurization to 4.6 bar with N_2
- Pressurization from 4.6 bar to 5 bar with feed
- Measurement of 5 cycles

Calculations with p_{DES}= 0.5 bar

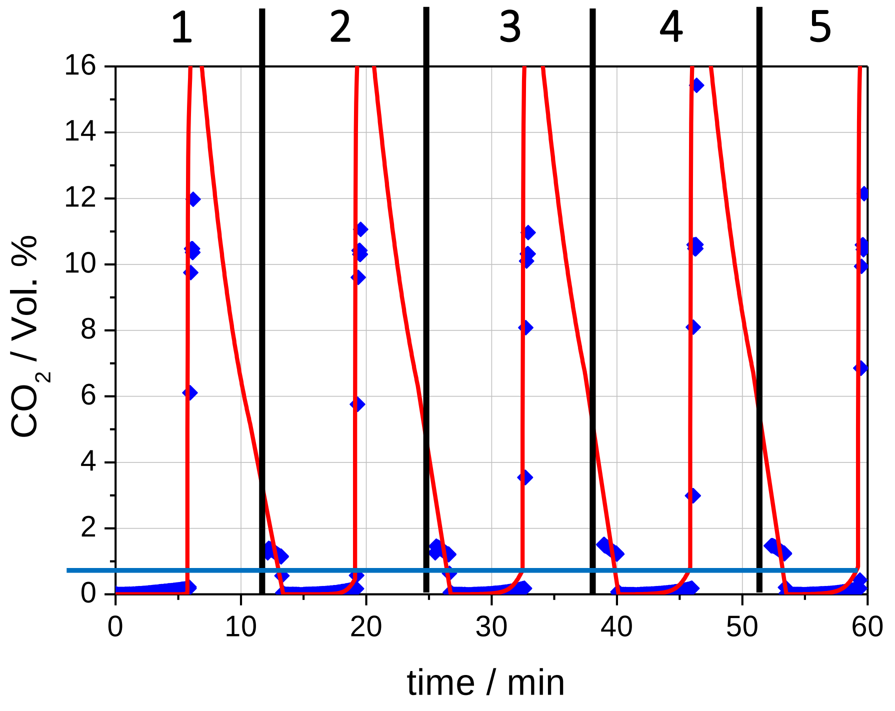
Predictions by modeling:

Regeneration conditions good enough
→ CO_2 impurity in effluent flow increases from cycle to cycle, but still below target (<1%)

Kinetics from Breakthrough Experiments – how to use?

Cycle times for modeling:

- Adsorption time 5.78 min
- Desorption time 5.03 min
- Calculating 5 cycles



Cycle times for experiment:

- Adsorption time 5.78 min @ 5 bar
- Blow down time ~ 0.25 min
- Desorption time 4.75 min
- Pressurization to 4.6 bar with N_2
- Pressurization from 4.6 bar to 5 bar with feed
- Measurement of 5 cycles

Calculations with p_{DES}= 0.5 bar

Predictions by modeling:

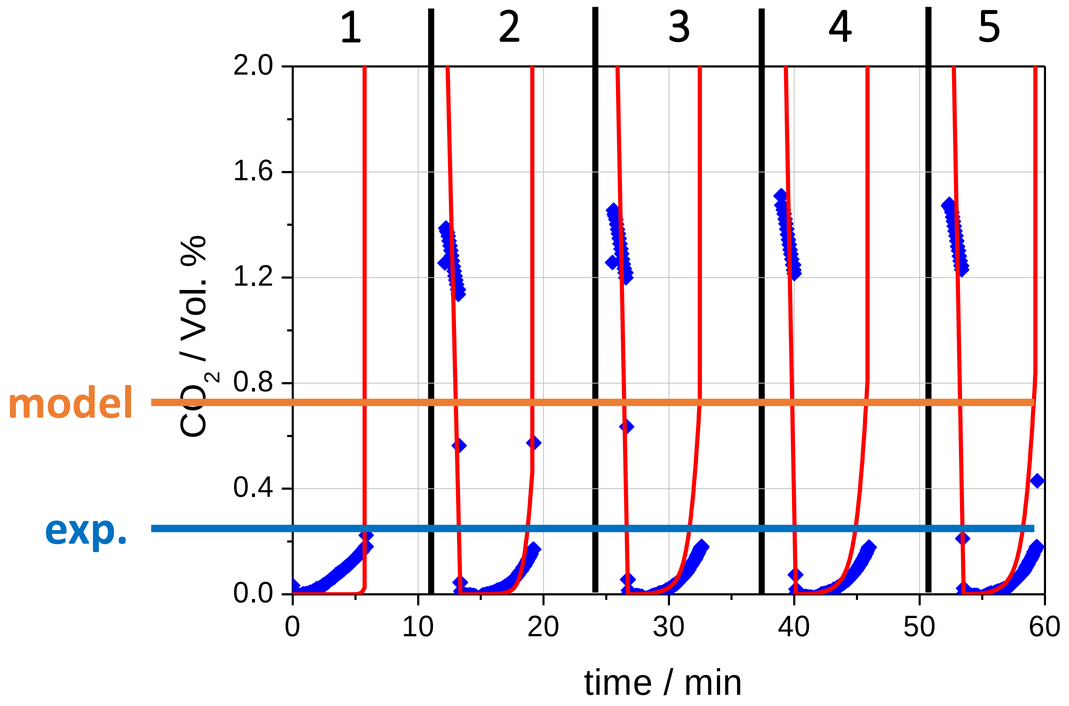
Regeneration conditions good enough
→ CO_2 impurity in effluent flow increases from cycle to cycle, but still below target (<1%)

Predictions were confirmed by experiment

Kinetics from Breakthrough Experiments – how to use?

Cycle times for modeling:

- Adsorption time 5.78 min
- Desorption time 5.03 min
- Calculating 5 cycles



Cycle times for experiment:

- Adsorption time 5.78 min @ 5 bar
- Blow down time ~ 0.25 min
- Desorption time 4.75 min
- Pressurization to 4.6 bar with N_2
- Pressurization from 4.6 bar to 5 bar with feed
- Measurement of 5 cycles

Calculations with p_{DES}= 0.5 bar

Modeling divers from experiment!

- Cycle steps in modeling strong simplified
- Variations experiment from model mainly in desorption part

→ Modeling can help to reduce experimental effort
→ final evaluation only by experiment!

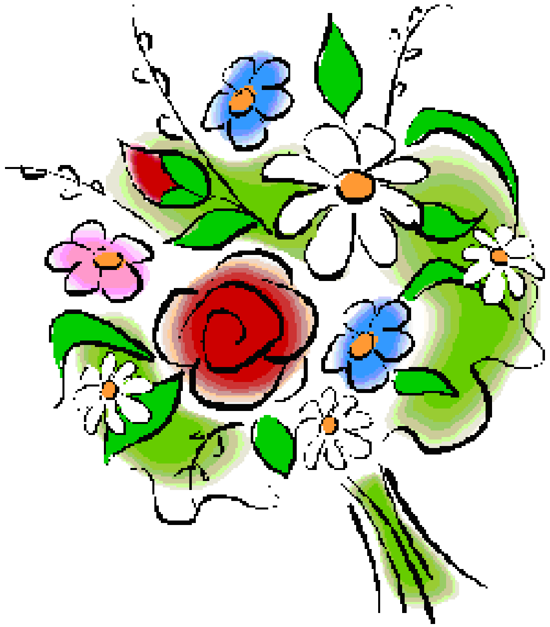
Summary Part II - Kinetics

- **Comparison of breakthrough slope** only qualitative → **can lead to wrong interpretation**
- Strong **nonisothermal effects must be considered** for evaluation of kinetics → influence of dissipation of heat
- **Measurement of desorption** part is **helpful** → influence of isotherm, heat dissipation etc.
- **Model is necessary to get** reliable **transport parameter** → k_{LDF} value
- **k_{LDF} values depend on concentration, total pressure** etc. → **measurements** under **same** conditions **like technical process**

- With well-known model parameter set **predictive calculations possible**
  - Results: technical useable sorption capacity, optimization of regeneration, cycle times etc.

    → **reducing experimental effort in bench scale**

    → **helpful for upscaling**
- But: Validation by some experiments necessary



Thank you for your attention!

Please visit our website for further information

www.dynamicsorption.com

[1] R.T. Yang, *Gas Separation by Adsorption Processes*, Imperial College Press,**1987**
[2] A.L. Myers, J.M. Prausnitz, *AIChe Journal*, **1965**, *11*
[3] T.W. Cochran, R.L. Kabel, R.P. Danner, *AIChe Journal,* 31, **1985**, *12*
[4] A. Möller, R. Eschrich, C. Reichenbach, J. Guderian, M-Lange, J. Möllmer, *Adsorption,* **2017,** *23*(2-3)
[5] M. Thommes, K. Kaneko, A.V. Neimark, J.P. Olivier, F. Rodriguez-Reinoso, J. Roquerol K.S.W. Sing, IUPAC Technical Report, *Pure Appl. Chem.* **2015**; 87(9-10)