Investigation of Mixed Gas Sorption in Lab-Scale – Experiment and Evaluation

Dr. Andreas Möller

Christian Reichenbach, Robert Eschrich

3P INSTRUMENTS GmbH & Co. KG

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Technical Necessity:

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.**

Characterization of Adsorbents

Number of Samples

Application Progress

Synthesis and First Characterization

Chemists

Nova Touch

- BET
- Pore Volume
- Pore Size Distribution

Determination of Thermodynamic Data

Chemists, Physicists

iSorb HP

- Isotherms
- Heat of Adsorption

Basic Process Design, Granulation of Adsorbents

Chemical Engineers

mixSorb L

- Techn. Useable Sorption Capacity
- Gas Mixtures
- Selectvities
- Kinetics for Process Conditions
- Cycle Stability

Detailed Process Design, Application

Engineers

Bench scale, Pilot plants, Industrial Plant

- Process Optimization
- Production

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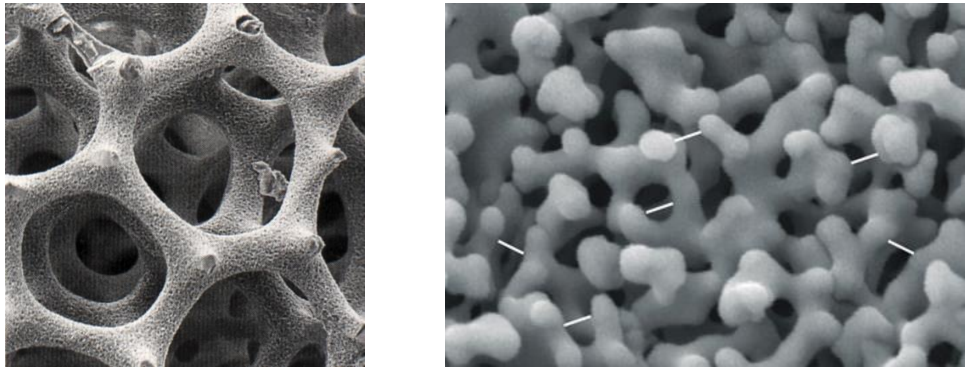
Why are Textural Properties not enough...?

Textural Properties of Adsorbents:

- BET-Surface
- Pore Size Distribution
- Micropore Volume



Textural properties allow only limited qualitative statements regarding:

- **expected sorption capacity (Micropore Volume)**
- **rough assessment of general sorption properties from Pore Size Distributuion**

Textural properties do not allow quantitative statements regarding:

- **sorption affinity**
- **selectivity**
- **no sufficient information of surface chemistry**

Selectivity and Separation factor

Often different definition of selectivity (separation factor)!

Thermodynamic selectivity and limit of selectivity (p→0) α

Difference of shape of isotherms and of loadings important [1]

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

Y… mole ratio in gas phase

X… mole ratio in adsorbed phase

H… Henry constants

Sorbent selection parameter of Rege and Yang [2]

$$S = \frac{\Delta q_{CO_2}}{\Delta q_{CH_4}} \alpha_{CO_2,CH_4}$$

Δq… difference in loading between adsorption and desorption

Kinetic separation faktor β

Difference of sorption rates important [3]

$$\beta_{CO_2,CH_4} = \frac{H_{CO_2}}{H_{CH_4}} \cdot \sqrt{\frac{D_{CO_2}}{D_{CH_4}}}$$

H… Henry constants

D… Diffusion coefficients

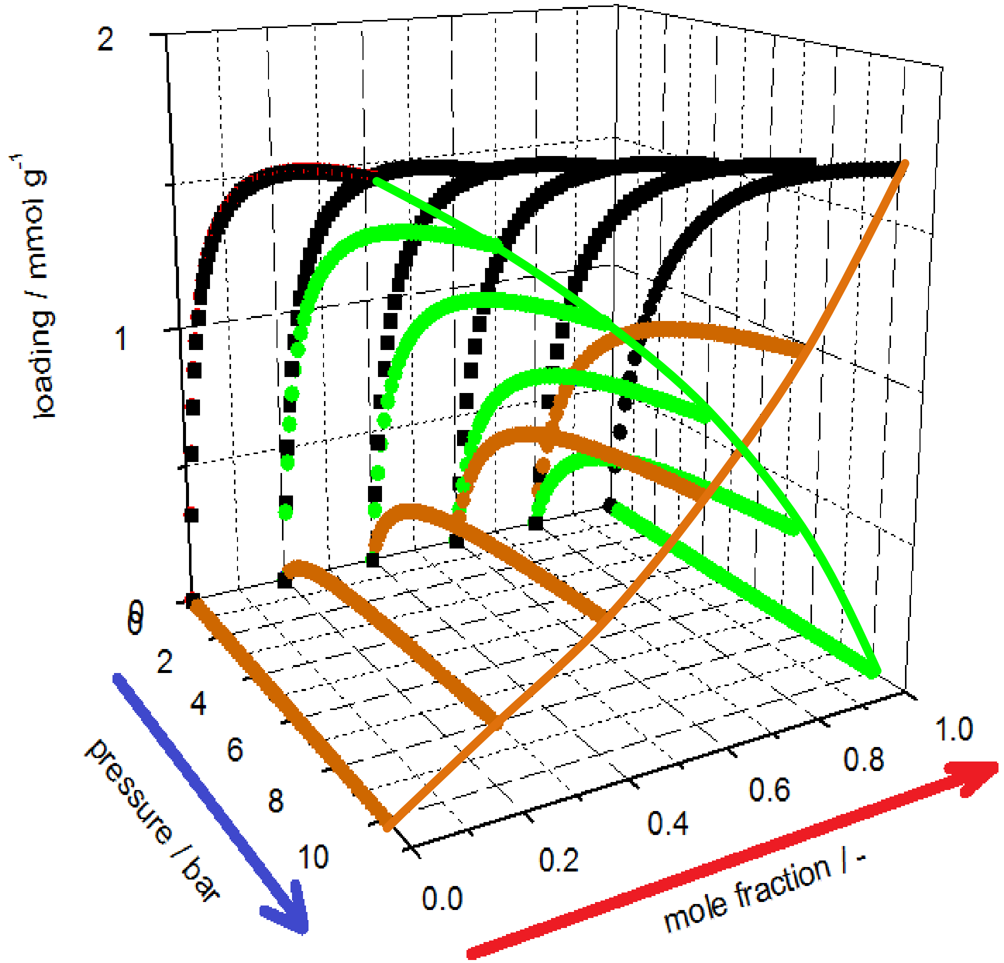
[1] R.T. Yang, *Gas separation by adsorption processes*, Imperial College Press, London, **1987**

[2] S.U. Rege, R.T. Yang, *Sep. Sci. & Technol.,* **2011**, *36*, 3355-3365

[3] D.M. Ruthven, S. Farooq, K.S. Knaebel, *Pressure Swing Adsorption*, Wiley-Verlag, New York **1994**.

Mixture Equilibria - Basics

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

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

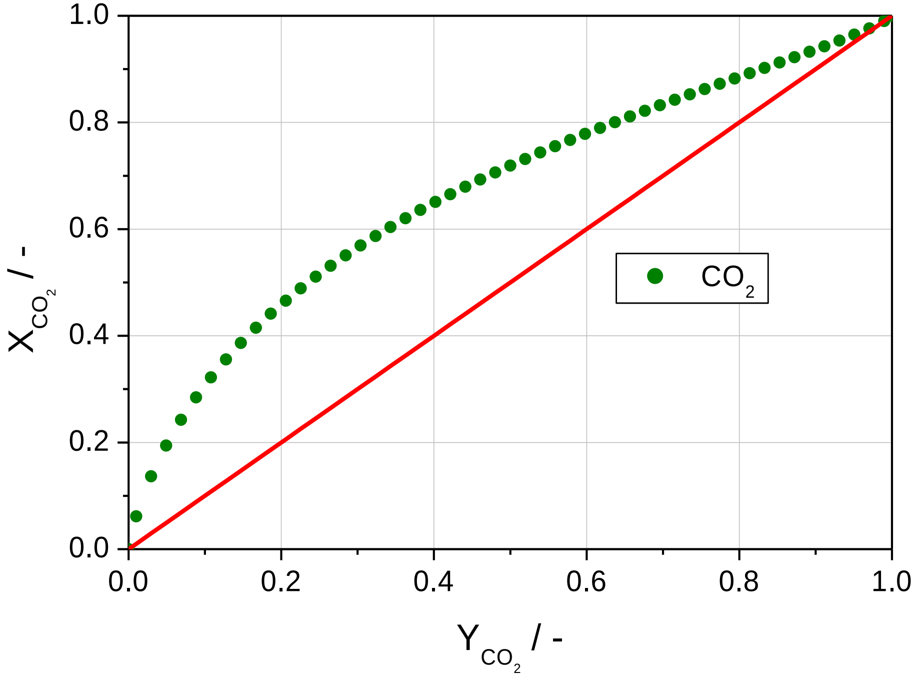
THE BLUE LINE – Case B

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

Mixture Equilibria - Basics

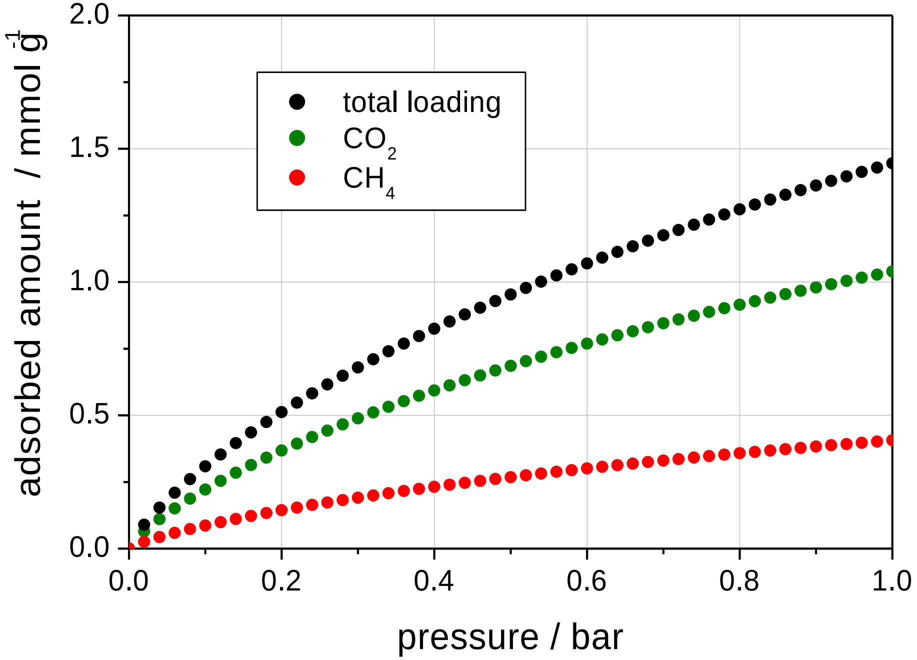
Typical presentation of sorption capacities for binary mixtures

Case A – variable gas composition



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

Case B – variable pressure



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

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

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

Mixture Equilibria - Basics

Typical presentation of sorption capacities for binary mixtures

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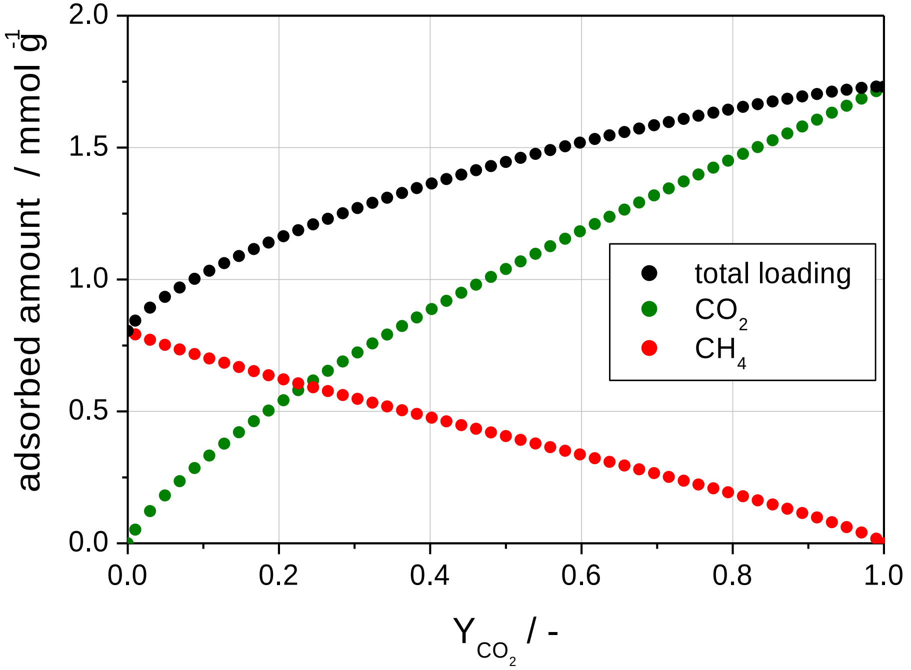

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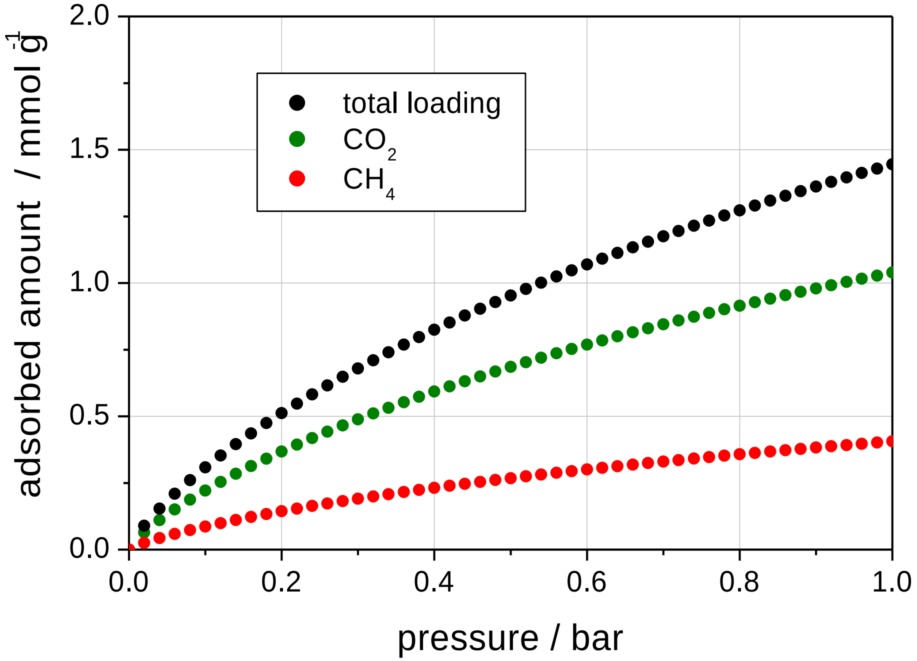
Case B – variable pressure



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

➡ **N-Y-Plot with statement to the partial loading at constant pressure**

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

Mixture Equilibria - Basics

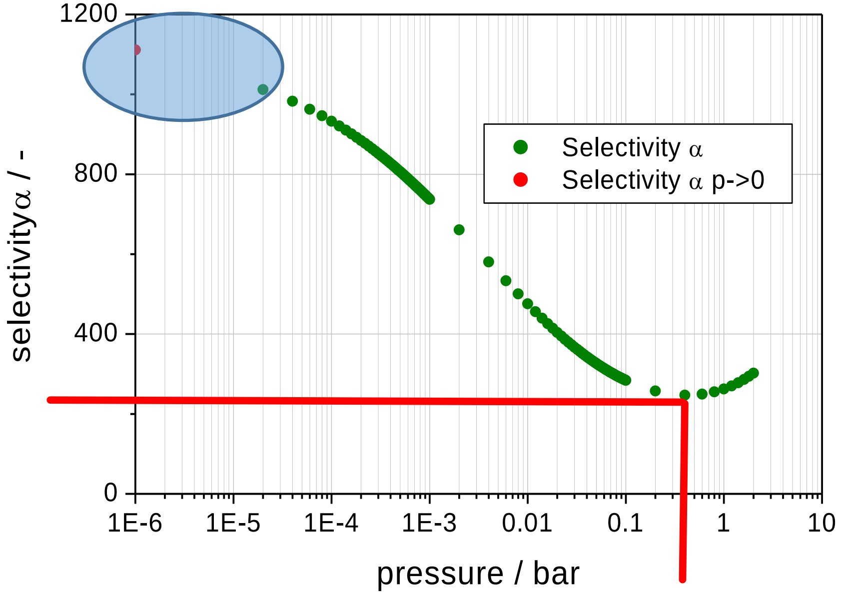
Dynamic Sorption

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** (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**

Mixture Equilibria - Basics

Models for mixture data

Requirements:

- Knowledge of pure component isotherms

Extended langmuir-like equations [1]

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

IAS-Theory [2]

- IAST with Langmuir
- IAST with Toth
- IAST with DSLAI

VS-Model [3]

- VS-Modell with Wilson

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

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

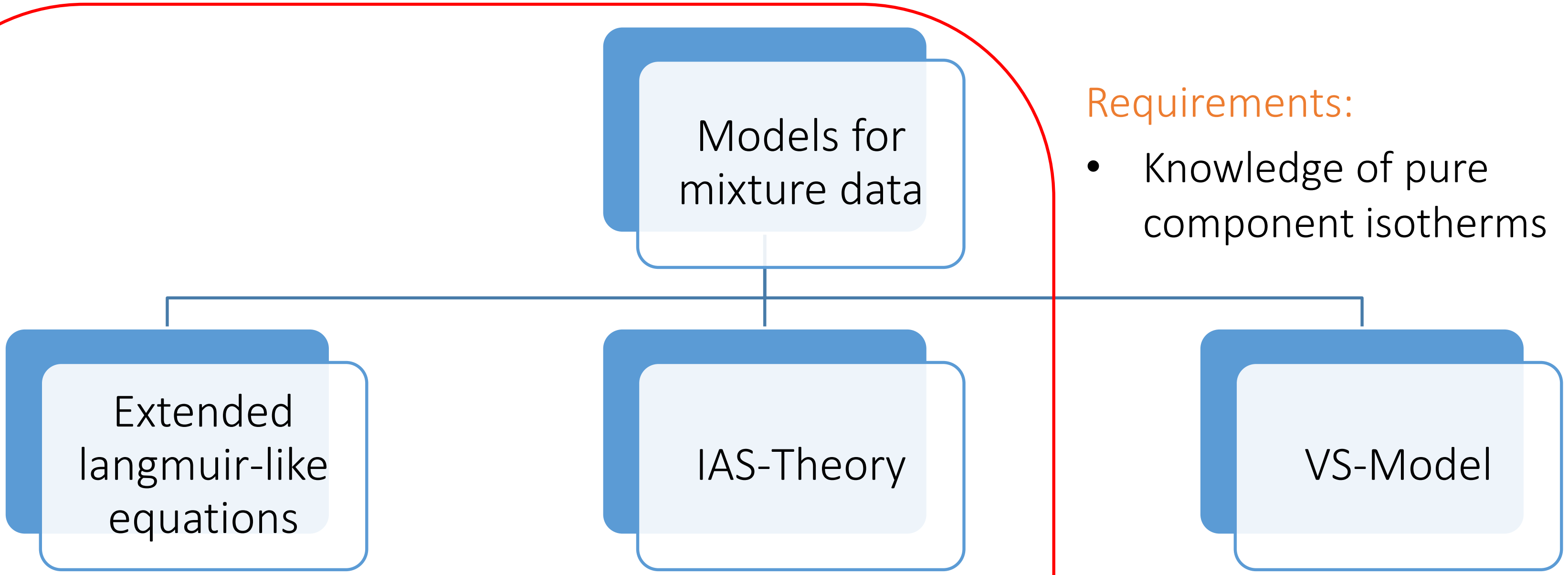
$$n = Isotherm(p_{io})$$

[1] R.T. Yang, *Gas Separation by Adsorption Processes*, Imperial College Press,**1987**

[2] A.L. Myers, J.M. Prausnitz, *AIChe Journal,* **1965**, *11*, 129

[3] T.W. Cochran, R.L. Kabel, R.P. Danner, *AIChe Journal,* 31, **1985**, *12*, 2075

Mixture Equilibria - Models



Models for mixture data

Extended langmuir-like equations

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MCSIPS

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

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

predictive calculations with **3P-Sim** possible

General Solution Algorithm for IAST

Nonlinear Equation System can be solved by Newton Algorithm

Formulation of equation system

$$\sum X_i = 1$$

$$\sum Y_i = 1$$

$$Y_i \cdot p = X_i \cdot p_i^0$$

$$\int_0^{p_i^0} \frac{n_i(p)}{p} dp - \frac{\pi A}{RT} = 0$$

Build up of Jacobian matrix *J*

Define starting Values (as vector)

Calculate of negative Functions (as vector)

$$\begin{pmatrix} \frac{\partial f_1}{\partial p_1^0} & \frac{\partial f_1}{\partial p_2^0} & . & \frac{\partial f_1}{\partial \pi} \\ . & . & . & . \\ . & . & . & . \\ \frac{\partial f_N}{\partial p_1^0} & . & . & \frac{\partial f_N}{\partial \pi} \end{pmatrix} \bullet \begin{pmatrix} p_1^0 \\ . \\ p_i^0 \\ \pi \end{pmatrix} = \begin{pmatrix} -FKT_1(p_i^0, \pi) \\ . \\ . \\ -FKT_i(p_i^0, \pi) \end{pmatrix}$$

Solving of lin. Equation system by **Gaussian elimination**

$$J(p_i^0, \pi) \cdot \Delta(p_i^0, \pi) = -FKTN(p_i^0, \pi)$$

Calculate a new vector

$$p_{i,N+1}^0, \pi_{N+1} = p_{i,N}^0, \pi_N + \Delta(p_i^0, \pi)$$

The whole procedure will be repeated till $\left|\Delta(p_{i,N}^0, \pi_N)\right| < \varepsilon$

Most Important Problem:

Finding of suitable starting values for convergence!

Hint:

Testing the solution by inserting into equation system

General Solution Algorithm for IAST

Example with Langmuir (3 Components)

Formulation of equation system and elimination of X_i

$$\frac{Y_1 \cdot p}{p_1^0} + \frac{Y_2 \cdot p}{p_2^0} + \frac{Y_3 \cdot p}{p_3^0} - 1 = 0$$

$$\int \frac{n_{m1} \cdot b_1}{1 + b_1 \cdot p_1^0} - \Pi = 0$$

$$\int \frac{n_{m2} \cdot b_2}{1 + b_2 \cdot p_2^0} - \Pi = 0$$

$$\int \frac{n_{m3} \cdot b_3}{1 + b_3 \cdot p_3^0} - \Pi = 0$$

Build up of Jacobian matrix *J*

Define starting Values (as vector)

Calculate of negative Functions (as vector)

$$\begin{pmatrix} \frac{Y_1 \cdot p}{\left(p_1^0\right)^2} & \frac{Y_2 \cdot p}{\left(p_2^0\right)^2} & \frac{Y_3 \cdot p}{\left(p_3^0\right)^2} & 0 \\ \frac{n_{m1} \cdot b_1}{1 + b_1 \cdot p_1^0} & 0 & 0 & -1 \\ 0 & \frac{n_{m2} \cdot b_2}{1 + b_2 \cdot p_2^0} & 0 & -1 \\ 0 & 0 & \frac{n_{m3} \cdot b_3}{1 + b_3 \cdot p_3^0} & -1 \end{pmatrix} \bullet \begin{pmatrix} p_1^0 \\ p_2^0 \\ p_3^0 \\ \pi \end{pmatrix} = -1 \cdot \begin{pmatrix} \frac{Y_1 \cdot p}{p_1^0} + \frac{Y_1 \cdot p}{p_1^0} + \frac{Y_1 \cdot p}{p_1^0} - 1 \\ n_{m1} \cdot \ln\left(1 + b_1 \cdot p_1^0\right) - \Pi \\ n_{m2} \cdot \ln\left(1 + b_2 \cdot p_2^0\right) - \Pi \\ n_{m3} \cdot \ln\left(1 + b_3 \cdot p_3^0\right) - \Pi \end{pmatrix}$$

Solving of lin. Equation system by **Gaussian elimination**

$$J\left(p_i^0, \pi\right) \cdot \Delta\left(p_i^0, \pi\right) = -FKTN\left(p_i^0, \pi\right)$$

$$p_{i,N+1}^0, \pi_{N+1} = p_{i,N}^0, \pi_N + \Delta\left(p_i^0, \pi\right)$$

The whole procedure will be repeated till $\left|\Delta\left(p_{i,N}^0, \pi_N\right)\right| < \varepsilon$

Hint:

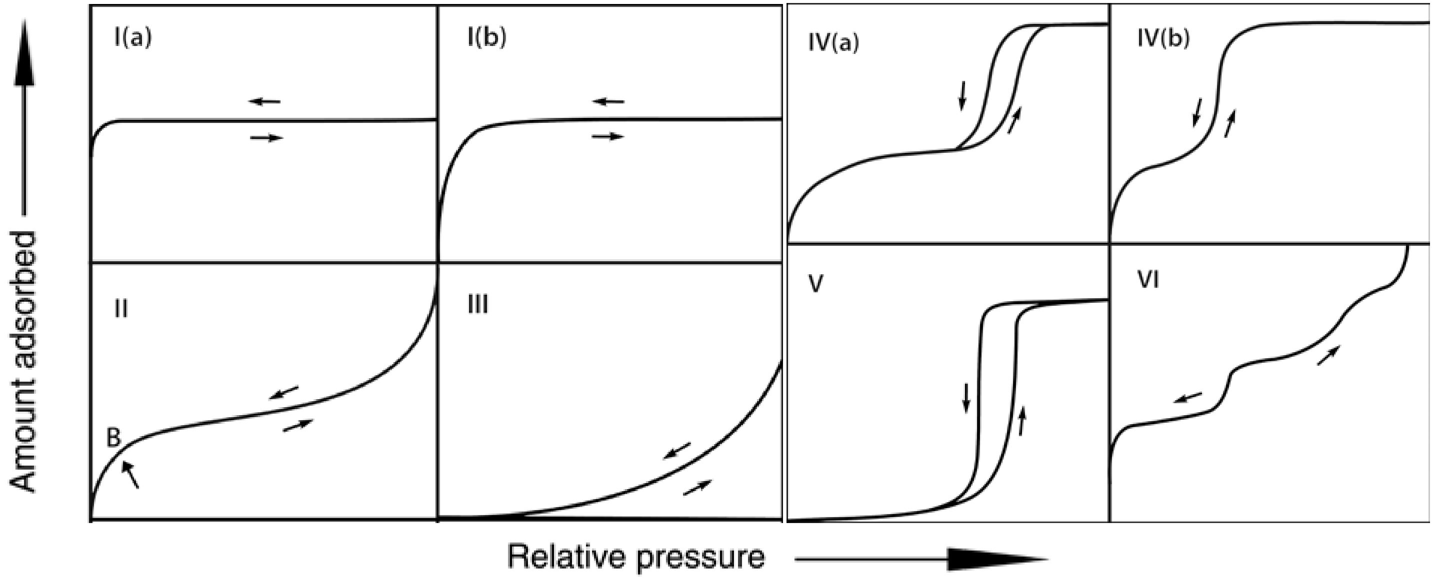
In case of Langmuir isotherm an analytical solution exists:

$$p \cdot \left(\frac{Y_1}{\exp\left(\frac{\Pi}{n_{m1}}\right) - 1} + \frac{Y_2}{\exp\left(\frac{\Pi}{n_{m2}}\right) - 1} + \frac{Y_3}{\exp\left(\frac{\Pi}{n_{m3}}\right) - 1} \right) - 1 = 0$$

Mixture Equilibria - Calculations

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

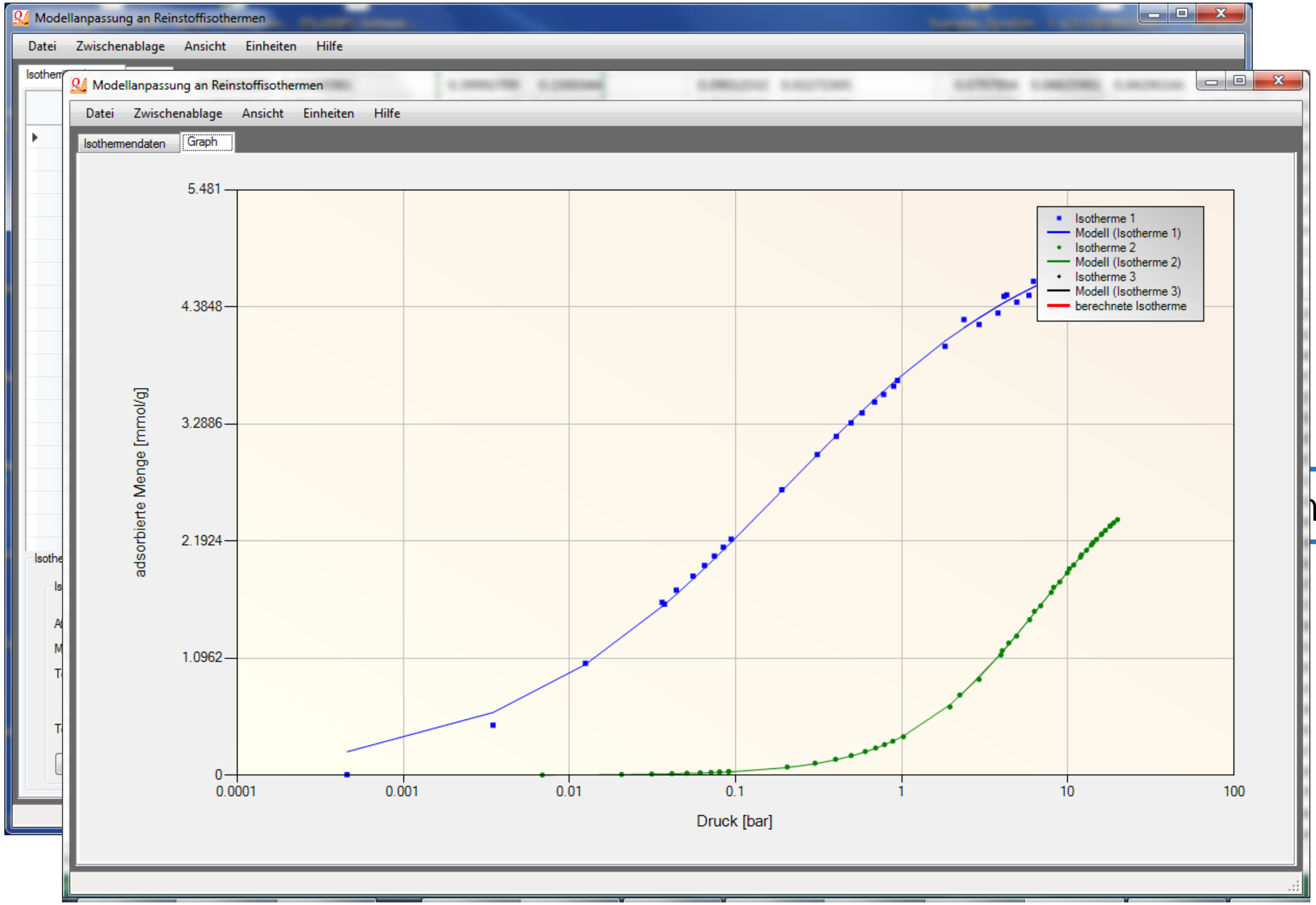
Typ II: (Freundlich)

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

IUPAC Technical Report, Pure Appl. Chem. 2015; 87(9-10), 1051-1069

Mixture Equilibria - Calculations

Calculations of mixture data with **3P-Sim** – fitting of pure components

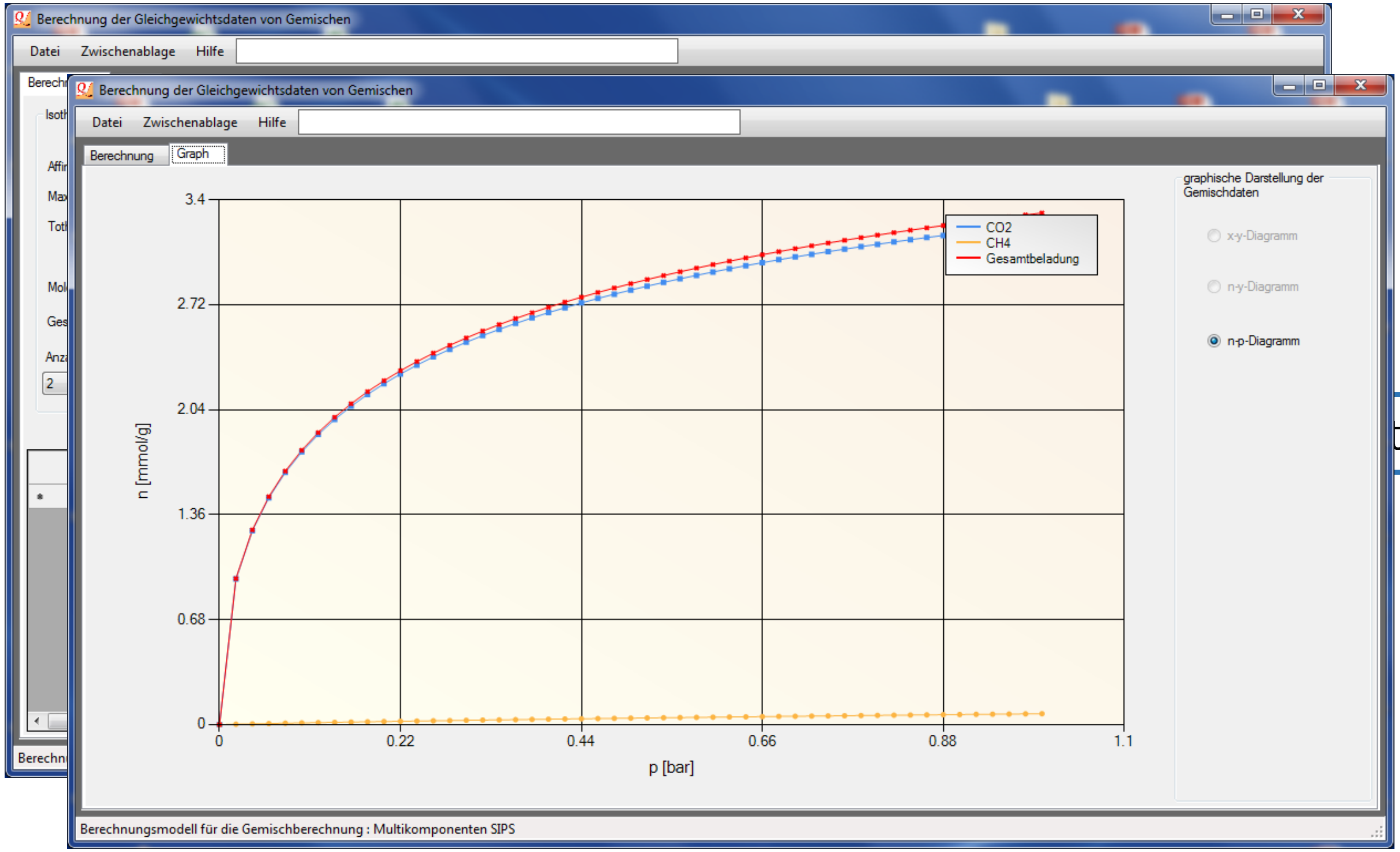


eter

Example: CO_2, CH_4 on NaMSX at 40°C

Mixture Equilibria - Calculations

Calculations of mixture data with **3P-Sim** – calculation of mixture data



Berechnungsmodell für die Gemischberechnung : Multikomponenten SIPS

t isotherms

➡ **The selected mixture model must include the pure component isotherm model!**

i.e.: with SIPS only the Multicomponent-SIPS approach is available

Static versus Dynamic Methods

Static-volumetric Method

- Sorption in closed chamber
- Measurement of pressure drop
- Pure component isotherms, mixed gas sorption hard to realize
  - Standard characterization (BET, Pore volume, pure component isotherms)

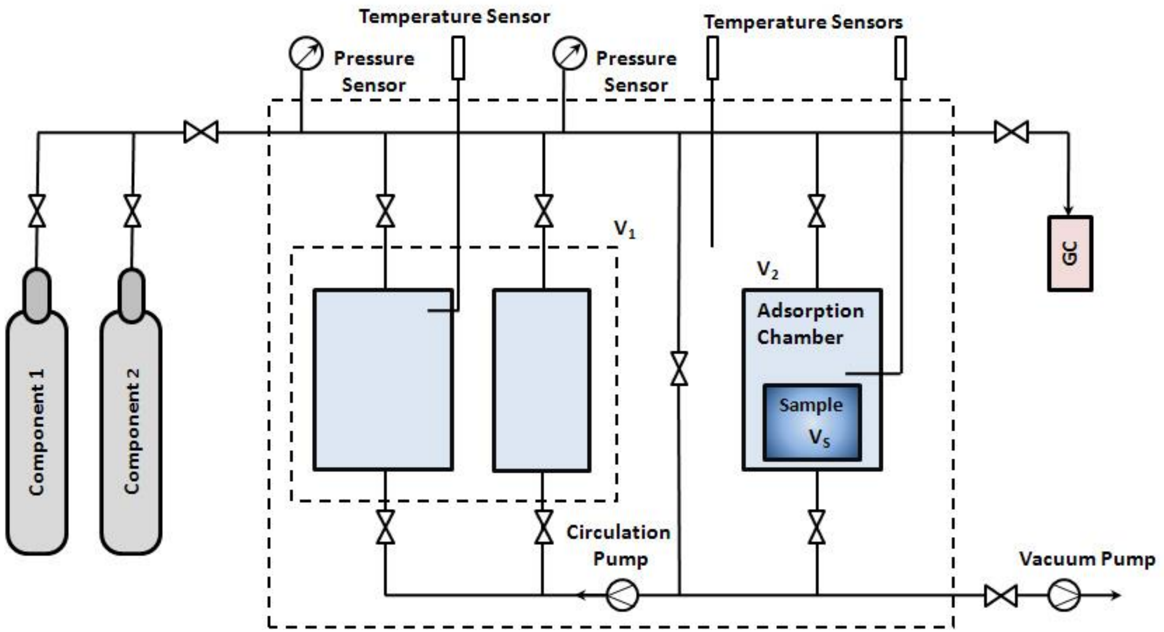
iSorb HP 1

Dynamic Method

- Sorption in an open system at constant pressure
- Time resolved measurement of effluent gas composition
- Mainly for mixed gas sorption, pure component data only with some approaches possible
- Technical processes in „Labscale“
  - Investigations to technical relevant parameters (**selectivity**, sorption kinetic, regenerability, cycle stability …)

mixSorb L

Measurement Techniques – Static Volumetry



R.Bazan et al., *Adsorption,* **2011,** *17*(2), 371-383

- Dosing and **mixing of a predefined gas mixture** in V1 by circulation pump
- Switch to **adsorption chamber V2 and continuous mixing** by circulation pump
- Recording of pressure drop and **analysis of gas phase** after achievement of equilibrium
- Calculation of partial loading based on **mass balance**

→ Precalculations necessary for a desired equilibrium point

Measurement Techniques – Headspace

Headspace Method (HS):

- **Special case** of a static-volumetric setup
- **Higher sample throughput** as classical volumetry
- Primarily for vapor mixtures suitable

Headspace GC at INC e.V.

Principle:

- Regeneration under N_2 at 150 °C (AC)
- Sometimes preloading with component 1 (i.e. H_2O)
- Loading of HS-Vial with sample and **VOC (with µl-Syringe)**
- **Equilibration for several days** in tempered bath
- **Analysis of gas phase** via GC and performing of a mass balance

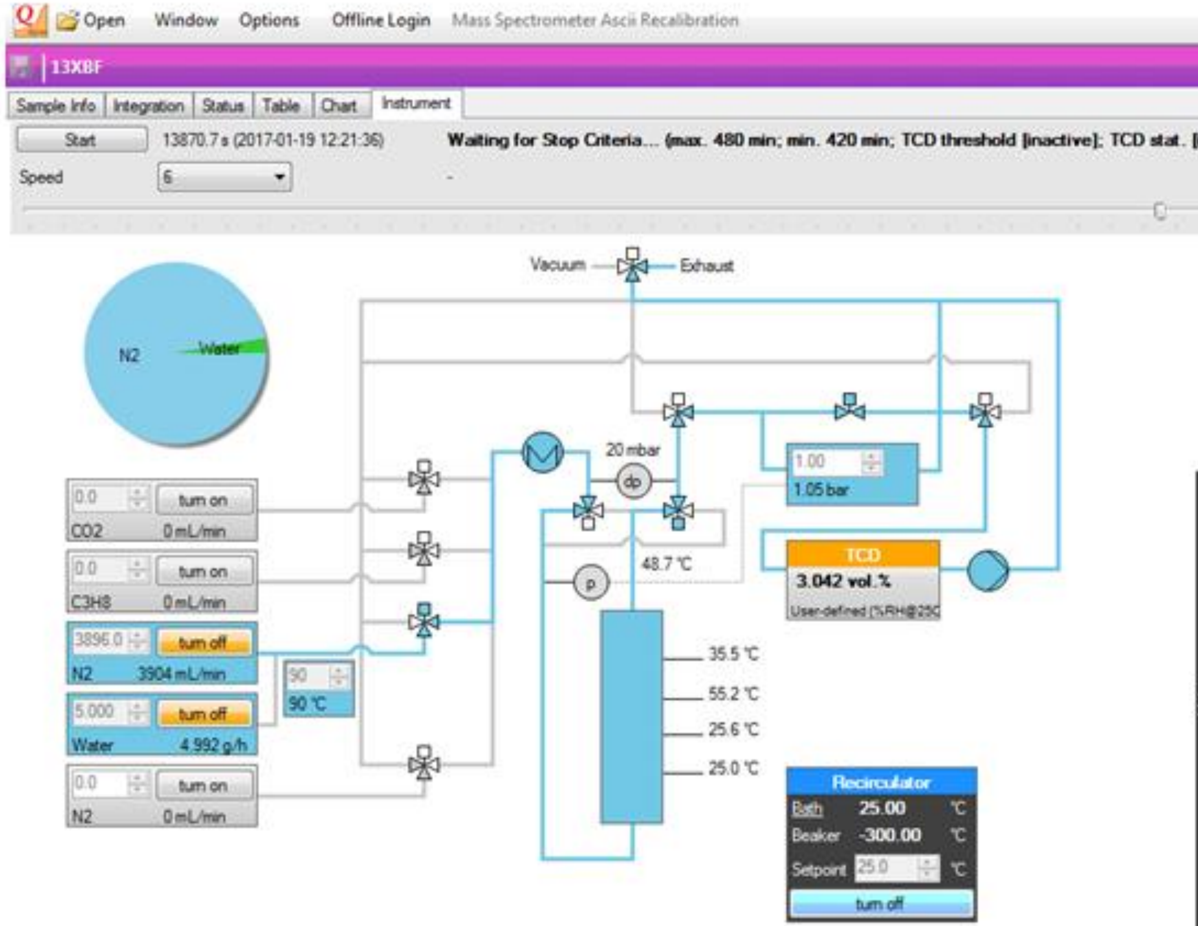
Vials

→ Precalculations necessary for a desired equilibrium point

M.J.G.Linders et al., *AIChE Journal,* **2001,** *47*(8), 1885-1892

Measurement Techniques – Dynamic Setup

Flow plot of a setup for the dynamic method



13870.7 s (2017-01-19 12:21:36)

Waiting for Stop Criteria... (max. 480 min; min. 420 min; TCD threshold [inactive]; TCD stat. [inactive]; Temp. stat. [10 min, <0.1 K]; Pres

Speed 6

0.0 CO2 0 mL/min

0.0 C3H8 0 mL/min

3896.0 N2 3904 mL/min

5.000 Water 4.992 g/h

0.0 N2 0 mL/min

90 90 °C

48.7 °C

35.5 °C

55.2 °C

25.6 °C

25.0 °C

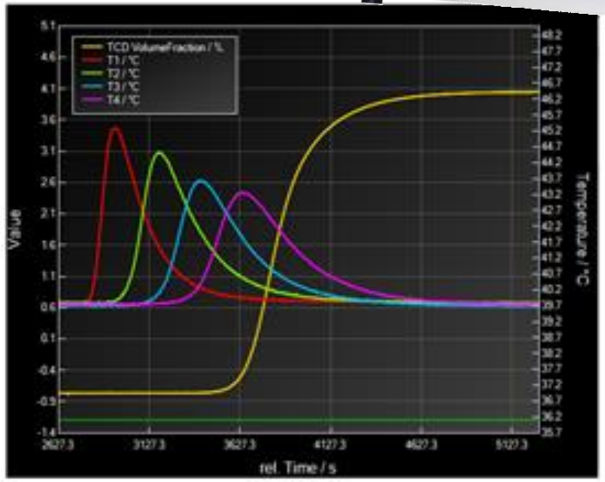
1.00 1.05 bar

TCD 3.042 vol.% User-defined (%RH@25C

Bath 25.00 °C

Beaker -300.00 °C

Setpoint 25.0 °C



- ➢ Flow through the regenerated sample with a predefined gas mixture
- ➢ Measurement of data at **a specified pressure and gas composition** → Advantage over static volumetry, no precalculations necessary

A.Möller et al., *Adsorption,* **2016,** *23*(2-3), 197-209

Measurement Techniques – Overview

Static-Volumetric	Headspace Method	Dynamic Method
➢ **Closed Chamber**	➢ **Closed Chamber**	➢ **Open System**
➢ no carrier gas necessary	➢ no carrier gas necessary	➢ carrier gas necessary, depending on the routine
➢ Suitable for gas mixtures and vapors	➢ Mainly for vapors	➢ Suitable for gas mixtures and vapors
➢ Experimentally complex	➢ **Precalculations necessary**	➢ **No precalculations** necessary
➢ **Precalculations necessary**	➢ **Sequenced experiments hard** to perform	➢ **Sequenced experiments easy** to perform
➢ **Sequenced experiments hard** to perform		➢ **Experiments along the „Lines“ possible**

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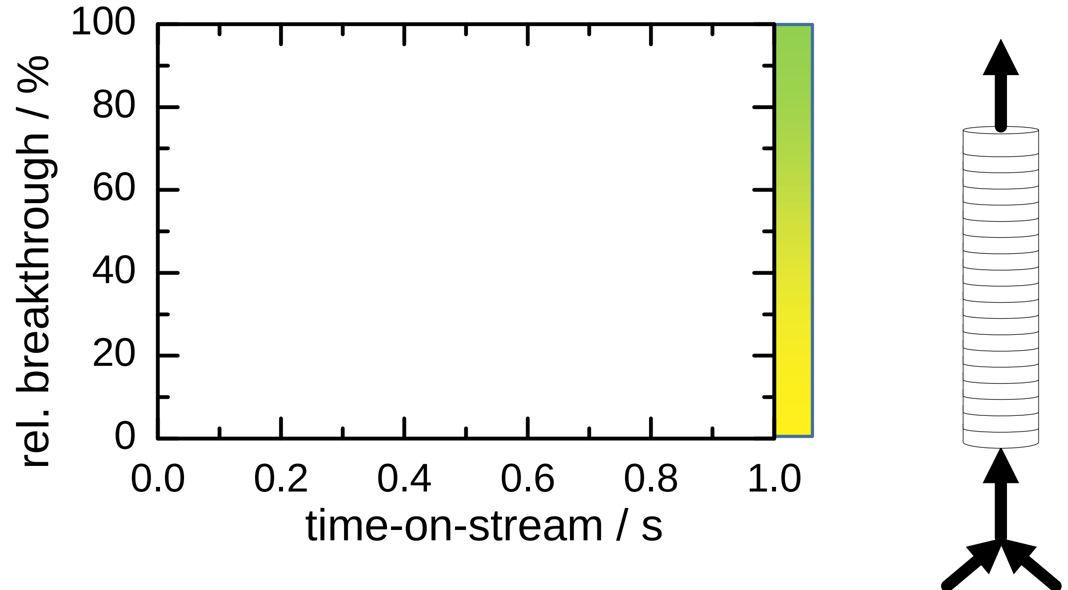
Measurement Techniques – Dynamic Method

Balancing of breakthrough experiments



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

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

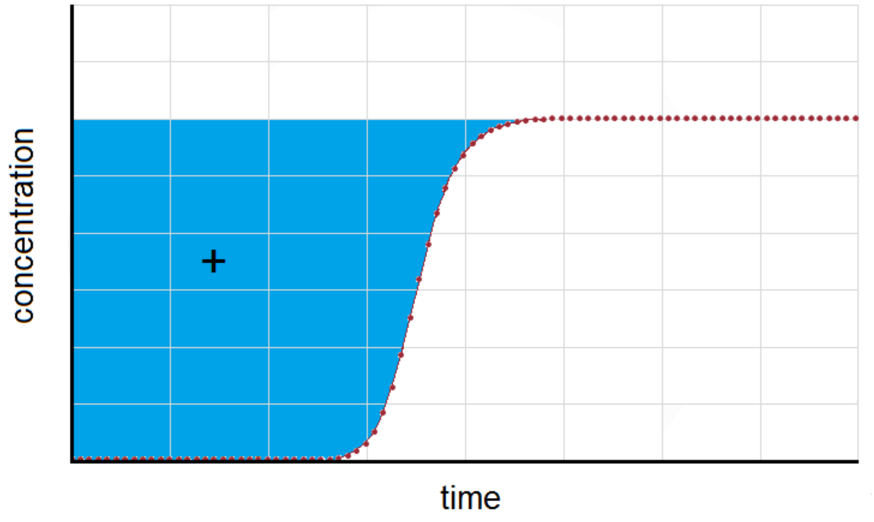
- Widely used approach and simplification for high diluted systems:

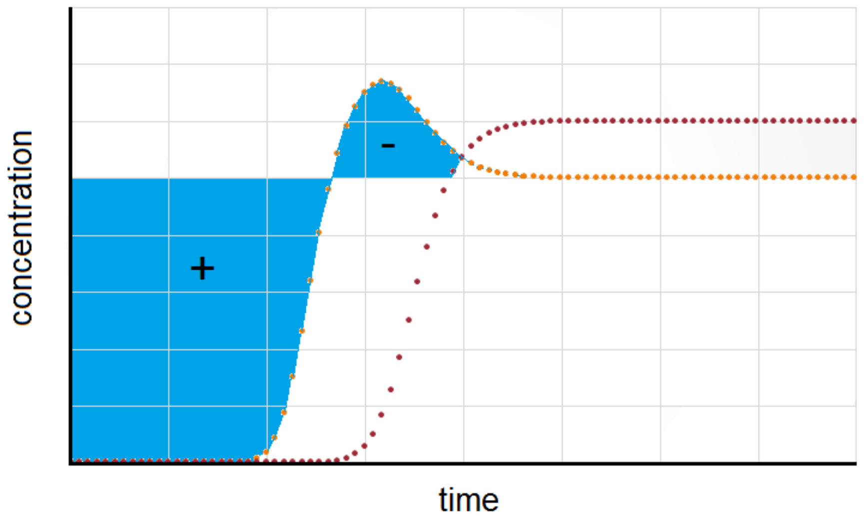
$$\dot{V}_{Out}(t) = \dot{V}_{In}(t) = const.$$

➡ **Small changes in concentration minimize this error**

➡ **High diluted systems easier to evaluate**

Measurement Techniques – Dynamic Method





- **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)

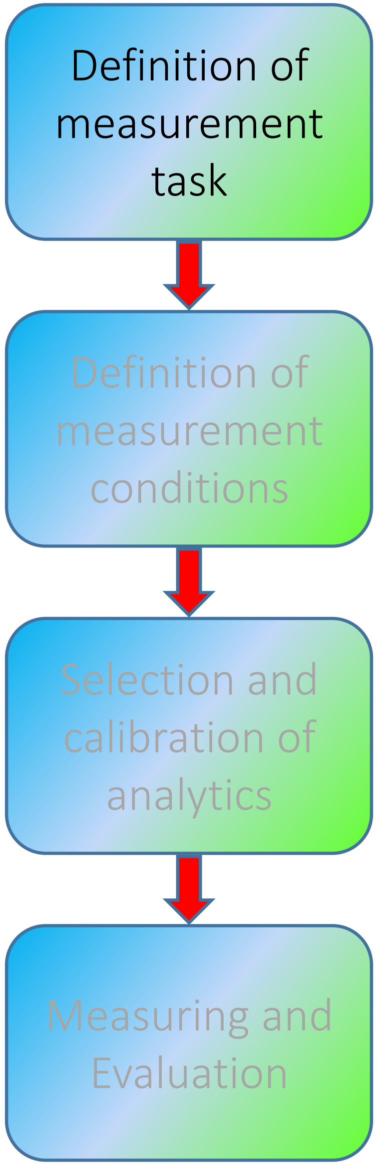
  → Preloading of sample with pure N_2

  → Partial loading for CO_2 and CH_4

  → Incomplete ternary mixture data

Planning of a Mixture Measurement

- **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)
  - → Check if any approach is valid, i.e. constant gas velocity …(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



Definition of measurement task

Definition of measurement conditions

Selection and calibration of analytics

Measuring and Evaluation

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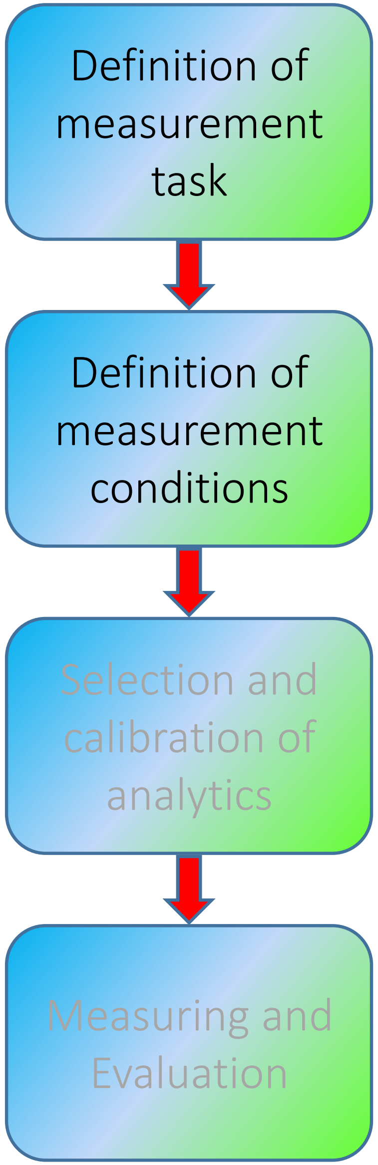

Definition of measurement task

Definition of measurement conditions

Selection and calibration of analytics

Measuring and Evaluation

Planning of a Mixture Measurement

- **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)
  - → Check if any approach is valid, i.e. constant gas velocity …(always)
- Sample preparation and definition of preparation conditions
  - → Temperature, carrier gas (always)
- Build up of a measurement routine
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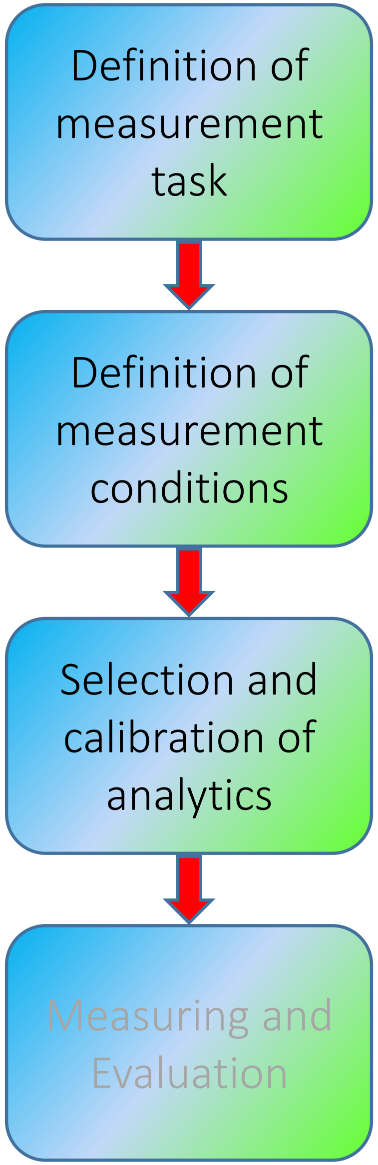

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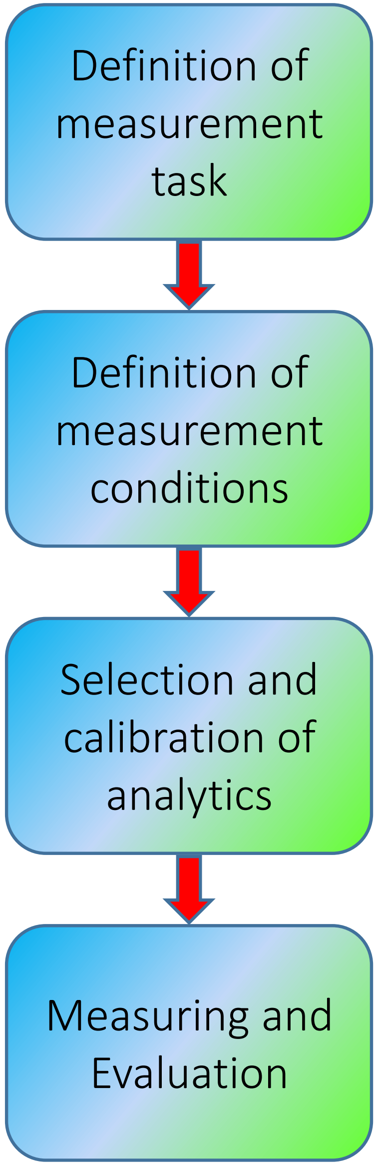
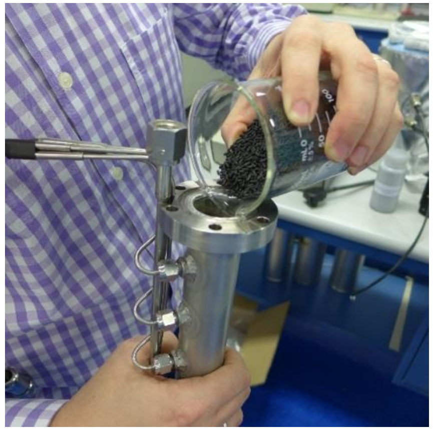


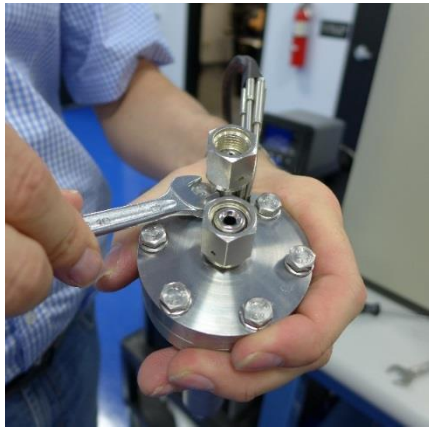
Example of a Measurement Routine

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:** 1l min^{-1} (STP) He, 0,75 l min^{-1} (STP) CH_4, 0,25 l min^{-1} (STP) CO_2
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**





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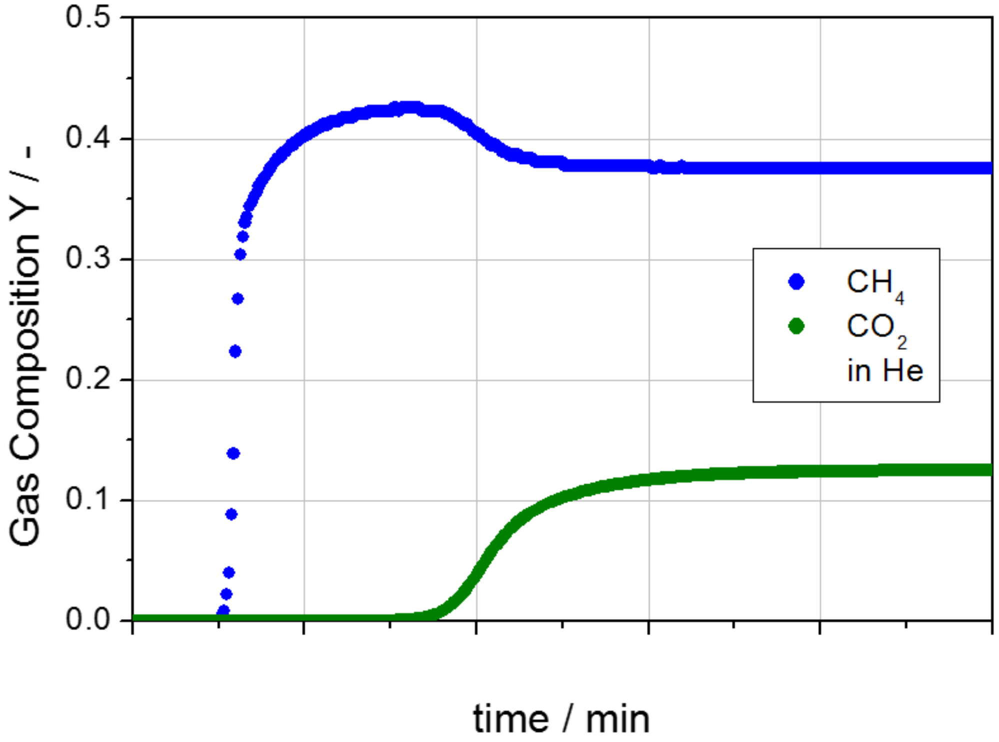


Result:

Breakthrough curve with “Role-Up” Effect

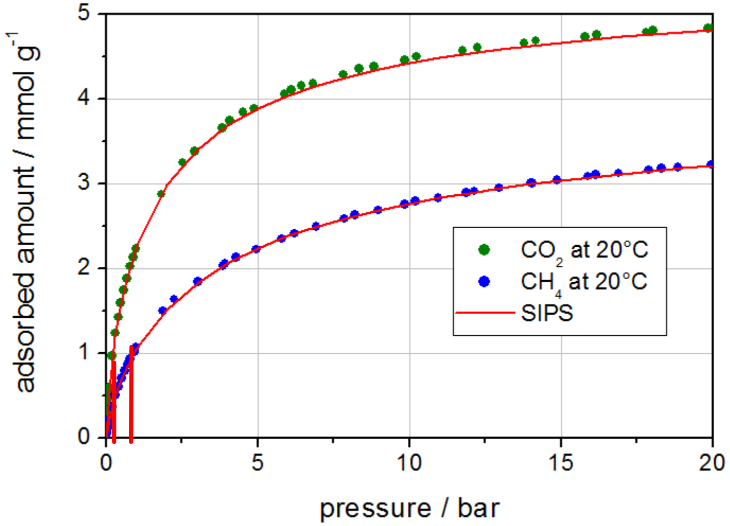
- Includes all partial loadings
- Reference on p_{CO2}=0,25 bar and P_{CH4}=3,75 bar
- Mole fraction: y_{CO2}=0,25; y_{CH4}=0,75
- **Helium will not be considered!**

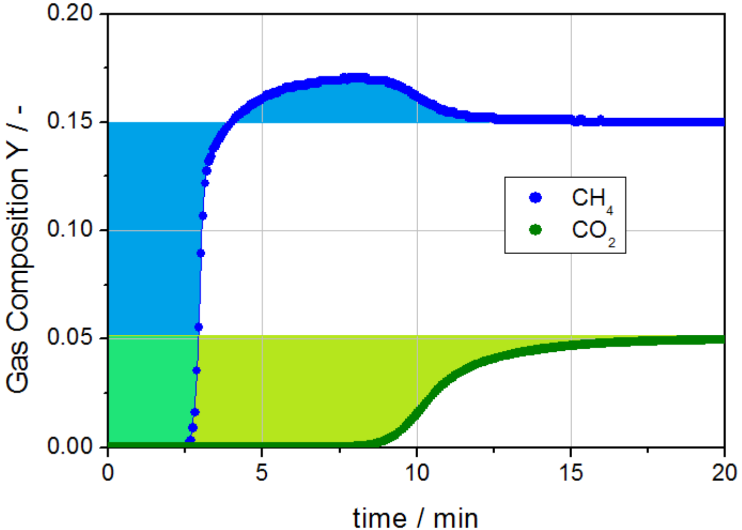
Integration of areas:

- $n(CO_2)$; $n(CH_4)$; n(total); α

An Example for a Complete Determined System

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



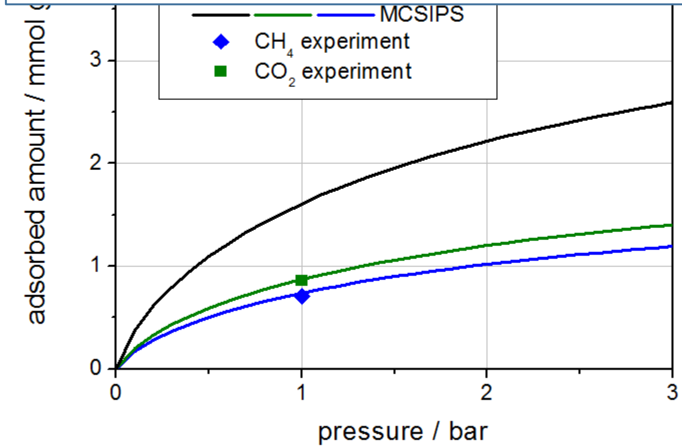


Thermodyn. Model (Multi component-SIPS)

Y_{CO2}=0,25
Y_{CH4}=0,75
P_{total}=1 bar

α_{Model}=3,53

A **complete determined** System!



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

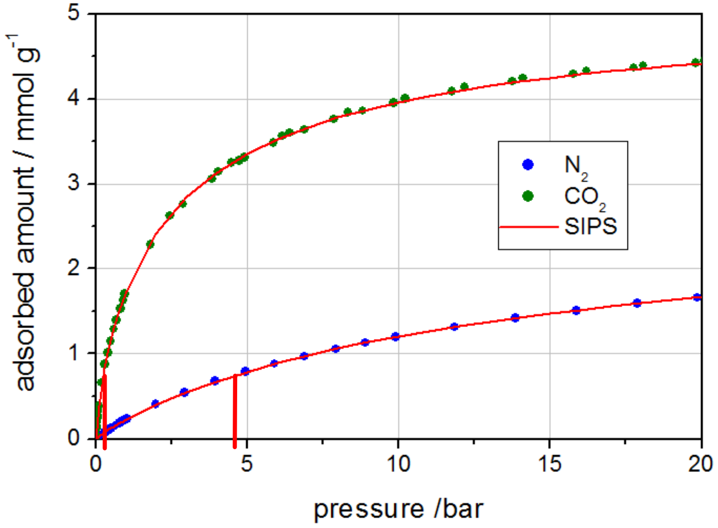
n_{CO2}= 0,86 mmol g^{-1}
n_{CH4}=0,71 mmol g^{-1}

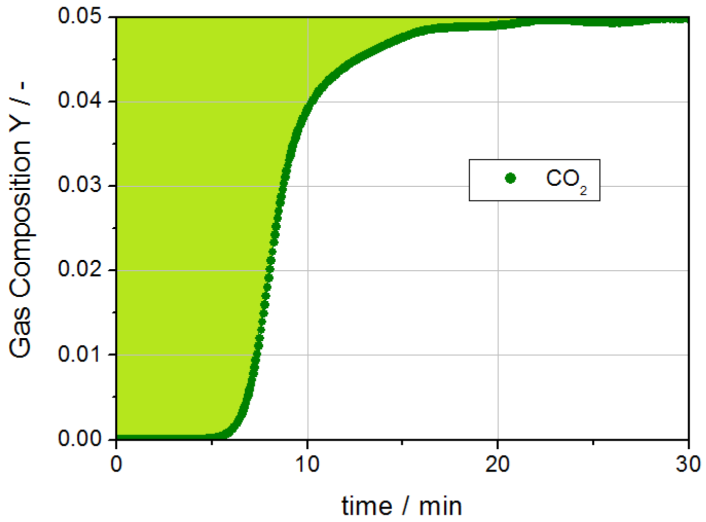
$\alpha_{Experiment}$=3,63

➡ **System** is **complete determined,** good agreement confirmed ideal behavior.

An Example for an Incomplete Determined System

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



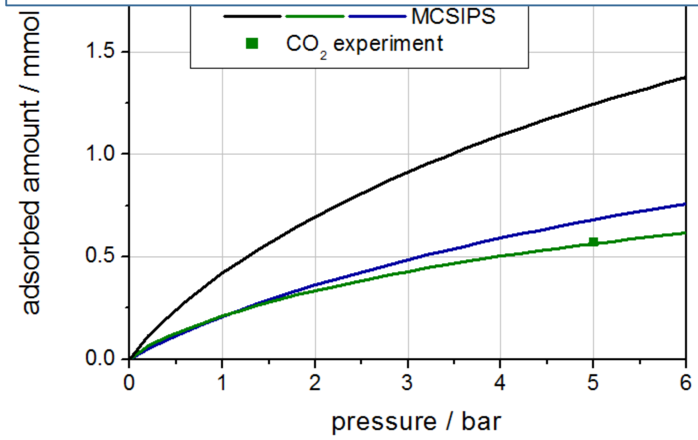


Thermodyn. Model
(Multi component-
SIPS)

Y_{CO2}=0,05
Y_{N2}=0,95
P_{total}=5 bar

α_{Model}=15,7

System is **not complete** determined!



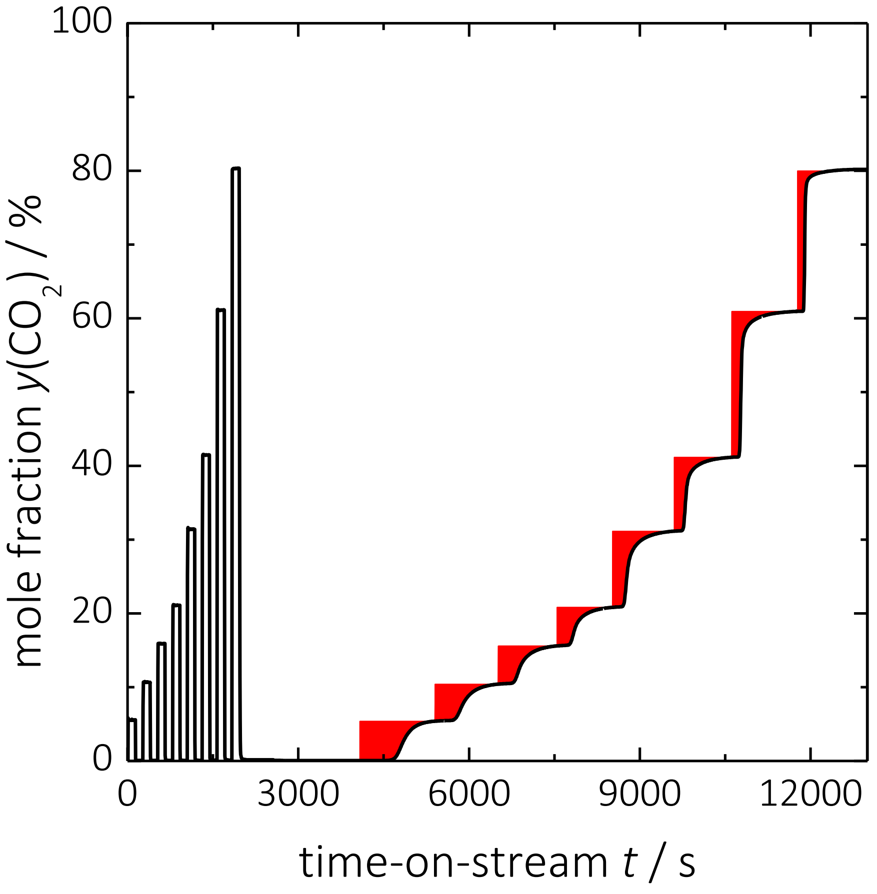
Dynamic Experiment
(Determination of
on partial loading)

n_{CO2}= 0,57 mmol g^{-1}
n_{N2}=not determined
$\alpha_{Experiment}$=not determined

System is only **incomplete determined.** Model is confirmed by experiment.

Measurement Techniques – Dynamic Method

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:

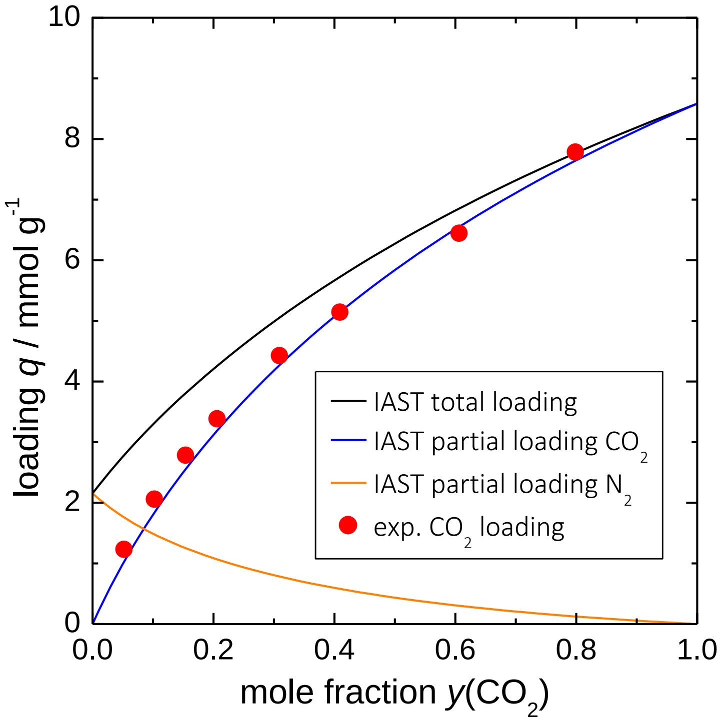
- Start further breakthroughs after equilibrium before
- **Integration** and **summation** results in partial loading data of CO_2
- Volume ratio and total pressure defines the partial pressure of CO_2

→ **Mixed isotherm data of CO_2 in N_2**

Measurement Techniques – Dynamic Method

Dynamic Sorption

Measured partial loading data for CO_2 on Activated Carbon D 55-1.5 at 10 bar



- Dynamic measured data (red)
- **IAST**-Model (Ideal Adsorbed Solution Theory) based on pure component isotherms (lines)
- Mixture of CO_2 and N_2 shows **ideal** behavior on AC

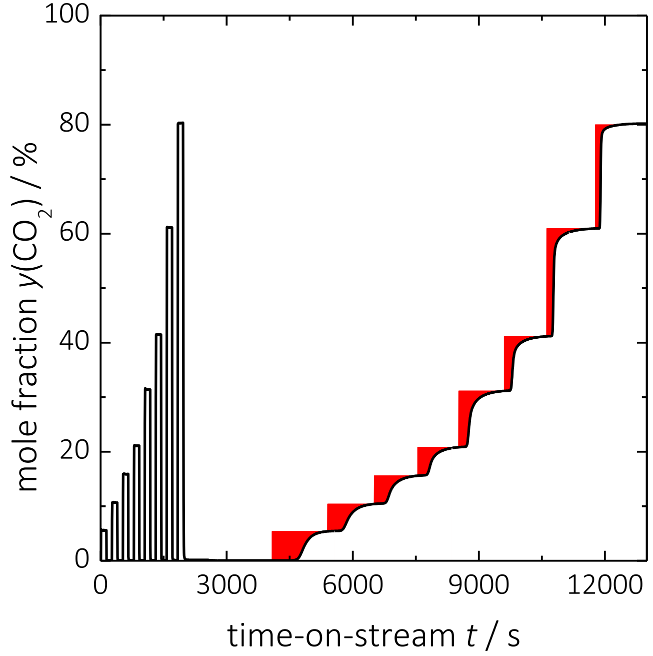
➡ Determination of partial loading data of CO_2 on AC D 55-1.5 by performing sequentially experiments along constant total pressure.

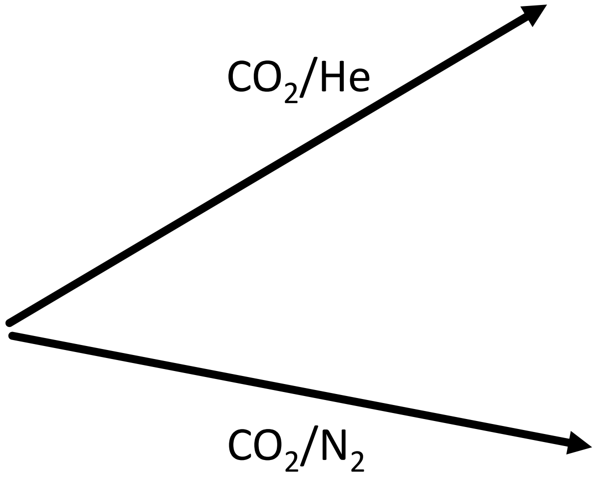
$$n_{CO_2,N_2,total}(p = const.) = FKT(Y_{CO_2}, Y_{N_2})$$

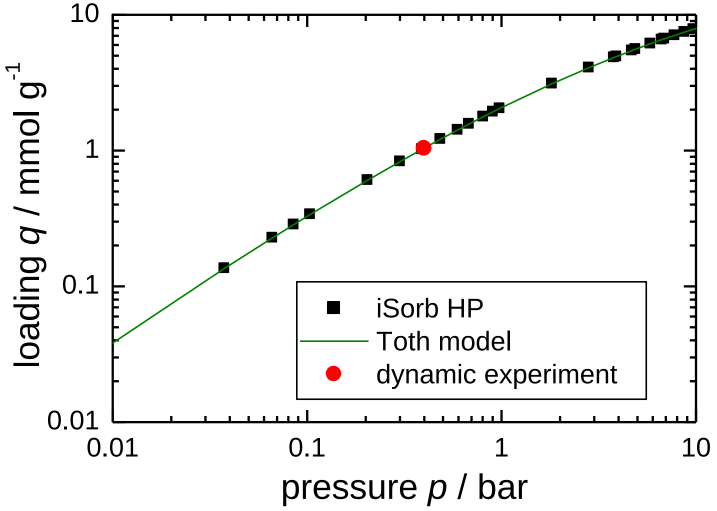
Measurement Techniques – Dynamic Method

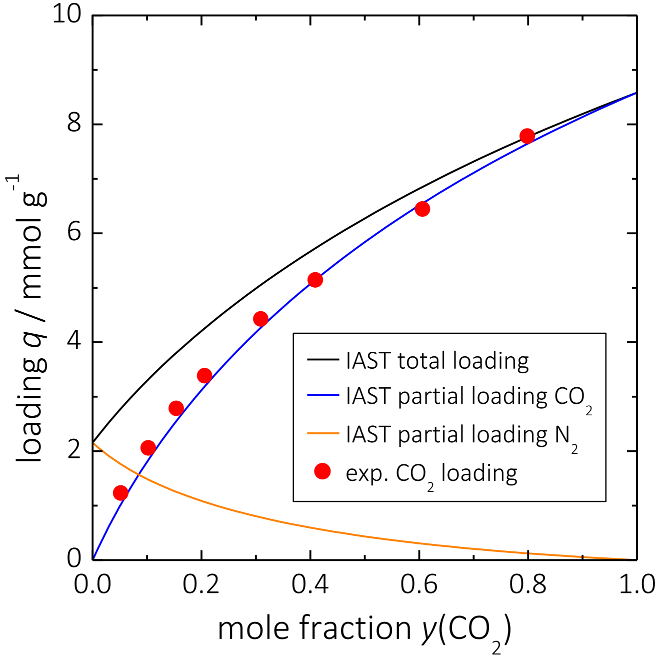
Sequence of several breakthrough curves on Activated Carbon D 55-1.5

- Assumption of **non-adsorbable Gas, i.e. Helium** as carrier gas will lead to pure component equilibria.
- Other, **adsorbable gases** results in mixture sorption data.



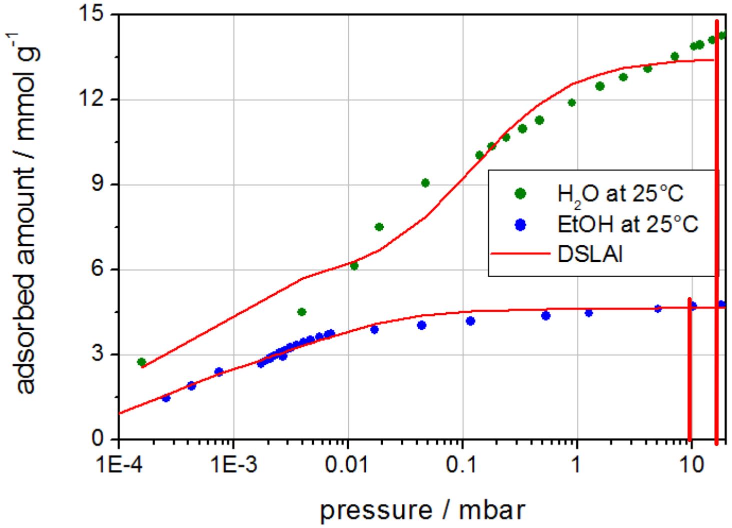


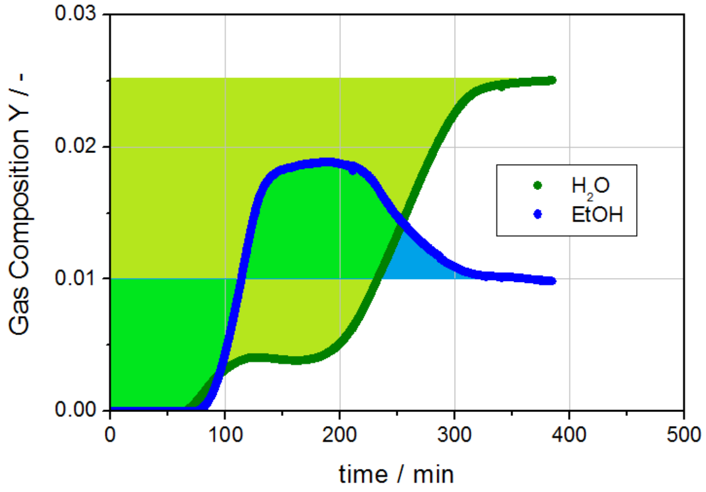




Vapor Mixture Measurement – Dynamic Method

1% EtOH 2,5% H_2O (approx. 80% RH) in N_2 at 25°C, 1 bar, 4000 ml/min on NaMSX

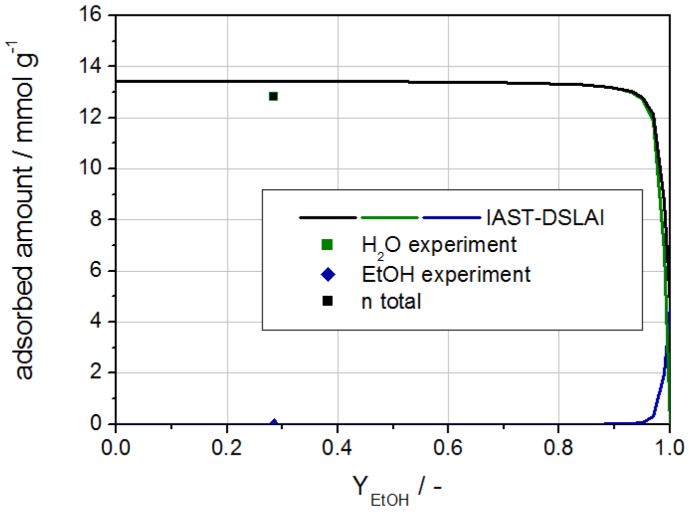




Thermodyn. Model (IAST-DSLAI)

Y_{EtOH}=0,322
Y_{H2O}=0,678
P_{total}=0.033 bar

α_{Model}>20000



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

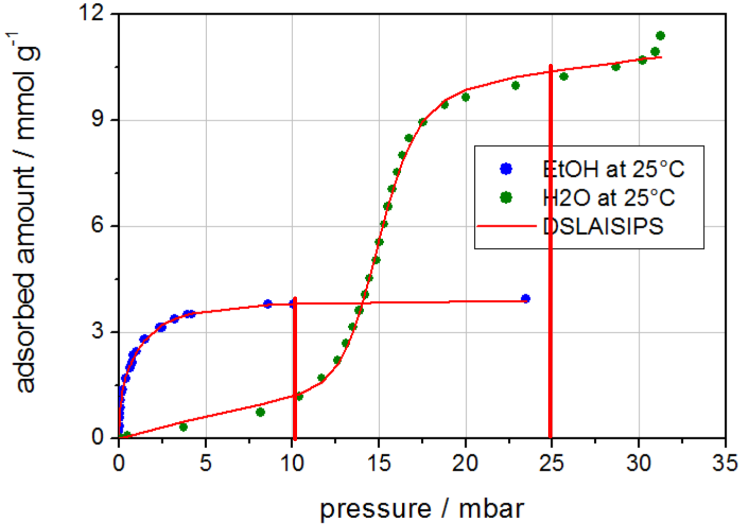
n_{EtOH}= ca. 0 mmol g^{-1}
n_{H2O}=12,9 mmol g^{-1}

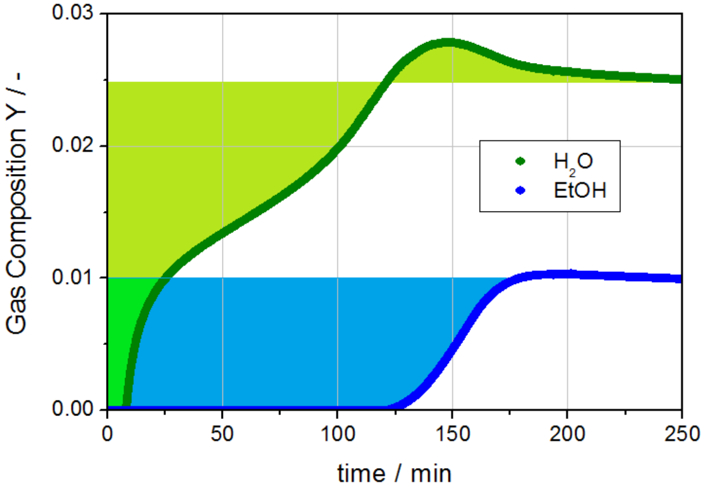
$\alpha_{Experiment}$=not determined (>20)

➡ **Very high selectivity of model confirmed by experiment**

Vapor Mixture Measurement – Dynamic Method

1% EtOH 2,5% H_2O (approx. 80% RH) in N_2 at 25°C, 1 bar, 4000 ml/min on D 55/1.5

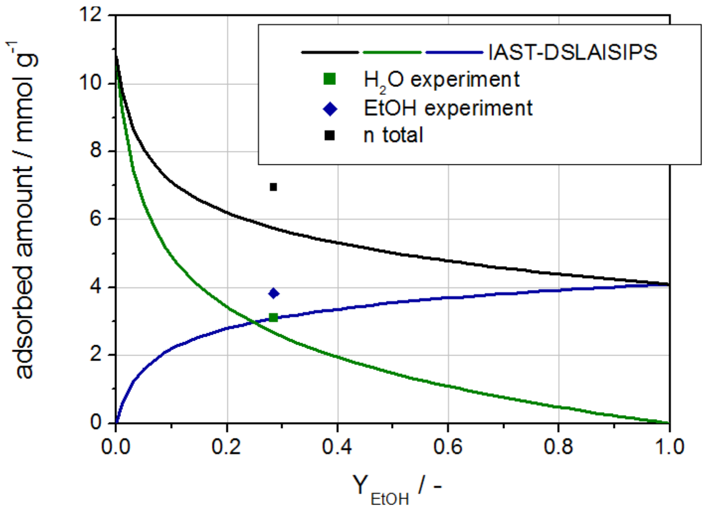




Thermodyn. Model
(IAST-DSLAISIPS)

Y_{EtOH}=0,286
Y_{H2O}=0,714
P_{total}=0.035 bar

α_{Model}=2,9



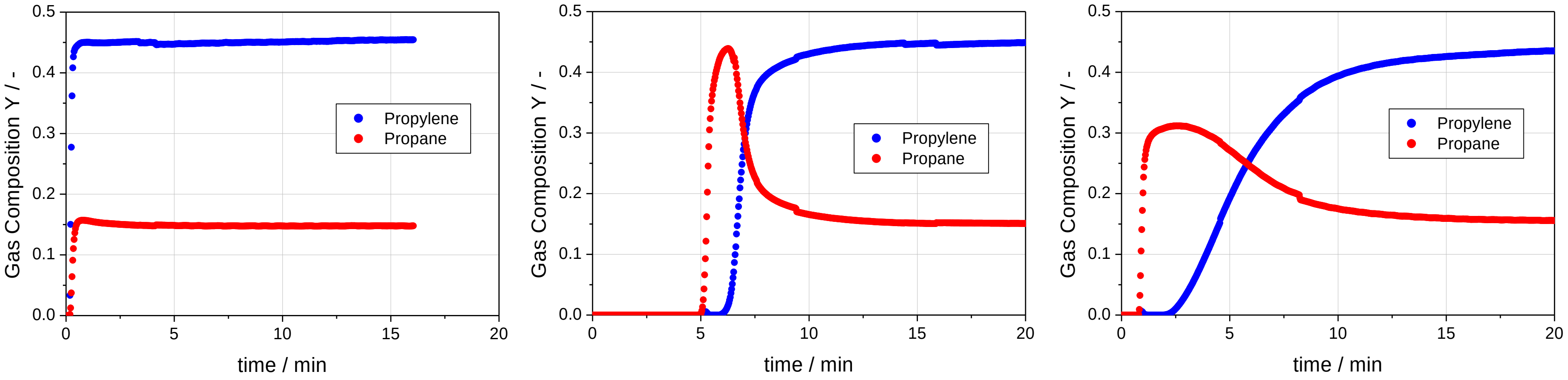
Dynamic experiment
(determination of **all**
partial loadings)

n_{EtOH}= 3,82 mmol g^{-1}
n_{H2O}= 3,11 mmol g^{-1}
$\alpha_{Experiment}$=3,1

➡ **Deviation between model and experiment** → no prediction, experiment necessary!

Comparable Measurements of Mixture Sorption

15% Propane 45% Propylene in He at 25°C, 5 bar, 1000 ml/min on A1, A2, A3



Sample: A1

$Y_{Propane}$=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: A2

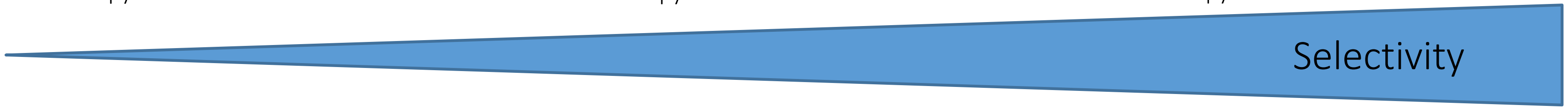
$Y_{Propane}$=0,25
$Y_{Propylene}$=0,75
$n_{Propane}$= 0,2 mmol g^{-1}
$n_{Propylene}$=1,7 mmol g^{-1}

$\alpha_{Propylene}$=2,83

Sample: A3

$Y_{Propane}$=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)



- Statements on selectivity also possible without modeling from pure component data
- Determination of sorption capacities and selectivities, recording of kinetic

What can we do with such data?

- Relevance for materials / science and production
  - Assessment of porous materials
  - R&D of tailor made materials for certain separation issues
  - Evaluation of Influence of some secondary components

Zeolite for gas purification
Source: www.cwk-bk.de

- Relevance for engineering / Process design
  - Modeling and Calculation of fixed bed adsorbers
  - Determination of Kinetics (Linear driving force constants)
  - Calculation of breakthrough curves, upscaling by modeling
  - Calculation of PSA and TSA processes

Process gas purification plant
source www.silica.de

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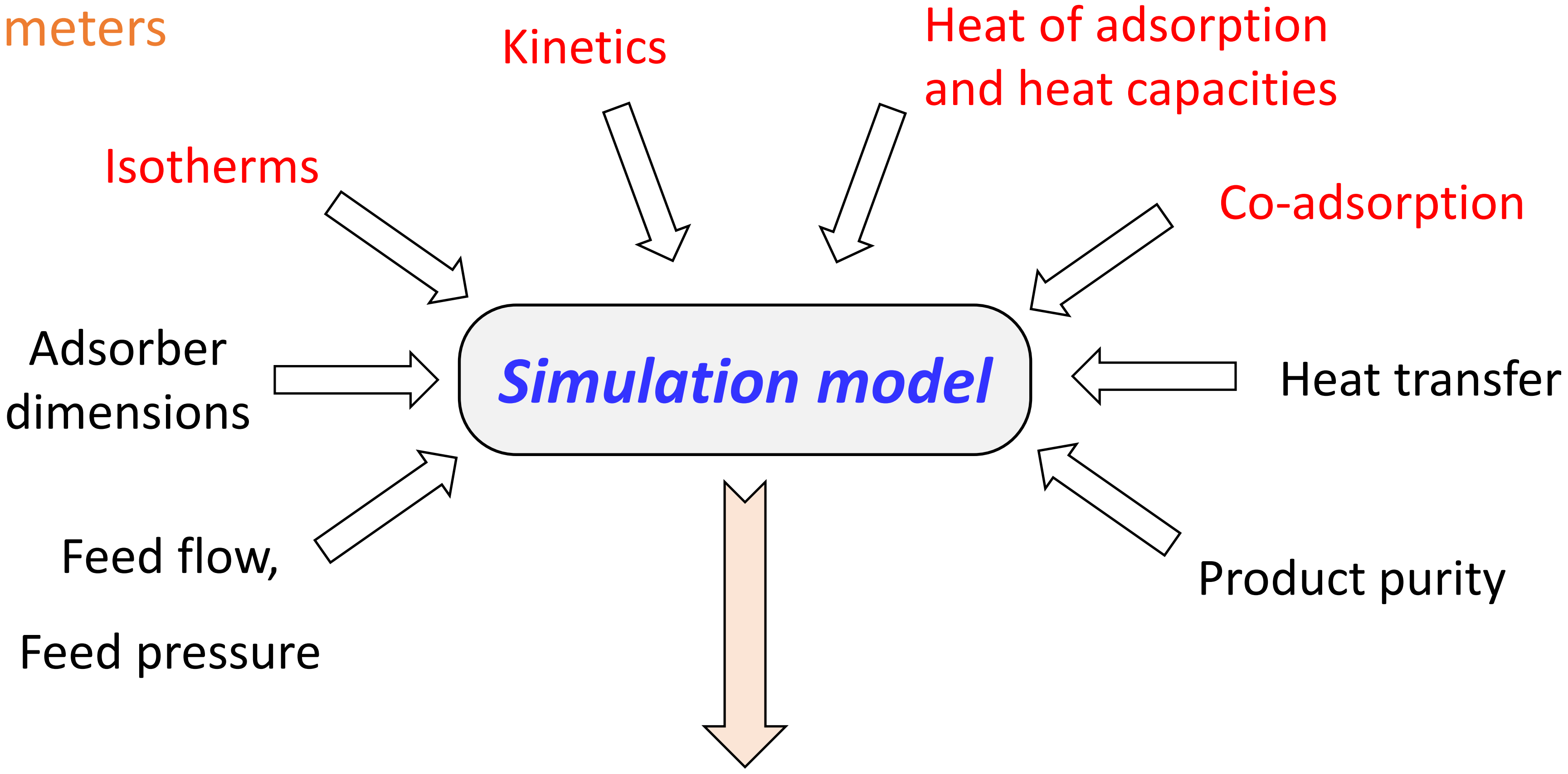
Modeling – necessary Input Parameters

Input Parameters



Kinetics

Heat of adsorption and heat capacities

Isotherms

Co-adsorption

Adsorber dimensions

Simulation model

Heat transfer

Feed flow,

Feed pressure

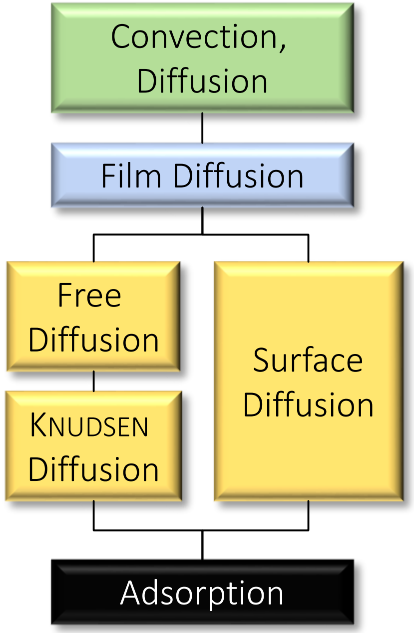
Product purity

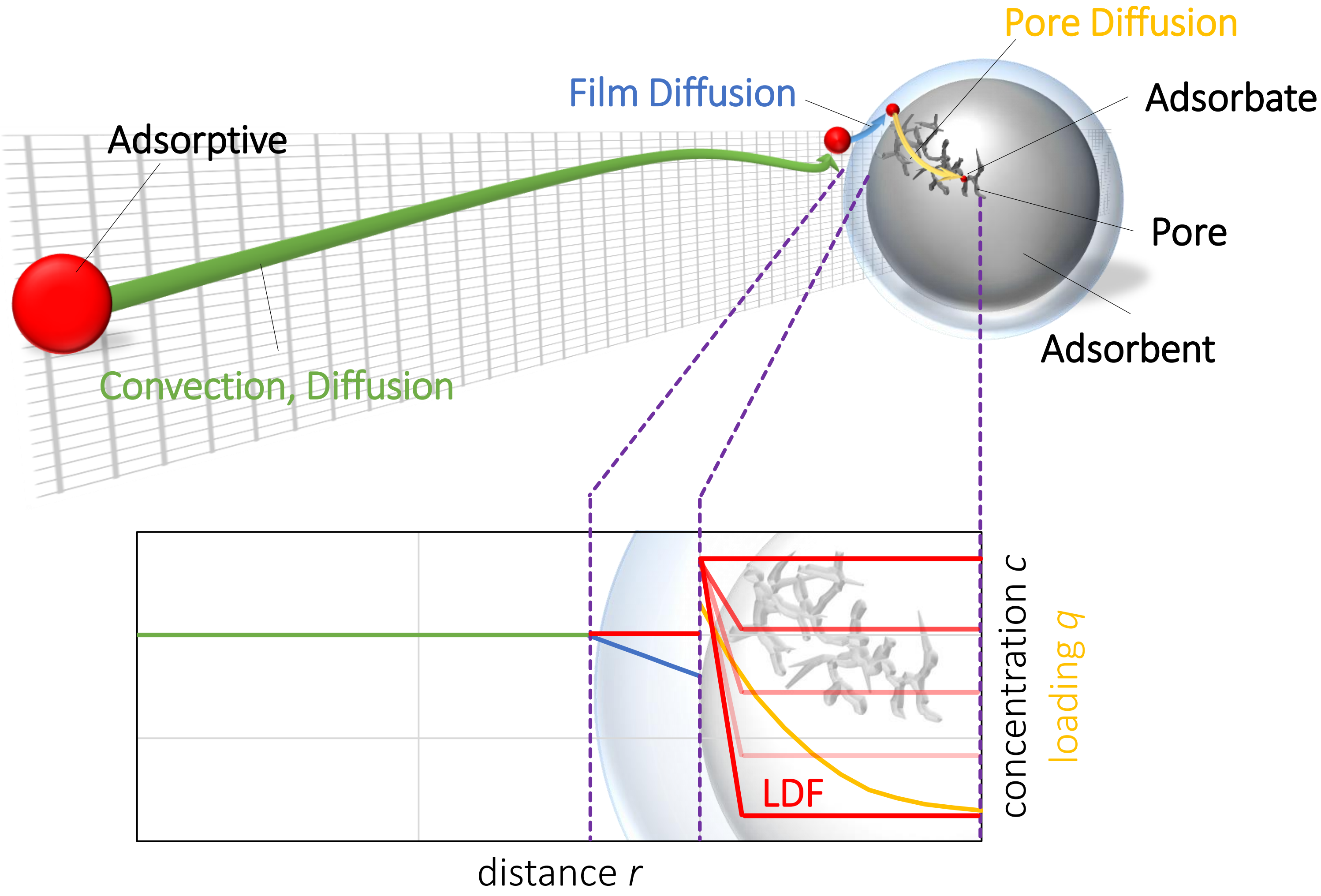
Cycle duration, pressure range…

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

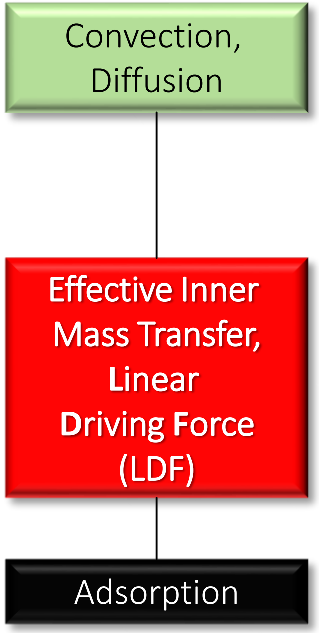
Modeling of Breakthrough Curves

Kinetic considerations - Mass Transfer coefficient k_{LDF}





Simplification

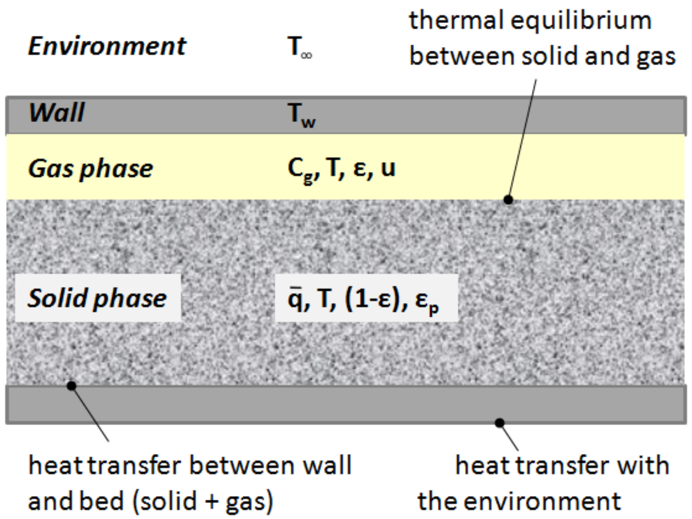


Modeling – Mass and Energy Balances

Mass Balance

$$\underbrace{\boxed{\frac{\partial C_{g,i}}{\partial t}+\frac{1-\varepsilon}{\varepsilon}\rho_{Part}\frac{\partial \bar{q}_i}{\partial t}}}_{\text{accumulation}}-\underbrace{\boxed{Dax\frac{\partial^2 C_{g,i}}{\partial z^2}}}_{\text{dispersion}}+\underbrace{\boxed{u\frac{\partial C_{g,i}}{\partial z}+C_{g,i}\frac{\partial u}{\partial z}}}_{\text{convection}}=0$$

$$\frac{\partial \bar{q}_i}{\partial t}=k_{LDF}\left(q_i^*-\bar{q}_i\right)$$ **LDF approach** $$q_i^*=f\left(Isotherms\right)$$



Energy Balances

$$\underbrace{\boxed{\frac{1-\varepsilon}{\varepsilon}\rho_{part}\sum_{i=1}^{n}\frac{\Delta H_i}{M_i}\frac{\partial \bar{q}_i}{\partial t}}}_{\text{generation}}-\underbrace{\boxed{\lambda\frac{\partial^2 T_g}{\partial z^2}}}_{\text{dispersion}}+\underbrace{\boxed{\left(\frac{1-\varepsilon}{\varepsilon}\rho_{part}cps+\rho_g cpg\right)\frac{\partial T_g}{\partial t}}}_{\text{accumulation}}+\underbrace{\boxed{u\rho_g cpg\frac{\partial T_g}{\partial z}+T_g\rho_g cpg\frac{\partial u}{\partial z}}}_{\text{convection}}+\underbrace{\boxed{4\frac{h_w}{d_i}\left(T_g-T_w\right)}}_{\text{transfer to wall}}=0$$

$$\underbrace{\boxed{\alpha_w h_w\left(T_g-T_w\right)}}_{\text{gas to wall}}-\underbrace{\boxed{\rho_w cpw\frac{\partial T_w}{\partial t}}}_{\text{accumulation}}-\underbrace{\boxed{\alpha_{wL}U_g\left(T_w-T_{Env}\right)}}_{\text{wall to environment}}=0$$

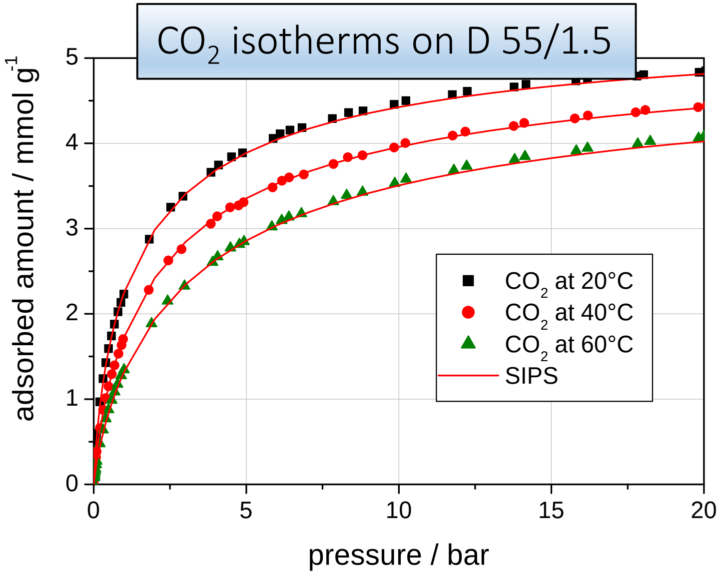
Equation for velocity / overall mass balance (isothermal)

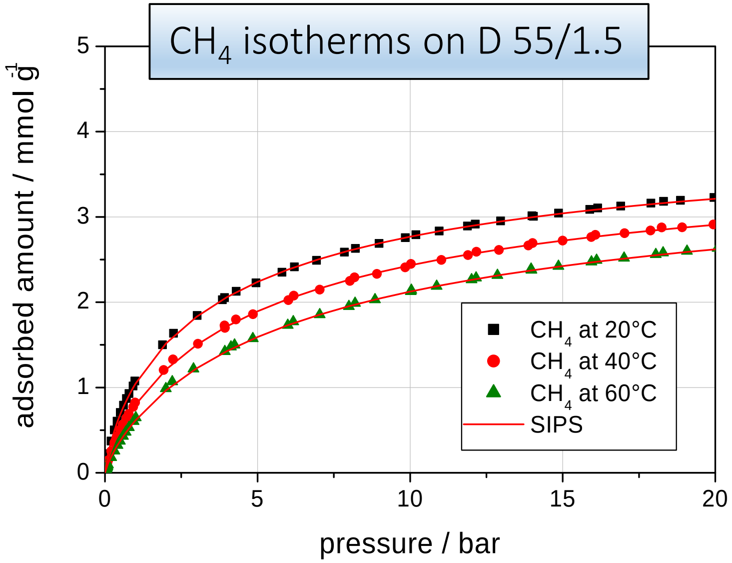
$$\frac{\partial u}{\partial z}+\underbrace{\boxed{\frac{RT}{p}\rho_{part}\frac{1-\varepsilon}{\varepsilon}\sum_{i=1}^{n}\frac{1}{M_i}\frac{\partial \bar{q}_i}{\partial t}}}_{\text{Change by adsorption}}+\underbrace{\boxed{\frac{1}{p}\frac{\partial p}{\partial t}}}_{\text{Change by compression}}=0$$

* A.M. Ribeiro et. al, *Chem. Eng. Sci.* 63 (**2008**)
* D.M. Ruthven, Principles of Adsorption (1984)
* M.S. Shafeeyan et. al, *Chem. Eng. Res. Des.* 92 (**2014**)

Working with the model – Example I

Replacement effects

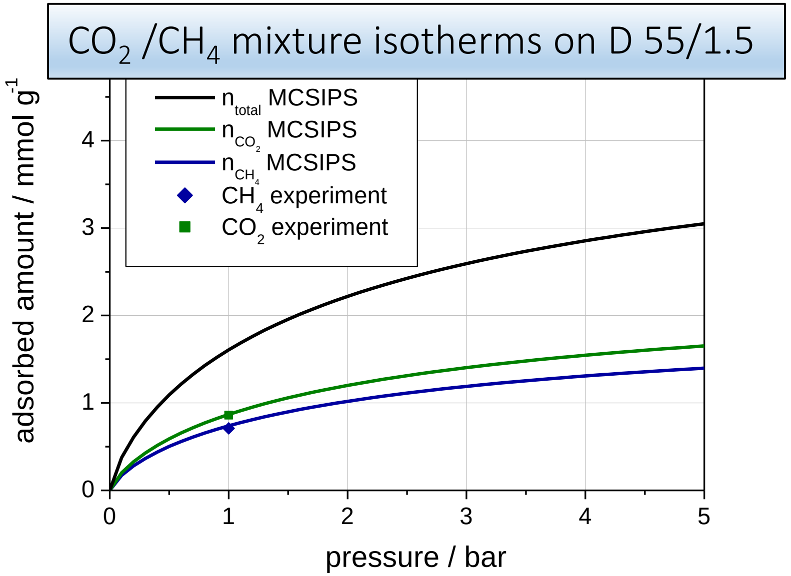

CO_2 isotherms on D 55/1.5

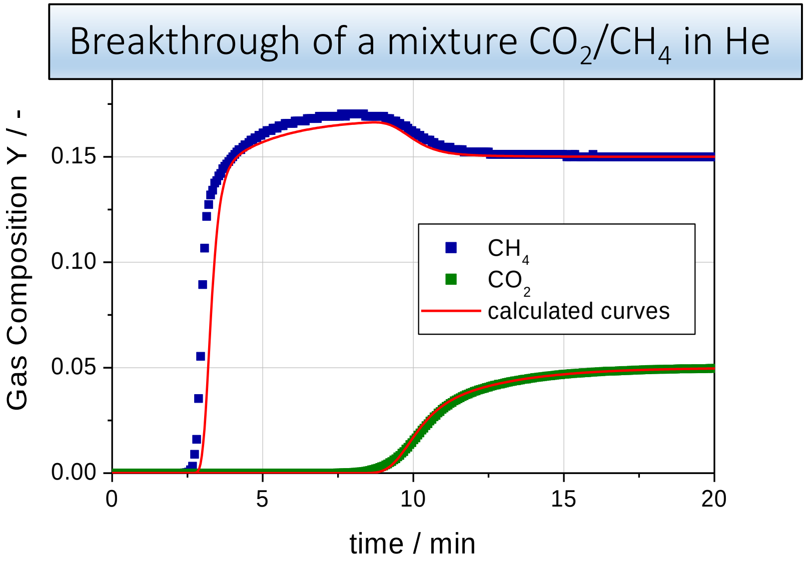

CH_4 isotherms on D 55/1.5

Input pure component Isotherms

Fitting k_{LDF}

Fitting Heat Transfer Coeff.


CO_2 /CH_4 mixture isotherms on D 55/1.5


Breakthrough of a mixture CO_2/CH_4 in He

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

Working with the model – Example I

Replacement effects – Temperature profiles

Use of integral heat of adsorption with Sips model (from isotherms):

$$q_{s,i} = q_{\max,i} \cdot \frac{(K_i \cdot c_i)^{t_i}}{1+\sum_{j=1}^{n}(K_j \cdot c_j)^{t_j}}$$

$$K_i = K_{i,0} \cdot \exp\left(\frac{Q}{R}\left(\frac{1}{T}-\frac{1}{T_0}\right)\right)$$

$$q_{\max,i} = q_{\max,i,0} \cdot \exp\left(\chi_i\left(1-\frac{T}{T_0}\right)\right)$$

$$t_i = t_{i,0} + \alpha_i\left(1-\frac{T_0}{T}\right)$$

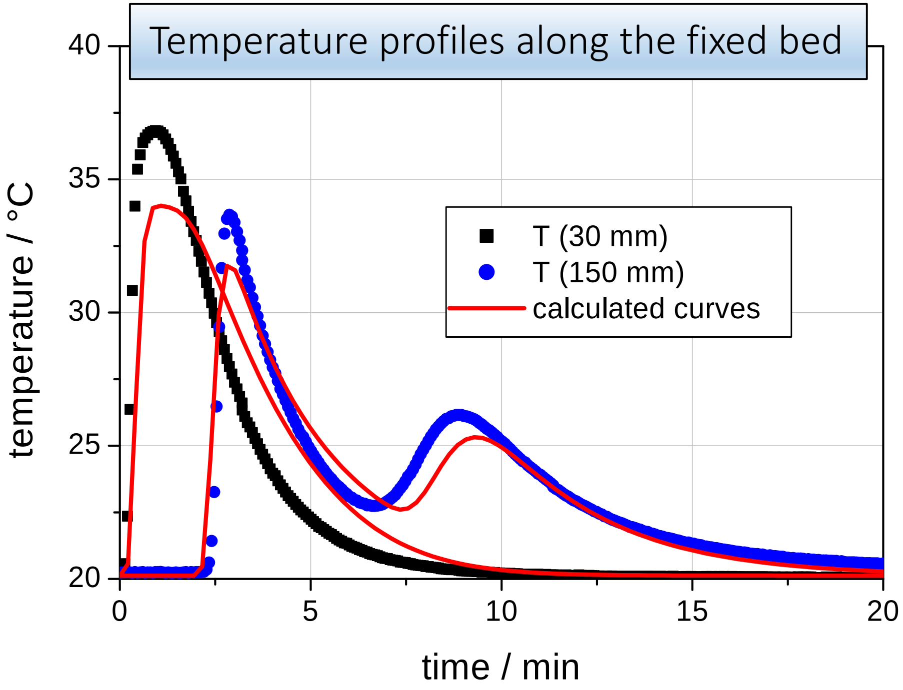
- Q (equivalent to $-\Delta H_{\Theta=0,5}$)
- Q_{CO2}: 15.9 kJ mol^{-1}
- Q_{CH4}: 11.9 kJ mol^{-1}

Input Q in energy balance

Input h_w, U_g in energy balance

Fitting Heat Transfer Coeff.

- h_w : ~ 30 W m^{-2} K^{-1} (Gas, Fixed Bed/Wall)
- U_g : ~ 400 W m^{-2} K^{-1} (Wall/Liquid)

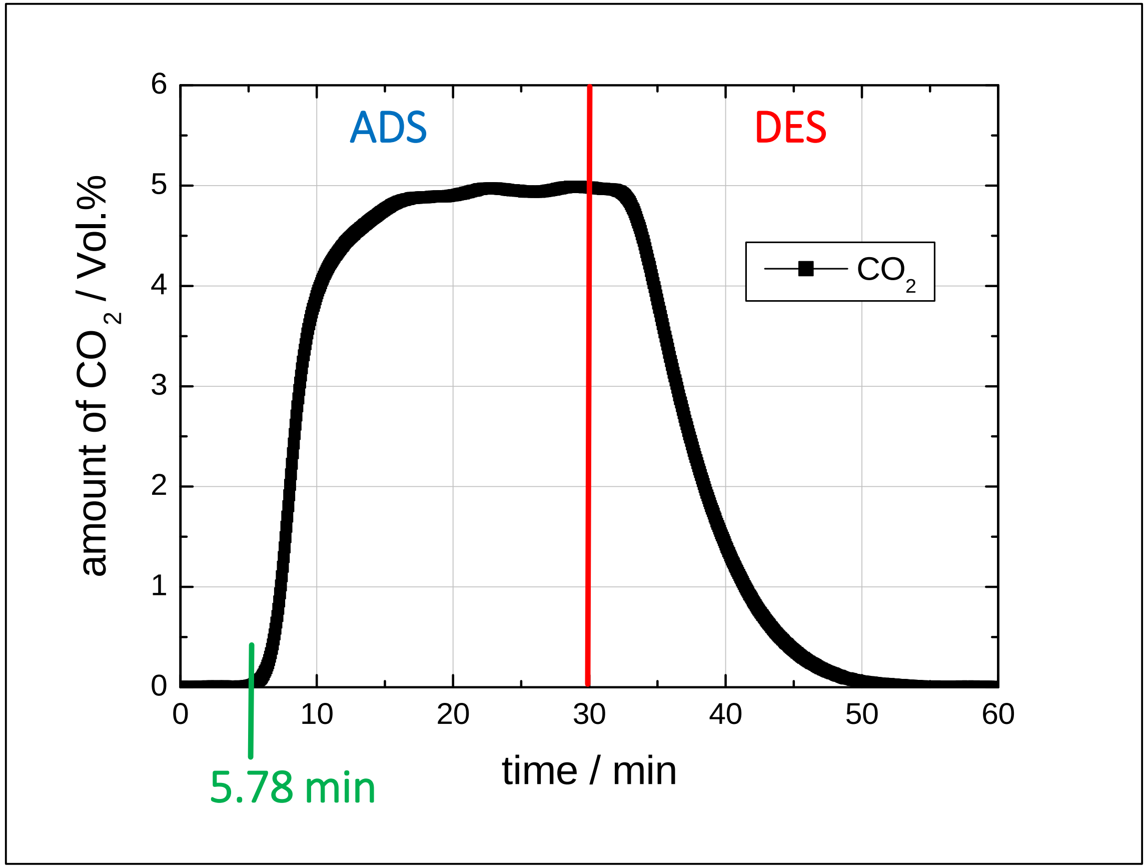


5% CO_2 15% CH_4 in He at 20°C, 5 bar, 2500 ml/min on D 55/1.5

- **CH_4 induced higher temperature effect**
- **Model can describe temperature profiles qualitatively**
- Underestimation of temperature peaks
- Experiment shows mostly sharper temperature profiles
  → differences due to simplification of no radial gradients
  → radial gradients in experiment expected due to external liquid cooling

Scope of Simulation

Example: CO_2 Adsorption on D55/1.5 in N_2-Carrier Gas



Observations:

1) Desorption curve flatter than Adsorption curve
2) Desorption time higher than Adsorption time
3) Adsorption time 5.78 min (c_{out}< 0.2 %)

Questions concerning:

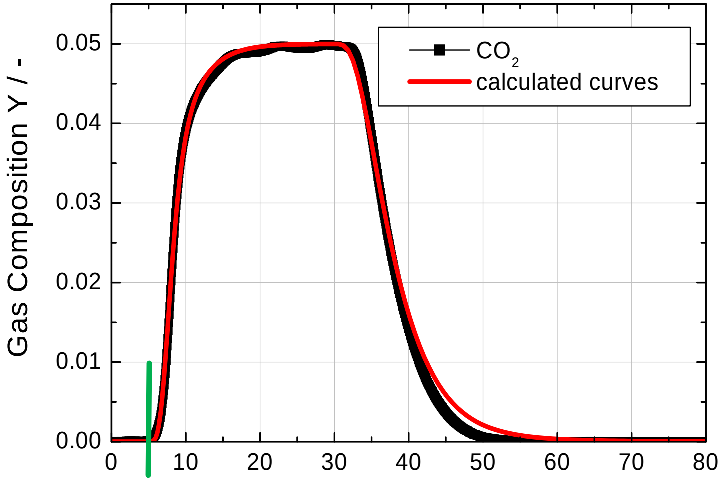
1) Kinetic parameter (k_{LDF})
2) Total pressure during each step
3) Adsorption/Desorption times
4) Purge flow during Desorption

Adsorption: 5% CO_2 in N_2 at 40°C, 5 bar, 2000 ml/min on D 55/1.5

Desorption: Purging with 2000 ml/min N_2 at 40°C, 5 bar

Working with the model – Example II

Regeneration / PSA



5.78 min

5% CO_2 95% N_2 at 40°C, 5 bar, 2000 ml/min on D 55/1.5

Model 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
- Purge Flow 2000 ml/min pure N_2

General Requirements for PSA:

- Purge Flow 500 ml/min pure N_2
- Desorption in counter current flow
- Max. CO_2 content in product 1%

Question concerning:

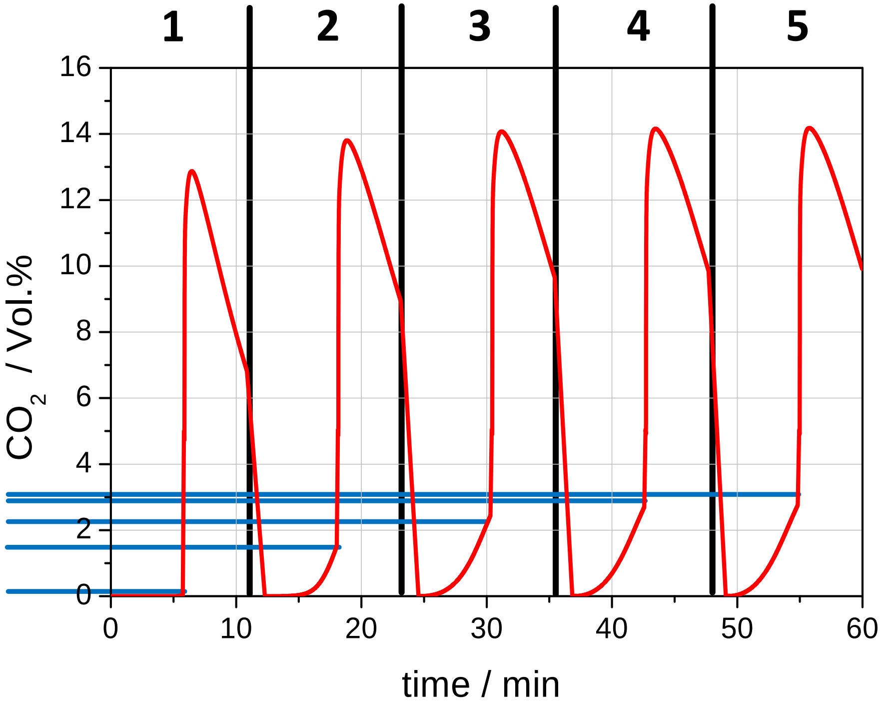
1) Desorption pressure?

Working with the model – Example II

Regeneration / PSA

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 %

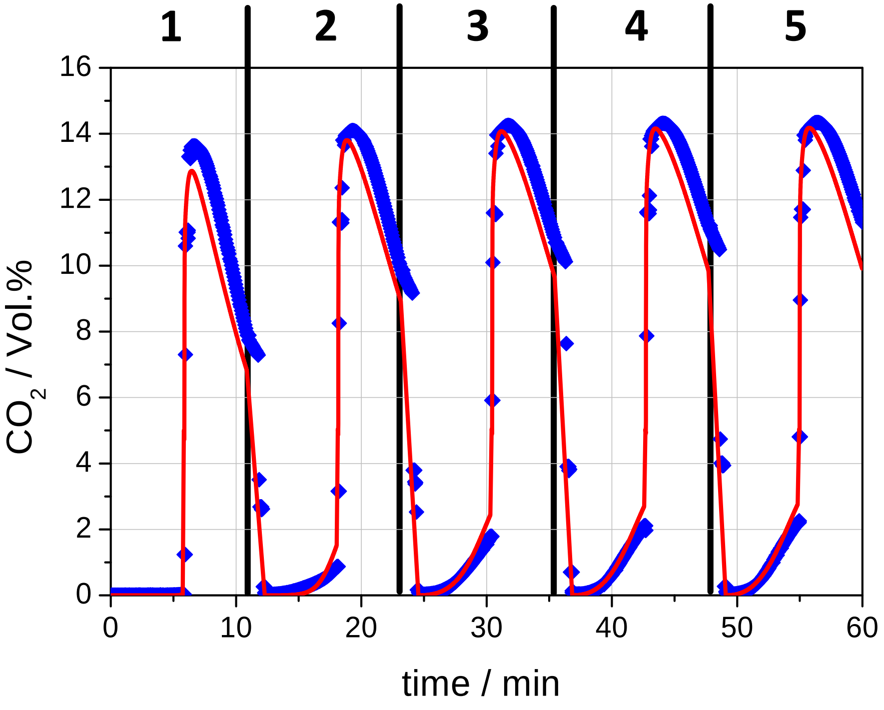
Working with the model – Example II

Dynamic orption

Regeneration / PSA

Cycle times for modeling:

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



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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

Working with the model – Example II

Regeneration / VPSA

Cycle times for modeling:

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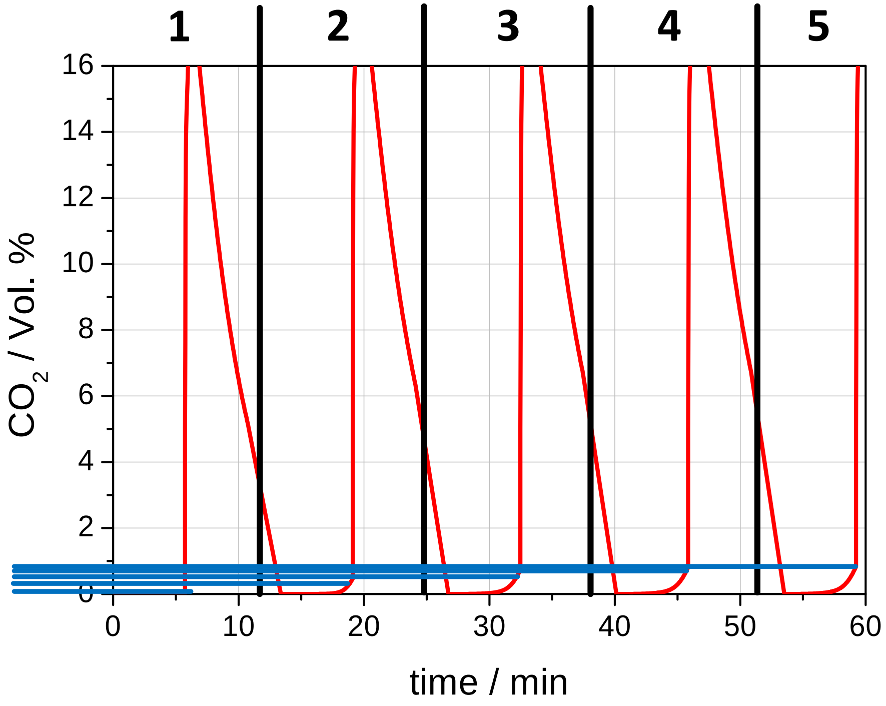

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- Pressurization from 4.6 bar to 5 bar with Feed
- Measurement of 5 cycles

Calculations with p_{DES}= 0.5 bar

Predictions by modeling:

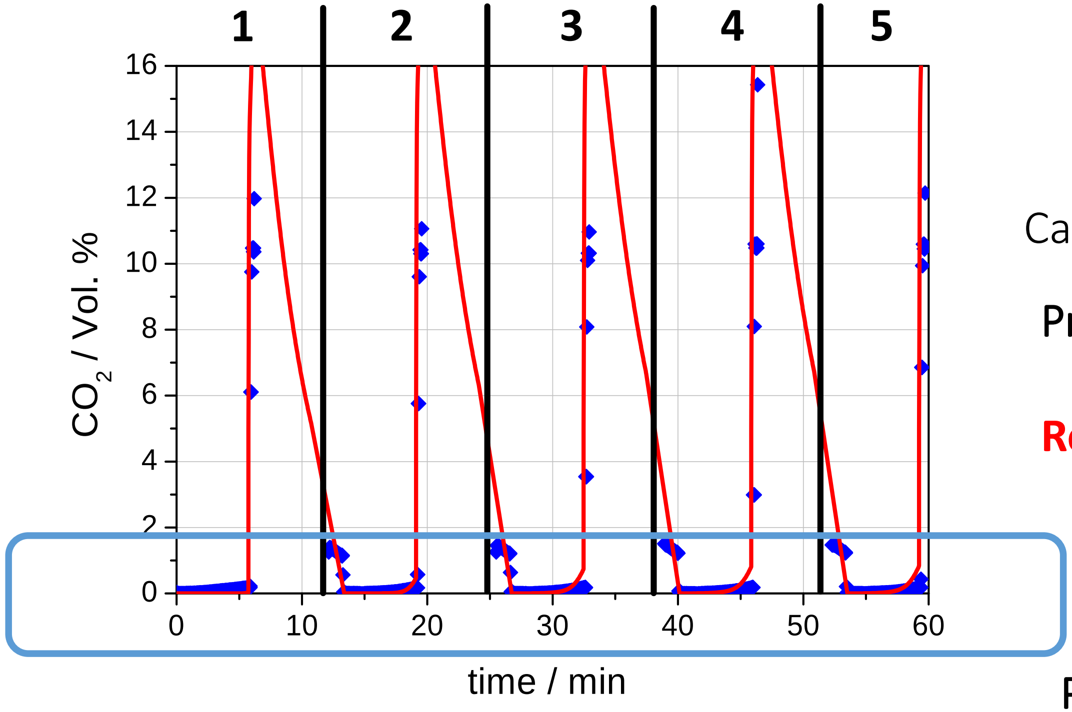
Regeneration conditions good enough
→ CO_2 impurity in effluent flow increases from cycle to cycle, but still below target (<1%)

Working with the model – Example II

Regeneration / VPSA

Cycle times for modeling:

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



Cycle times for Experiment:

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- Measurement of 5 cycles

Calculations with p_{DES}= 0.5 bar

Predictions by modeling:

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Working with the model – Example II

Dynamic orption

Regeneration / VPSA

Cycle times for modeling:

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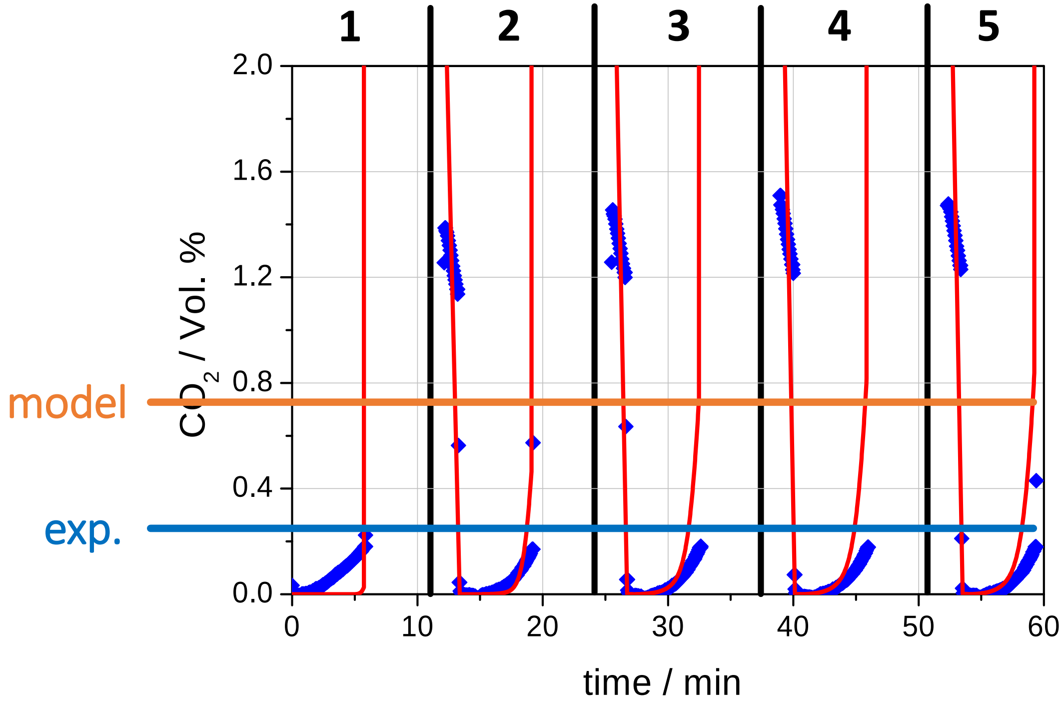

Cycle times for Experiment:

- Adsorption time 5.78 min @ 5 bar
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- Pressurization to 4.6 bar with N_2
- Pressurization from 4.6 bar to 5 bar with Feed
- Measurement of 5 cycles

But: 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!

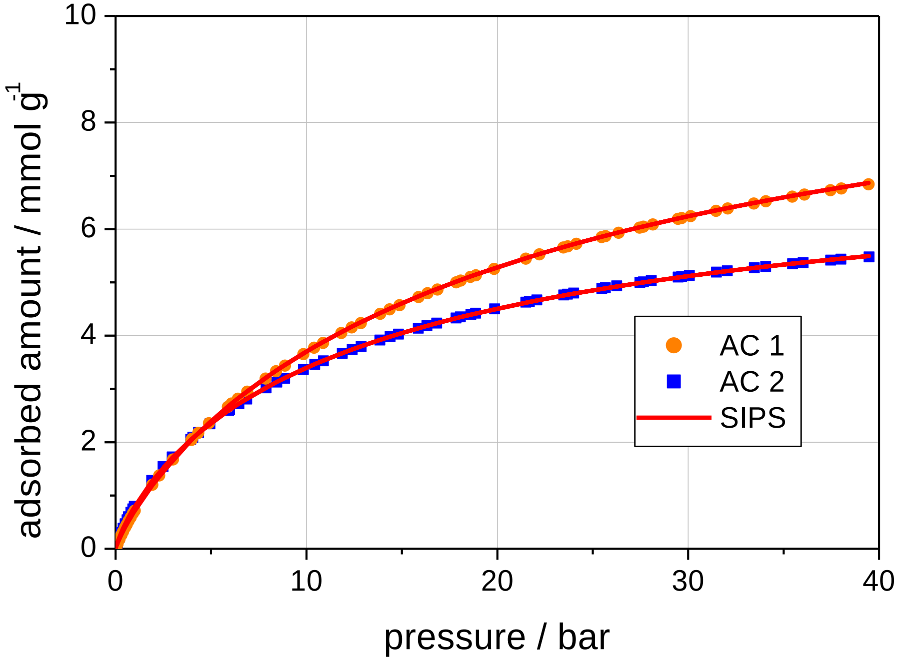
Working with the model – Example III

C_3H_8 removal from CH_4 (partial pressure range 0.01 bar and 0.50 bar)

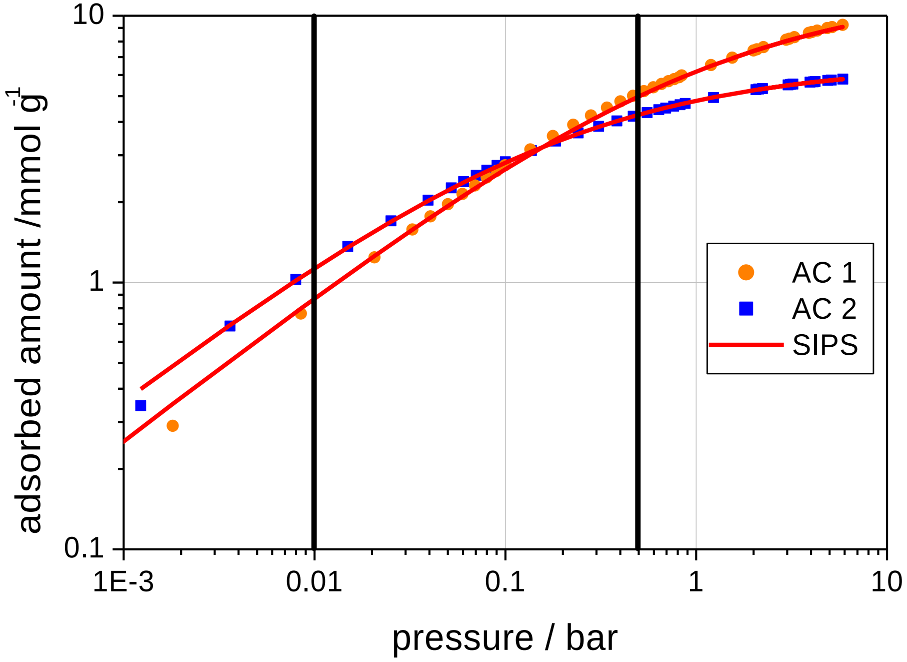
Selection of activated carbon with different BET-Surfaces, but from same raw material

- **AC 1** BET ~1800 m^2/g
- **AC 2** BET ~1300 m^2/g

CH_4 isotherms on **AC 1** and **AC 2** at 40°C



C_3H_8 isotherms on **AC 1** and **AC 2** at 40°C



Often AC with higher BET will be selected by user which is not always the best decision!

→ according to isotherms **AC 2** is better for low C_3H_8 concentrations

→ for high C_3H_8 concentrations **AC 1** is better

Working with the model – Example III

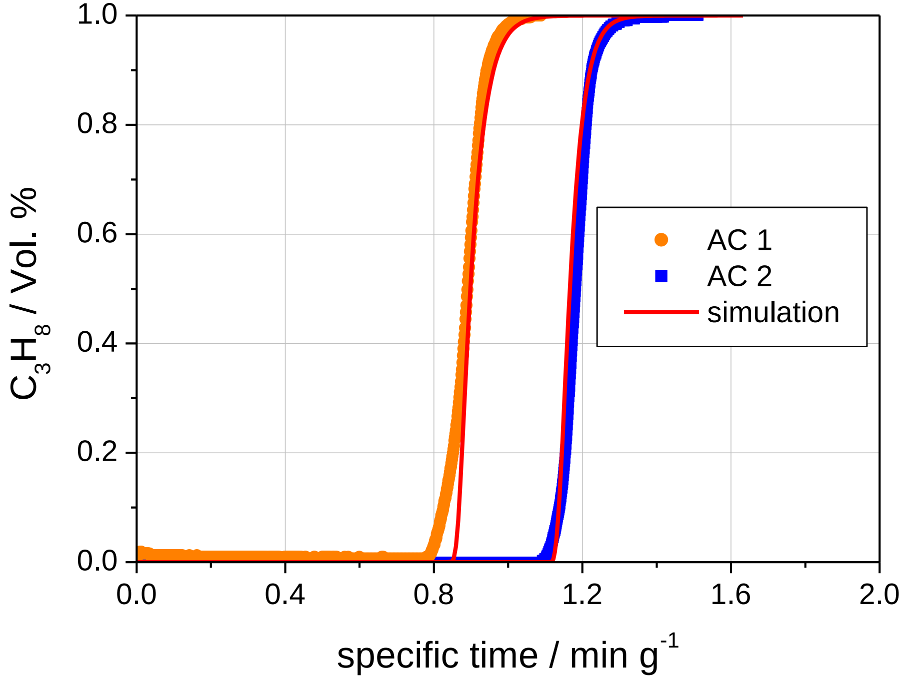
Dynamic Sorption

C_3H_8 removal from CH_4 (partial pressure range 0.01 bar and 0.50 bar)

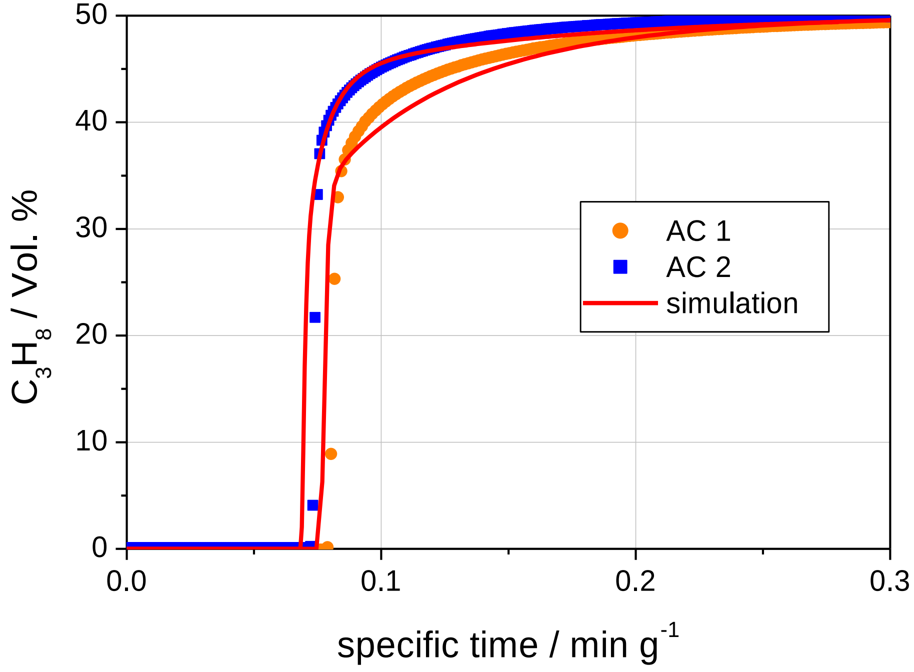
Selection of activated carbon with different BET-Surfaces, but from same raw material

- AC 1 BET ~1800 m^2/g
- AC 2 BET ~1300 m^2/g

breakthrough of 1% C_3H_8 in CH_4 at 40°C, 1 bar



breakthrough of 50% C_3H_8 in CH_4 at 40°C, 1 bar



Breakthrough experiments and simulations very sensitive for low concentrations!

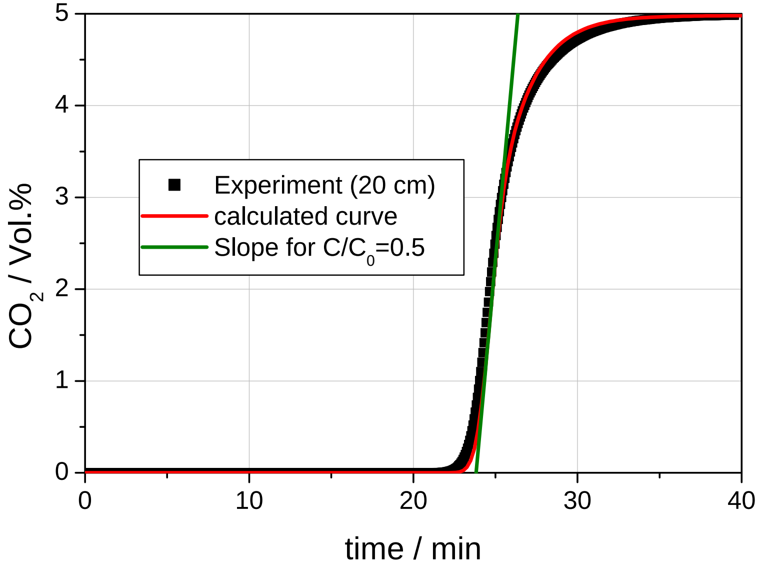
→ Observations made from isotherms were confirmed by dynamic experiments and calculations

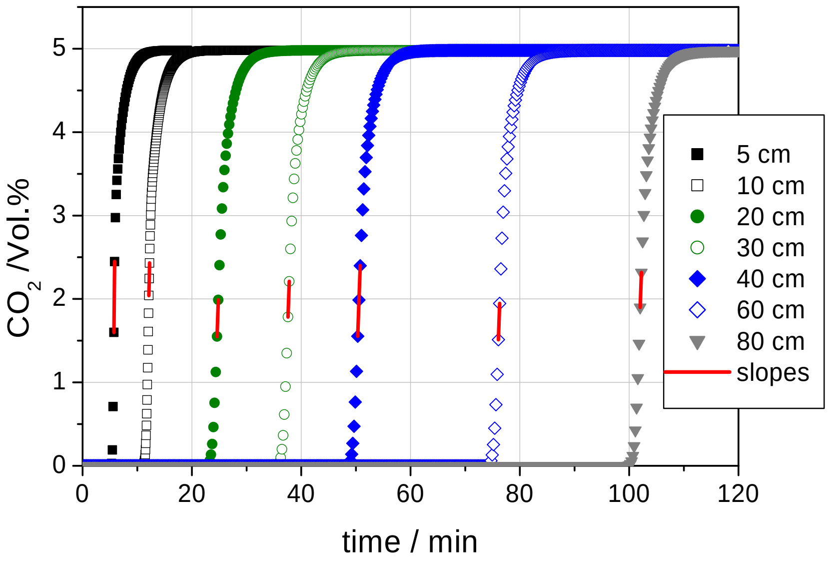
Working with the model – Example IV

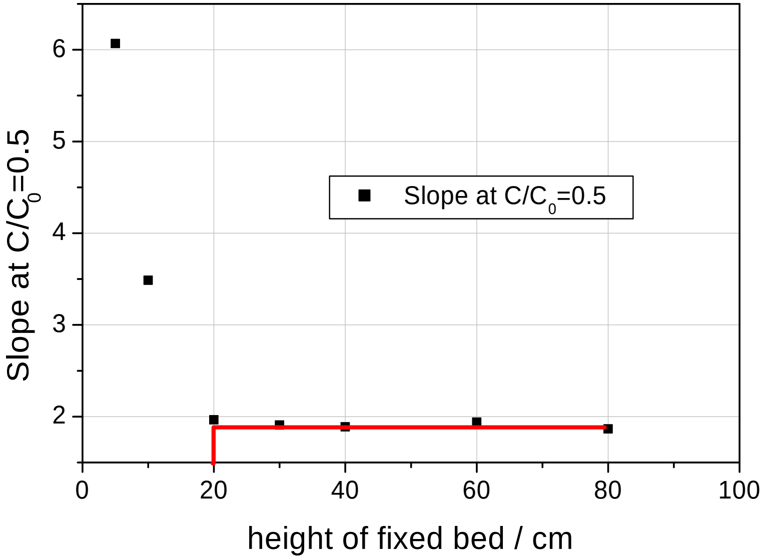
Calculation of Constant Pattern Profiles

For favored isotherms (Type I-Isotherms) a Constant Pattern Behavior can occur

- Shape of breakthrough will not change for longer elongation times or adsorber heights, respectively
- Based on compensation of flattening and rising effects
- Height for Constant Pattern = f(Shape of Isotherm, Dispersion, Kinetics)







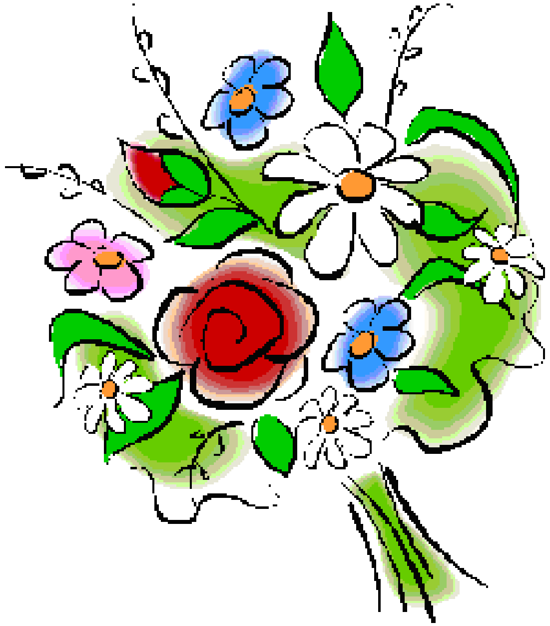
5% CO$_2$ in He at 40°C, 5 bar, 1000 ml/min on D 55/1.5

Experiment carried out at 20 cm, simulations were performed for different heights

→ Slopes at C/C$_0$=0.5 were used to evaluate steepness of breakthrough curves
→ Constant Pattern Behavior can be expect above 20 cm bed height

Conclusions

- **Equilibria of mixtures and selectivities** are **important** for applications
  - Knowledge of such data are highly valuable and of great interest
- however much **more difficult to measure**
  - There is a lack of data in literature
- Mixture equilibria can not calculated by textural properties but **partial predictive from pure component isotherms** based on classical thermodynamic Models.
- **Predictions have some limits! → Number of components, vapors, non-ideal systems…, experiments are mandatory**
- Mixture Models necessary for calculations of dynamic processes



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