Dynamische Methoden in der Adsorptionstechnik

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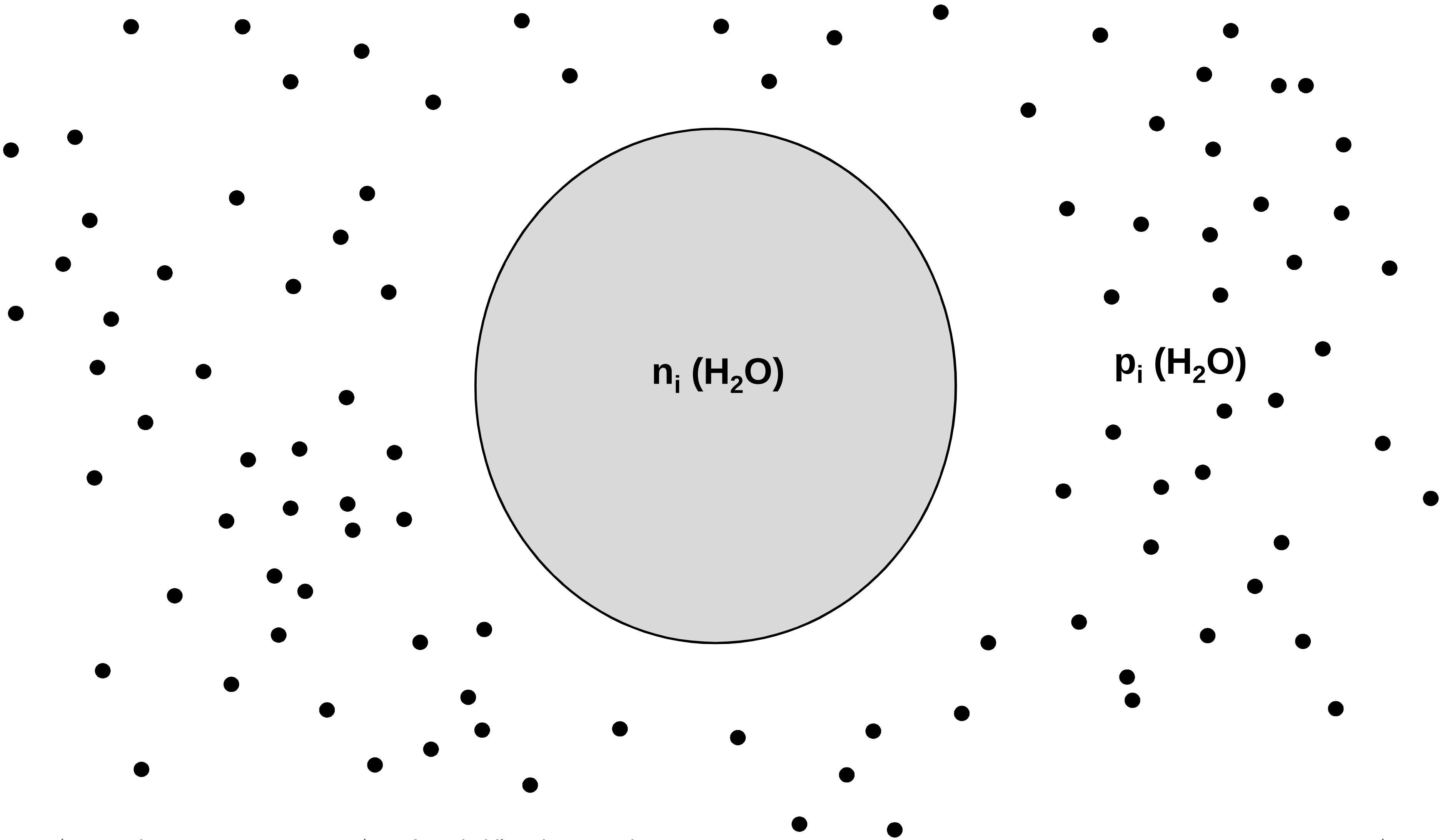
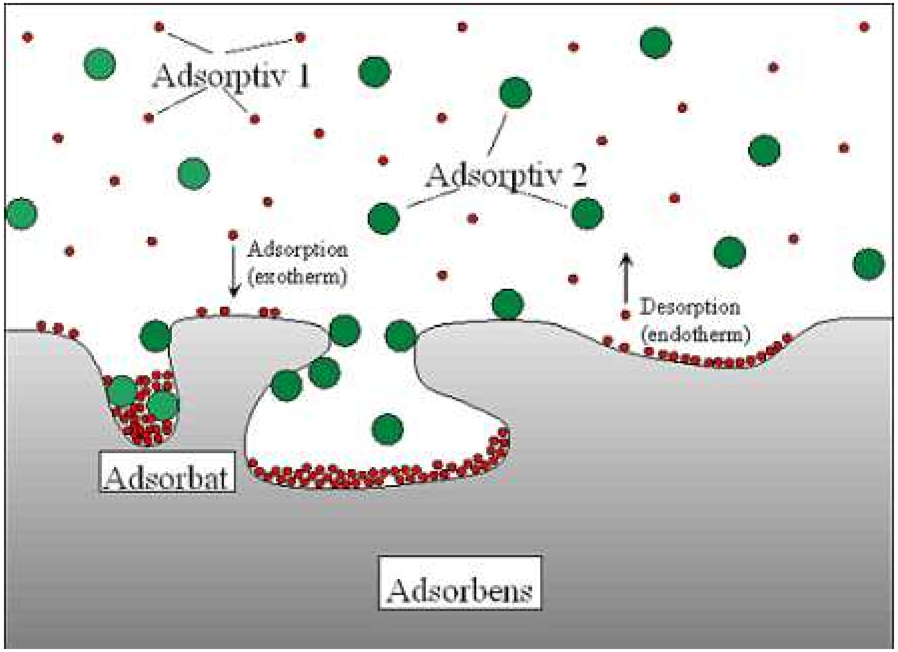
Gliederung

- **Einführung**
  Definitionen, Begriffe
- **Poröse Feststoffe**
  Materialcharakteristik
- **Isothermen**
  Experiment, Isothermengleichungen
- **Kinetik**
  effekt. Transportkoeffizient
- **Wärme**
  isosterische Wärme
- **Gemischadsorption**
  Experiment, Modelle
- **Reale Anwendungen**
  TSA, PSA, Wärme

Adsorption
Isothermal Equilibrium



Adsorption on surfaces / separation effects



Technical usable effects

Thermodynamic effect (differences between the sorption capacities)

Knowledge of Isotherms

Kinetic effect (differences between the sorption velocities)

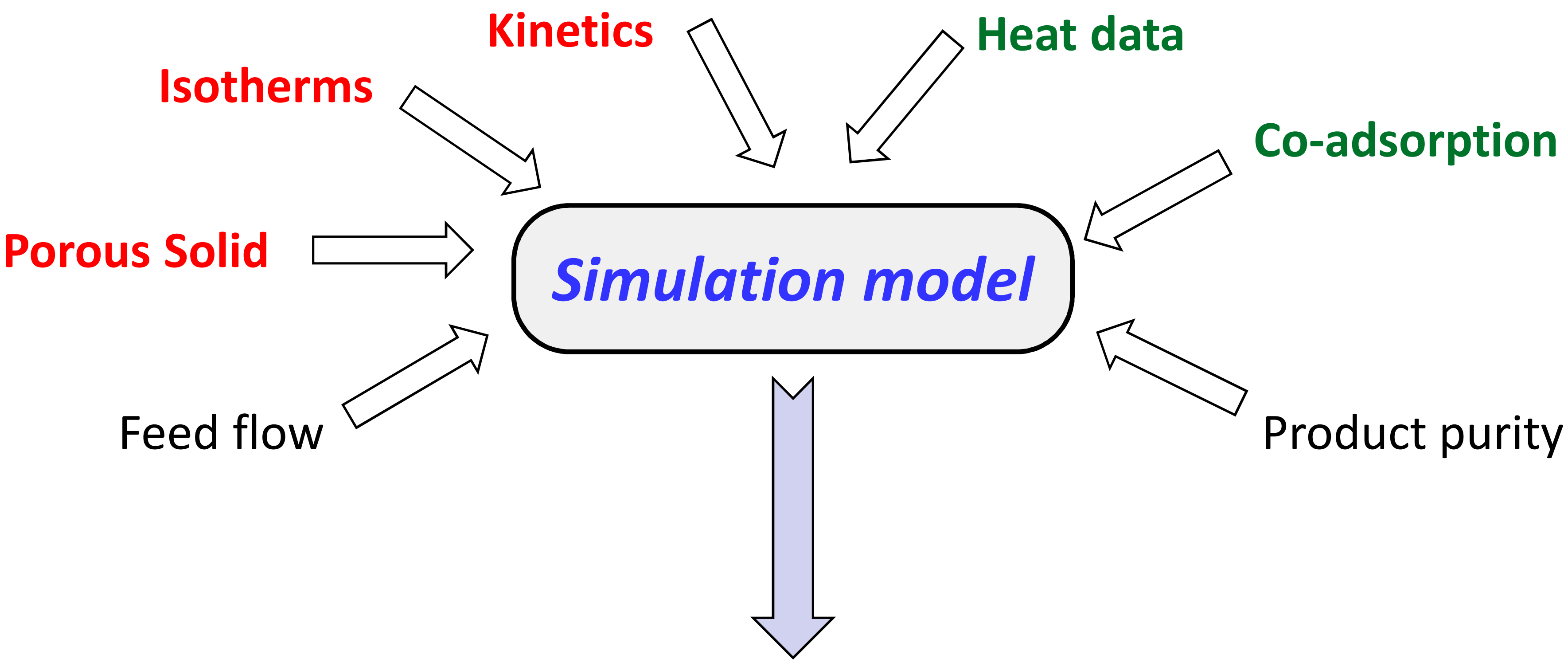
Knowledge of transport coefficients

Steric effect (molecular sieve effect)

Knowledge geometrical parameters

Adsorption process - Input Data

Prediction of breakthrough curves



Cycle duration, Dimension of adsorber…

Modeling – Unknown Parameter

Parameter		Get from	Alternative
Mass Balance			
D_{ax}	*Axial Dispersion Coefficient*	*Breakthrough on fixed bed (for example inert material)*	*Calculation from gas velocity particle size and other Parameters* [1,2]
k_{eff}	*Mass Transfer Coefficient*	*Fitting the model on breakthrough Curves*	*From Uptake rate experiments?*
$n(c_i)$	*Adsorbed amount*	*From Isotherms*	*Breakthrough exp.*
Energy Balances			
Δh	*Heat of adsorption*	*From Isotherms*	*Breakthrough exp.*
λ	*Dispersion Coefficient*	*Experiments on packed beds (Breakthrough exp.)* [3]	*Set Zero to simplify energy balance*
h_w, U_g	*Heat transfer Coefficients*	*Fitting the model on breakthrough Curves*	*Fitting the model on breakthrough Curves*

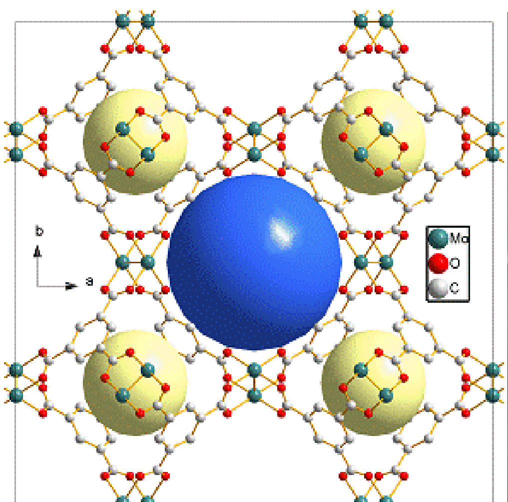
1) W. Kast, Adsorption aus der Gasphase, (1988)
2) F.V.S. Lopes et al., *Sep. Sci. Technol.* 44 (**2009**)
3) V.S. Prasad et al., *Int. J. of Heat and Mass Transfer* 45 (**2002**)

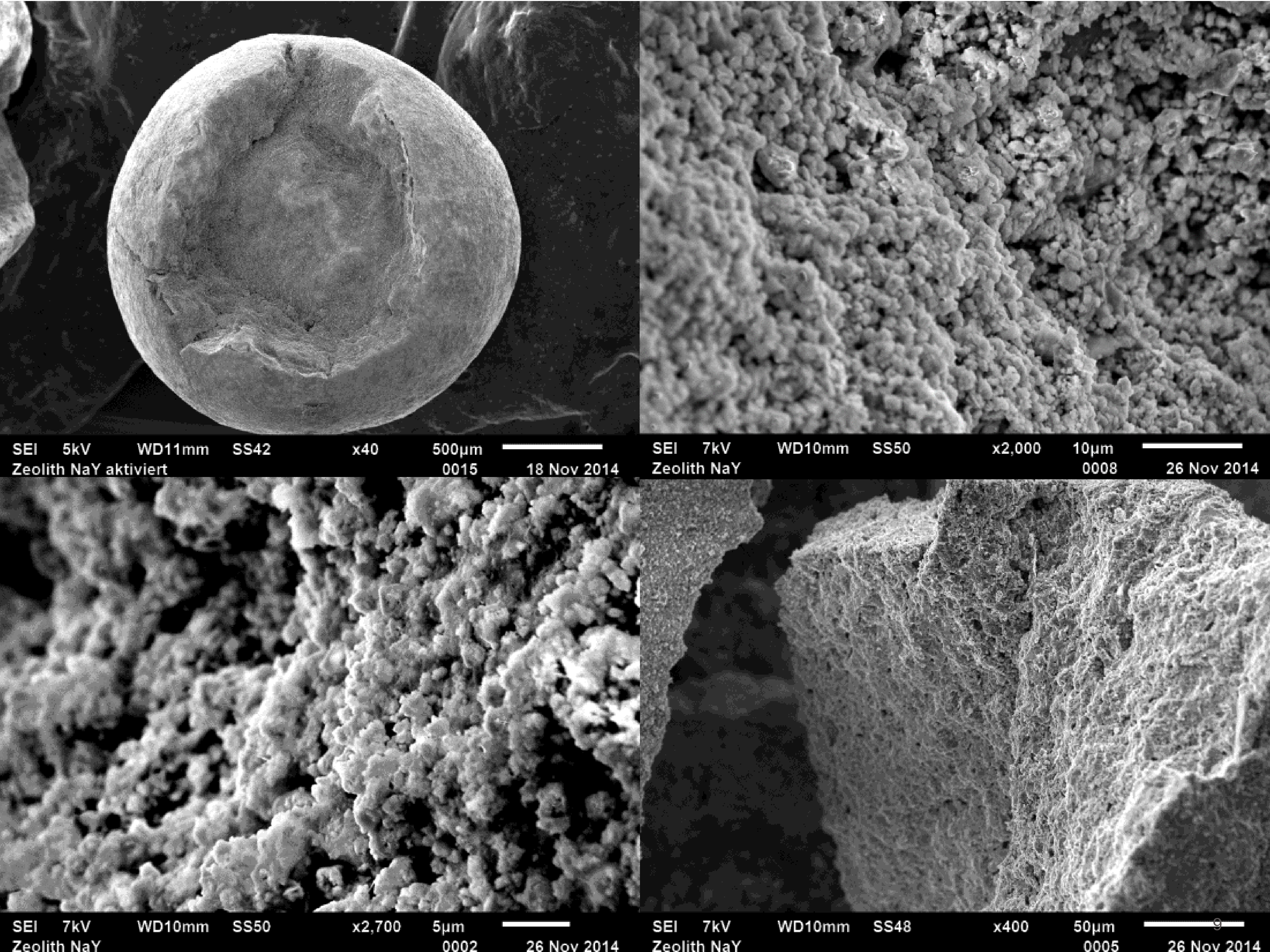
Modeling – Unknown Parameter

Parameter		Get from	Alternative
Thermophysical Properties			
c_{PS}	*Heat capacity of porous material*	*Literature*	*Experiments*
c_{PG}	*Heat capacity of gas phase*	*Literature*	*Experiments*
q_i^*	*Density of gas phase*	*Equation of State*	*Experiments*
ρ_W	*Heat capacity of wall*	*Literature*	*Experiments*
α_W α_{WL}	*Surface to Volume ratio*	*Geometry*	

Porous materials

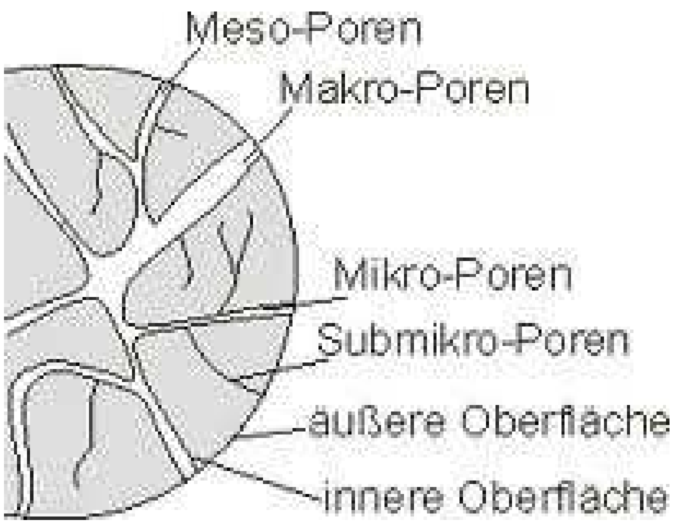
- Activated Carbon
- Zeolite
- Molecular sieve
- Silicagel
- MOF

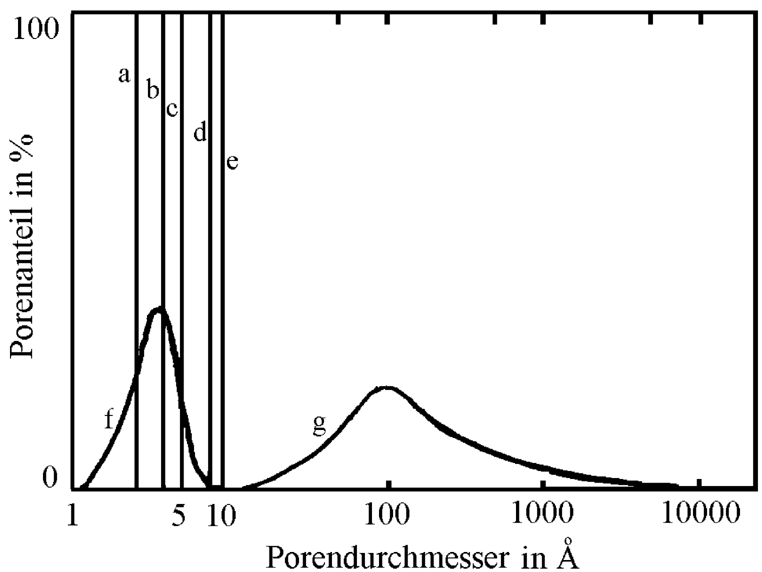



SEI 5kV WD11mm SS42 x40 500µm
Zeolith NaY aktiviert 0015 18 Nov 2014
SEI 7kV WD10mm SS50 x2,000 10µm
Zeolith NaY 0008 26 Nov 2014
SEI 7kV WD10mm SS50 x2,700 5µm
Zeolith NaY 0002 26 Nov 2014
SEI 7kV WD10mm SS48 x400 50µm
Zeolith NaY 0005 26 Nov 2014

Classification of pores

Submicropores	d ≤ 0,4 nm
Mikropores	0,4 < d ≤ 2,0 nm
Mesopores	2,0 < d ≤ 50 nm
Makropores	d > 50 nm



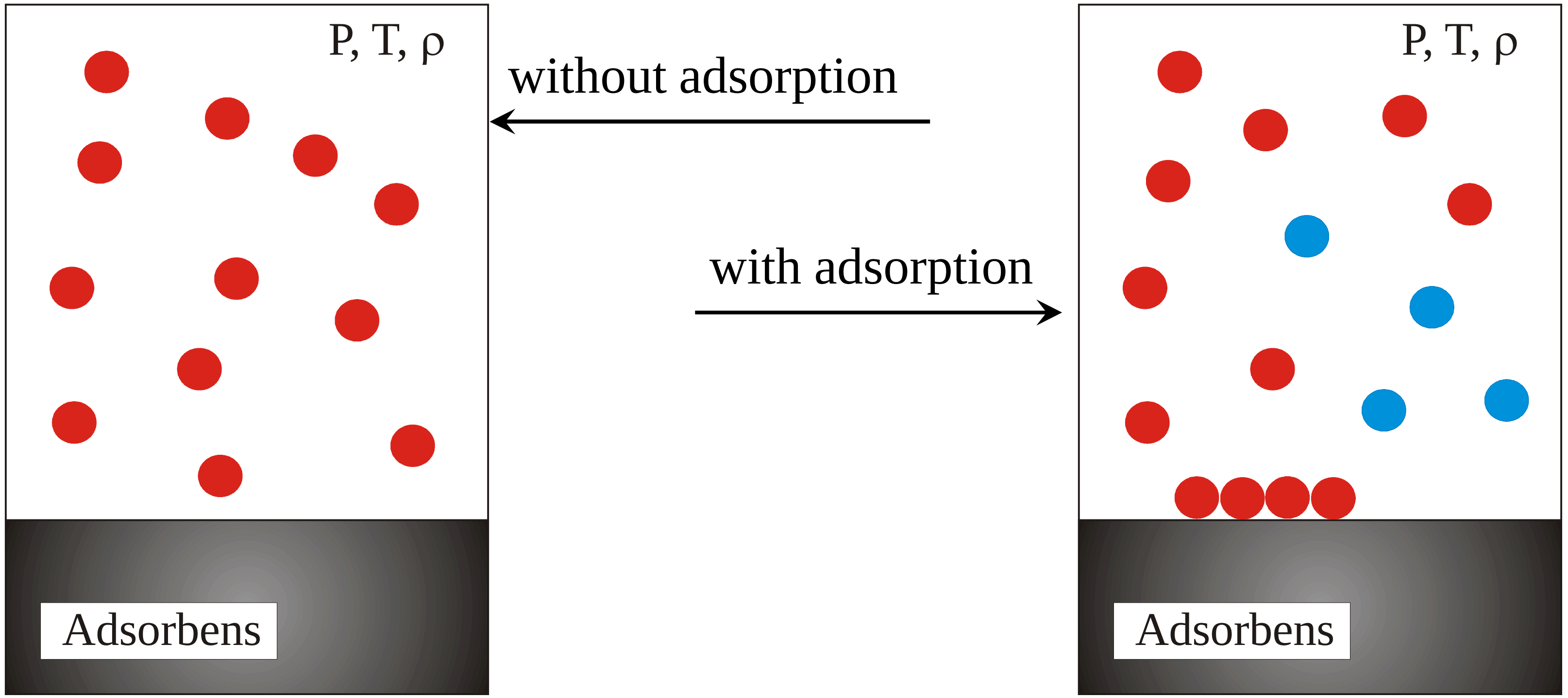


Quelle: VDI-Richtlinie 3674
http://www.chemgapedia.de

Characterisation of porous materials

- Pore size distribution: DIN 66135
- BET surface, pore radius: DIN 66135
- Iodine number: ASTM D4607 – 94
- Water content: DIN 51718
- Ashes content: DIN 51719
- Density (bulk, Helium)
- Abrasion, Paricle size distribution
- Benzole Adsorption at rel. Pressure: 0.9, 0.1, 0.01, 0.001
- VDI-Richtlinie 3674

Excess amount adsorbed

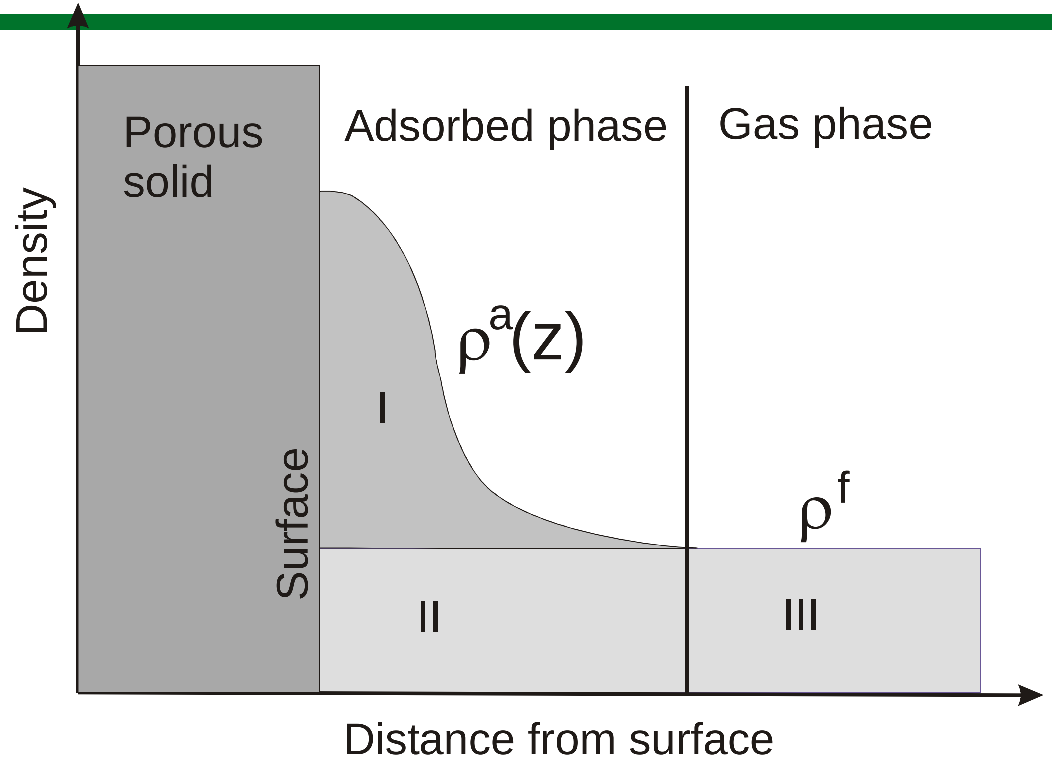


Gibbs definition of
excess amount adsorbed

$$m_{GE} = \left(\rho^{f} - \rho^{f'}\right)\left(V - V^{s}\right)$$

Total mass in system m_{total}	12 + 4
Mass in gas phase m^{f}	8 + 4
Gibbs excess mass m_{GE}	4

Excess amount adsorbed



Total mass in system m_{total} (I + II + III)

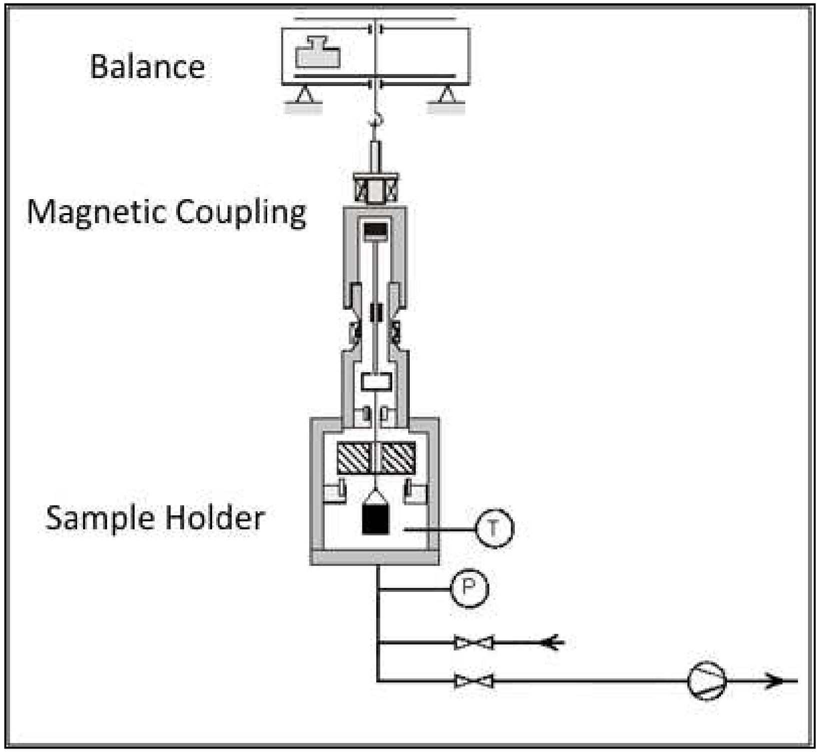
Volume of Gas phase $V^f = V - V^{Solid}$

Mass in gas phase m^f (II + III)

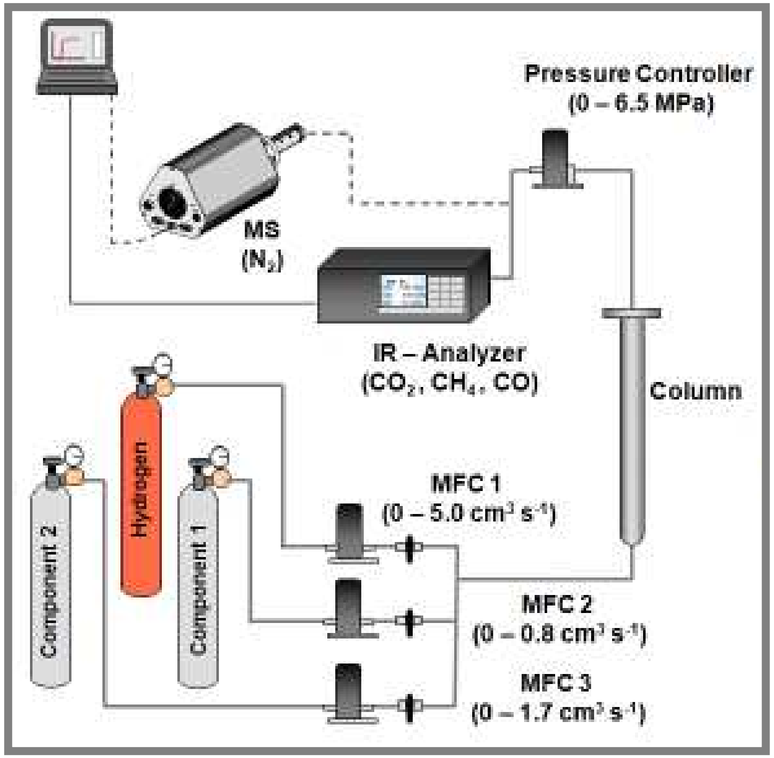
Gibbs excess mass $m_{GE} = m_{total} - m^f$ (I)

Experiment

Isotherms



Breakthrough Curves



- Isotherms of pure components
- Pressures up to 3.5 MPa
- Temperature range: 260 to 700 K

- Breakthrough curves
- Pressures up to 1.0 MPa
- Ambient temperature

Procedure of measurement I

Start: Calibration of instrument
→ Volume of Sample
→ Dead volume

Step 1: Measurements without sample
→ Value of unloaded microbalance
→ Value of unloaded adsorber

Step 2: Installation of sample

Step 3: Activation / regeneration of sample
→ Mass lost of sample by desorption

Procedure of measurement II

Regeneration Process:

- Time (cp. technical process)
- Temperature, Pressure (cp. technical process)
- Gas flow

In Dynamic experiment:

- Close to technical application / real process

Step 4: Measurement with non-adsorbing gas:

→ Helium volume

→ Gas velocity

Helium measurement = reference measurement

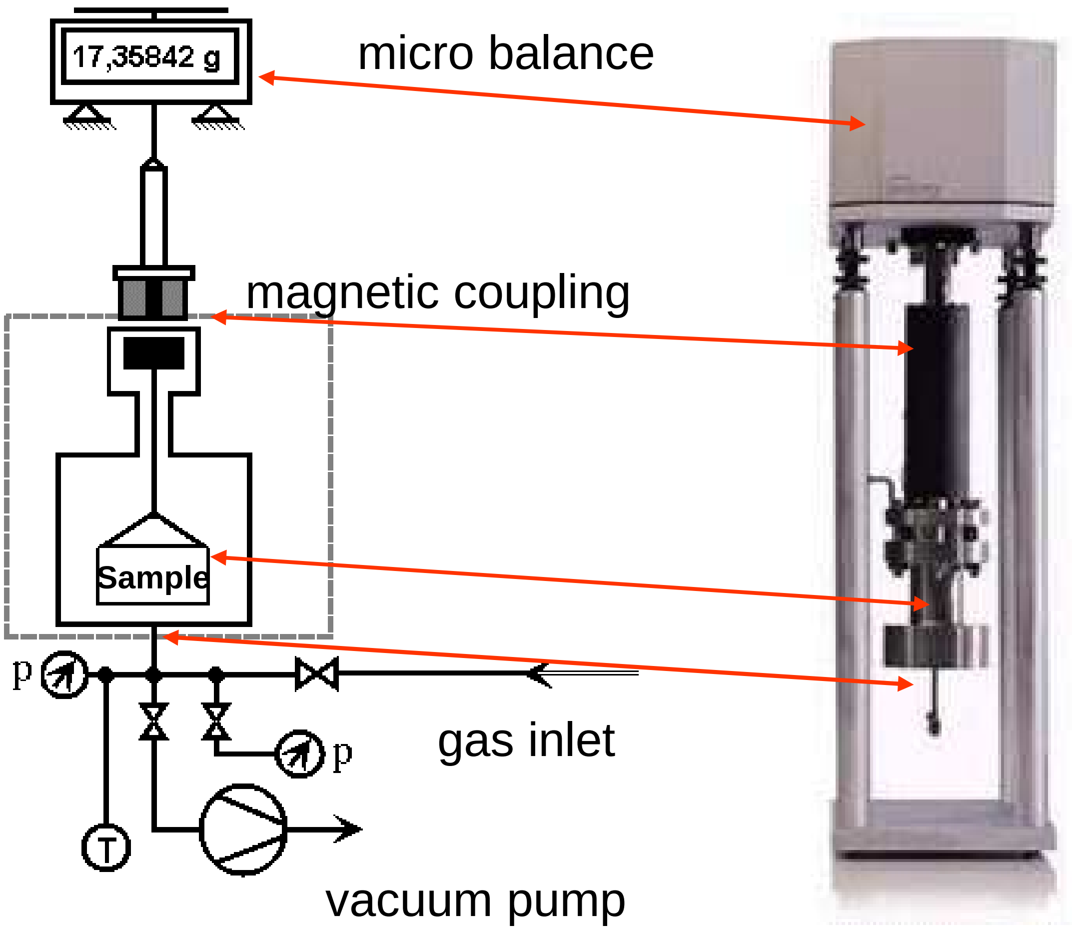
Procedure of measurement III

Step 5: Measurement of adsorption isotherm / break through curve
→ Excess amount adsorbed

Adsorption equilibrium
→ Time (cp. technical process)
→ Constant Microbalance signal

Step 6: Measurement of desorption / regeneration
→ regeneration time and conditions

Instrumental setup



balance

- time-resolution 1 sec
- mass-resolution 10 µg
- temperature RT-500 °C

pressure transducers

- 0.01 mbar – 10 mbar
- 1 mbar - 200 mbar
- 200 mbar - 30 bar

temperature sensor

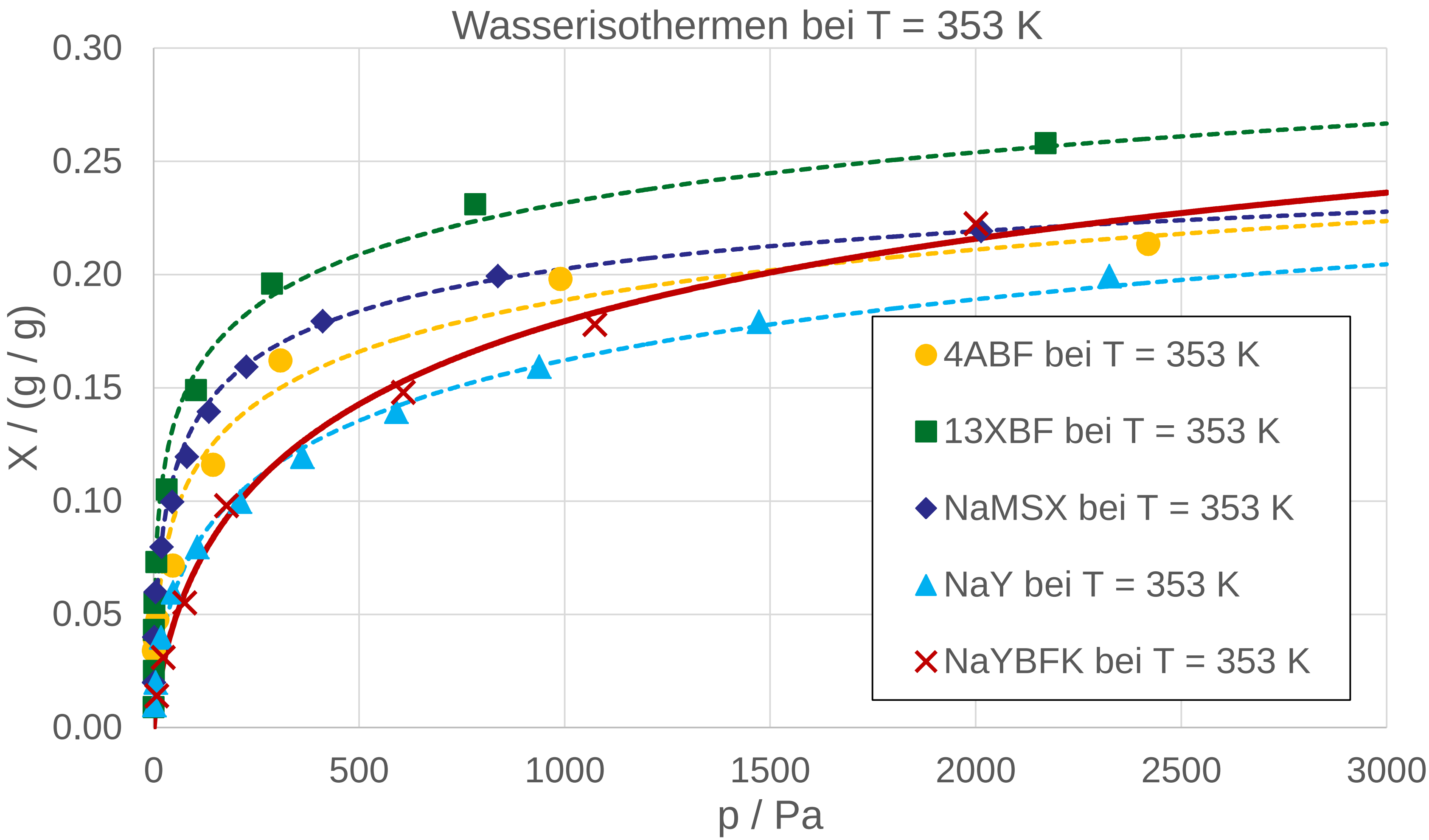
- PT 100 sensor

vacuum

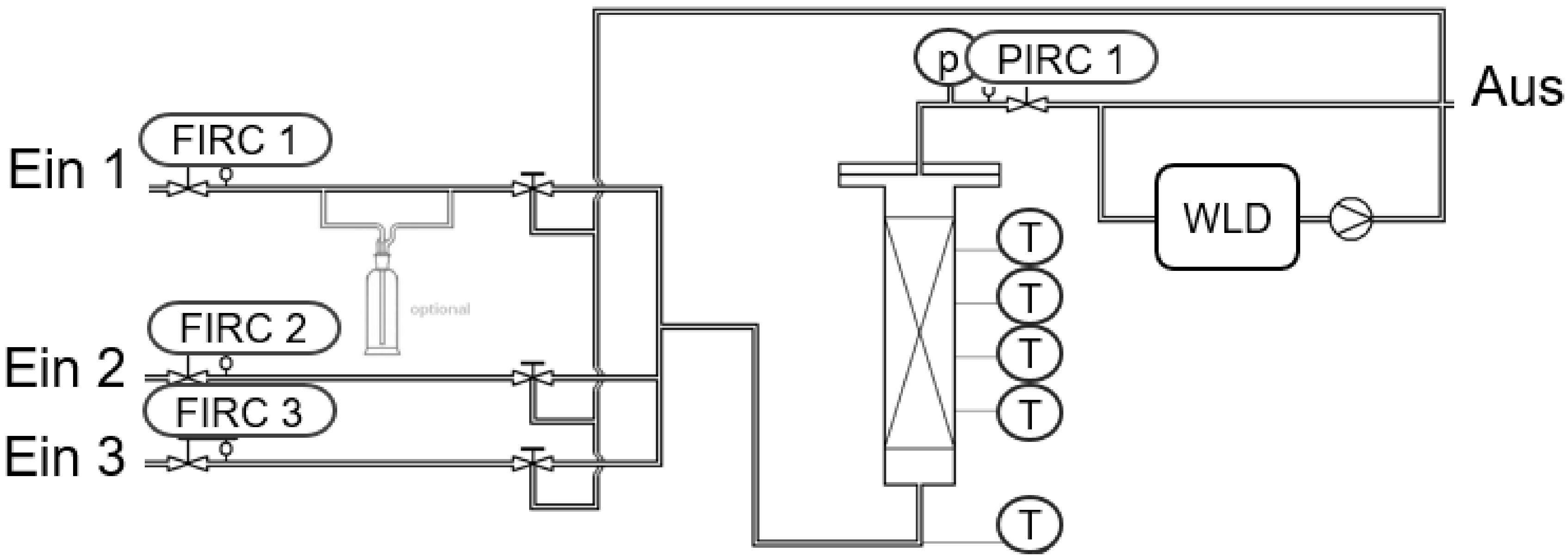
- turbomoleculare pump

Adsorption

Choice of zeolite



INCurves120



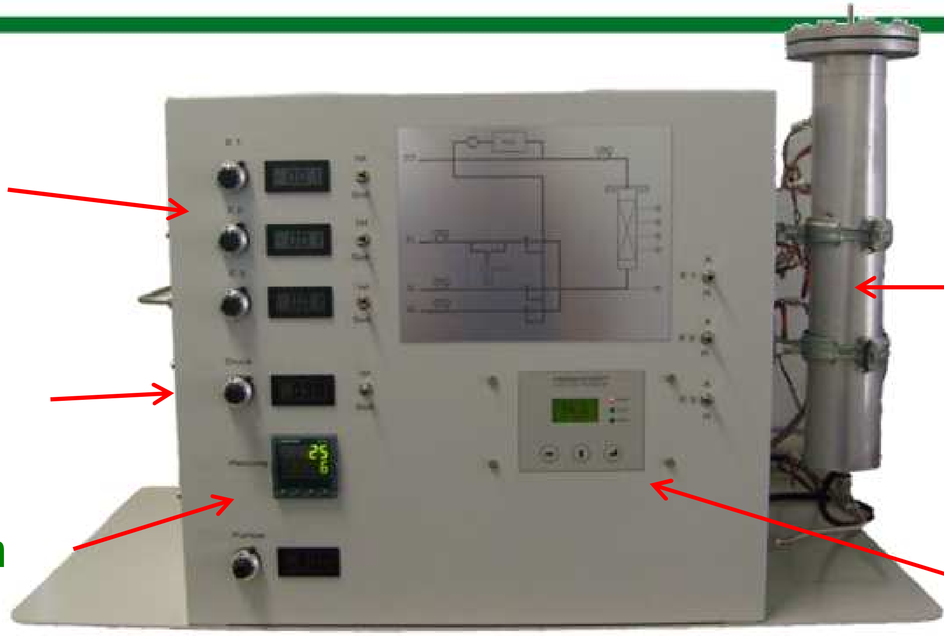
$$\Omega = m - V^{as} \rho^{f}$$

$$= \dot{m}_{flow} * t - V_{col} * \rho^{f}$$

Calibration of instrument: volume, WLD, …

Measurement: concentration c(t), massflow m_{flow} and time t

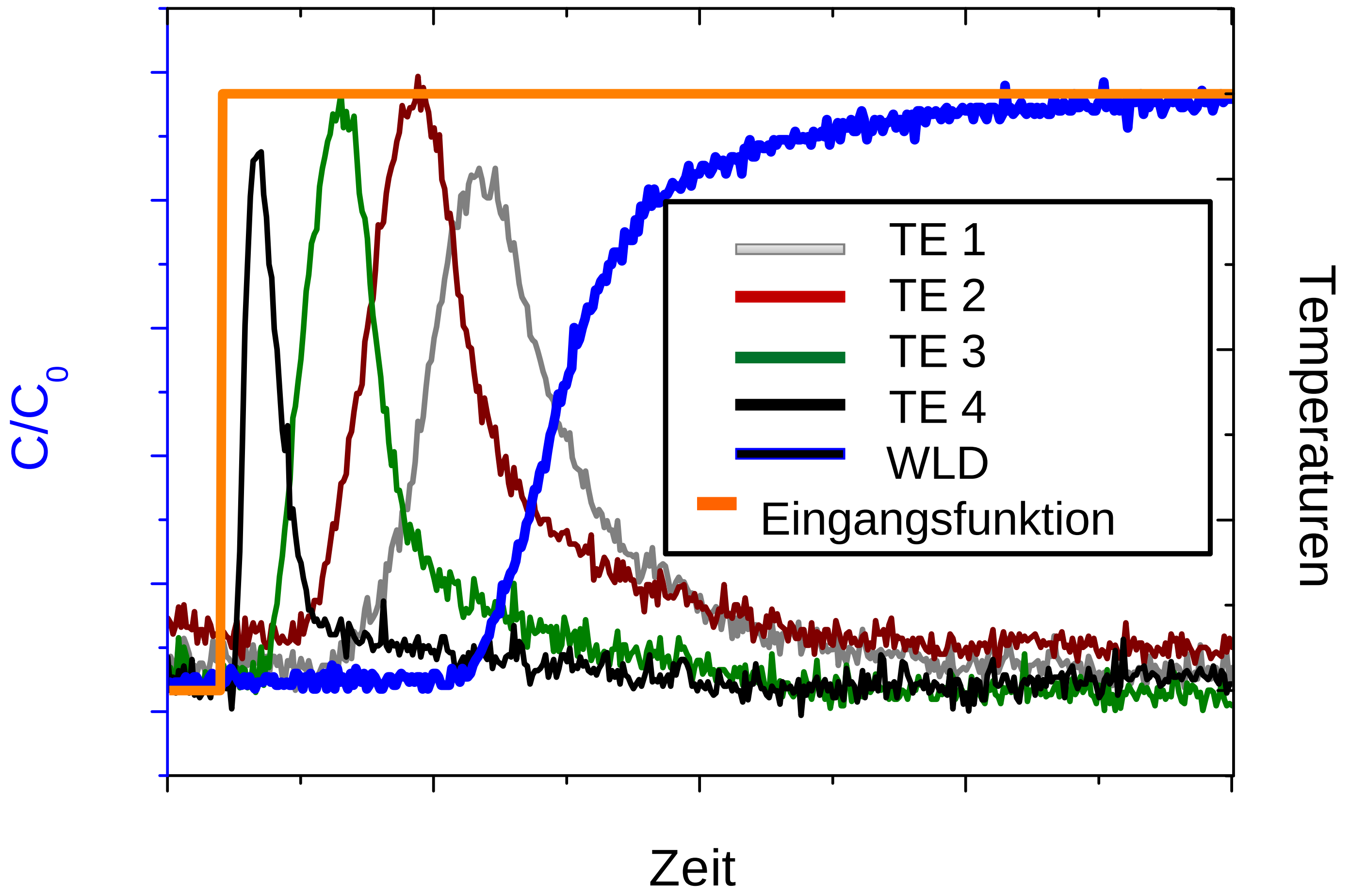
Breakthrough curves

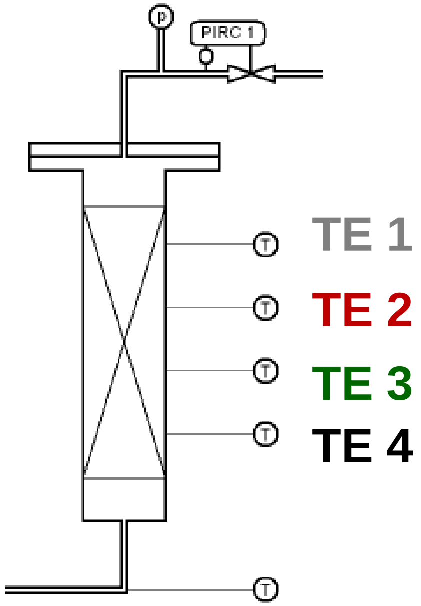


Measurement of breakthrough curves

- on approx. 100 g sample
- up to 10 bar, 3 different gas inlets (2 x 5 NL min^{-1}, 1 x 1 NL min^{-1})
- detection of gas composition with thermal conductivity detector
- measurement of temperature profiles (4 sensors)

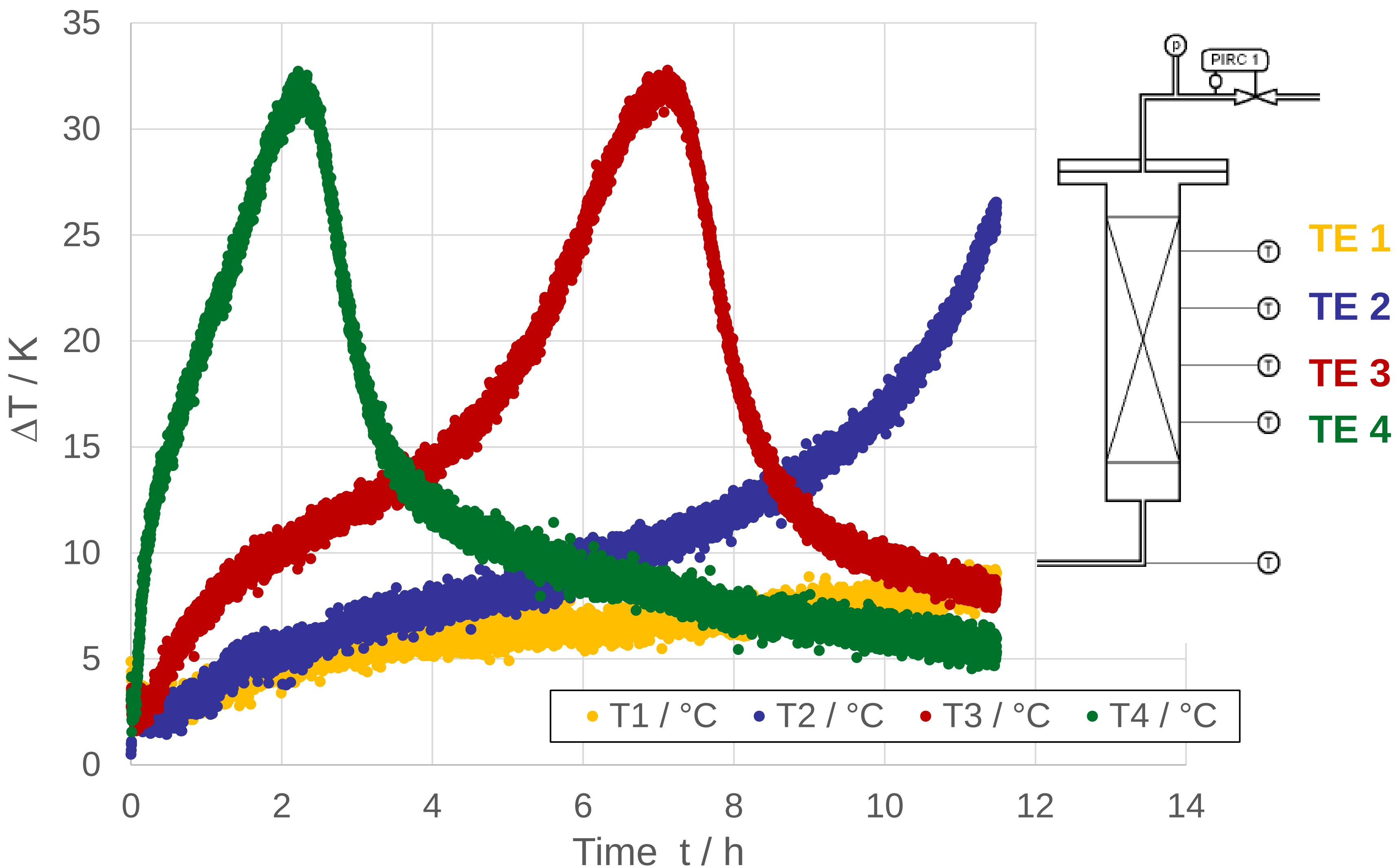
INCurves120





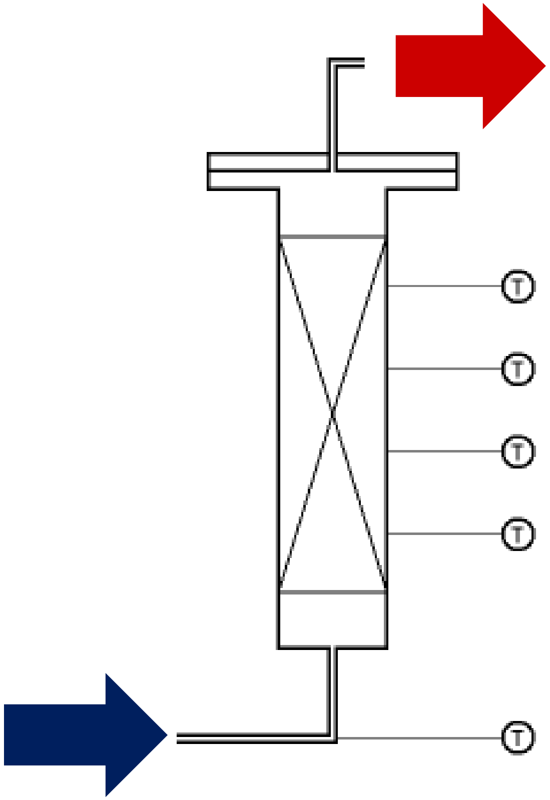
Dynamische Messanordnung für Untersuchungen an Festbett INCurves 120,
Dr. Andreas Möller, Faltblatt DBK (Brochüre INC); 2013

Reactor without isolation

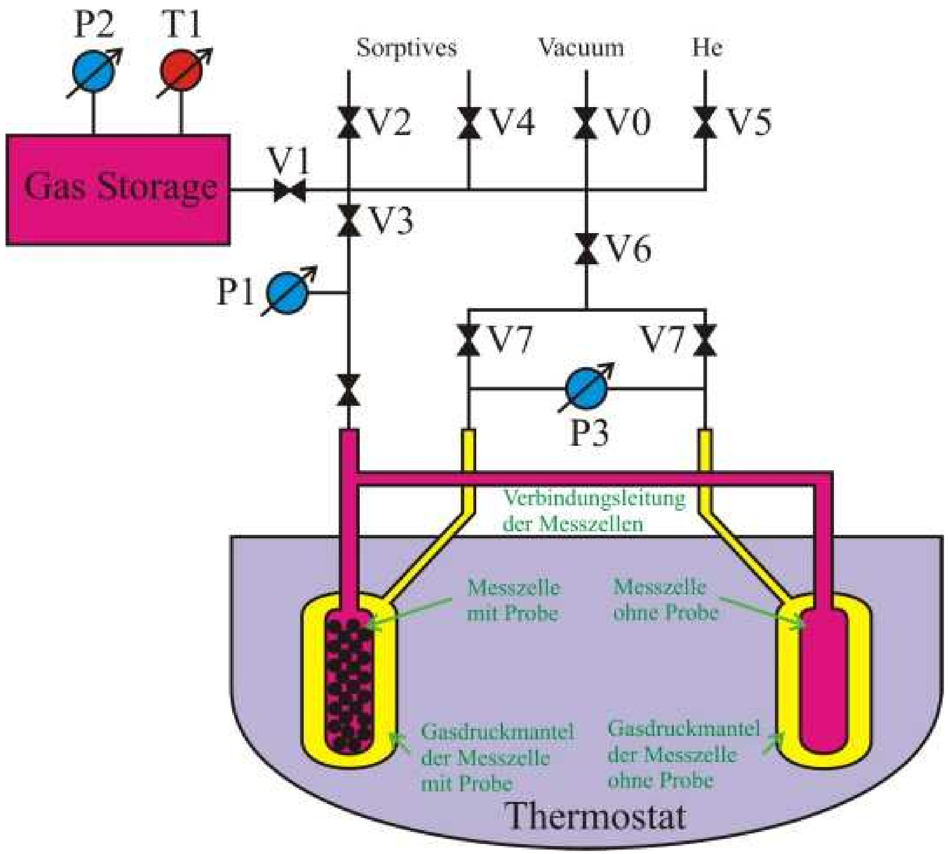


Fascination

Zeolite - Water

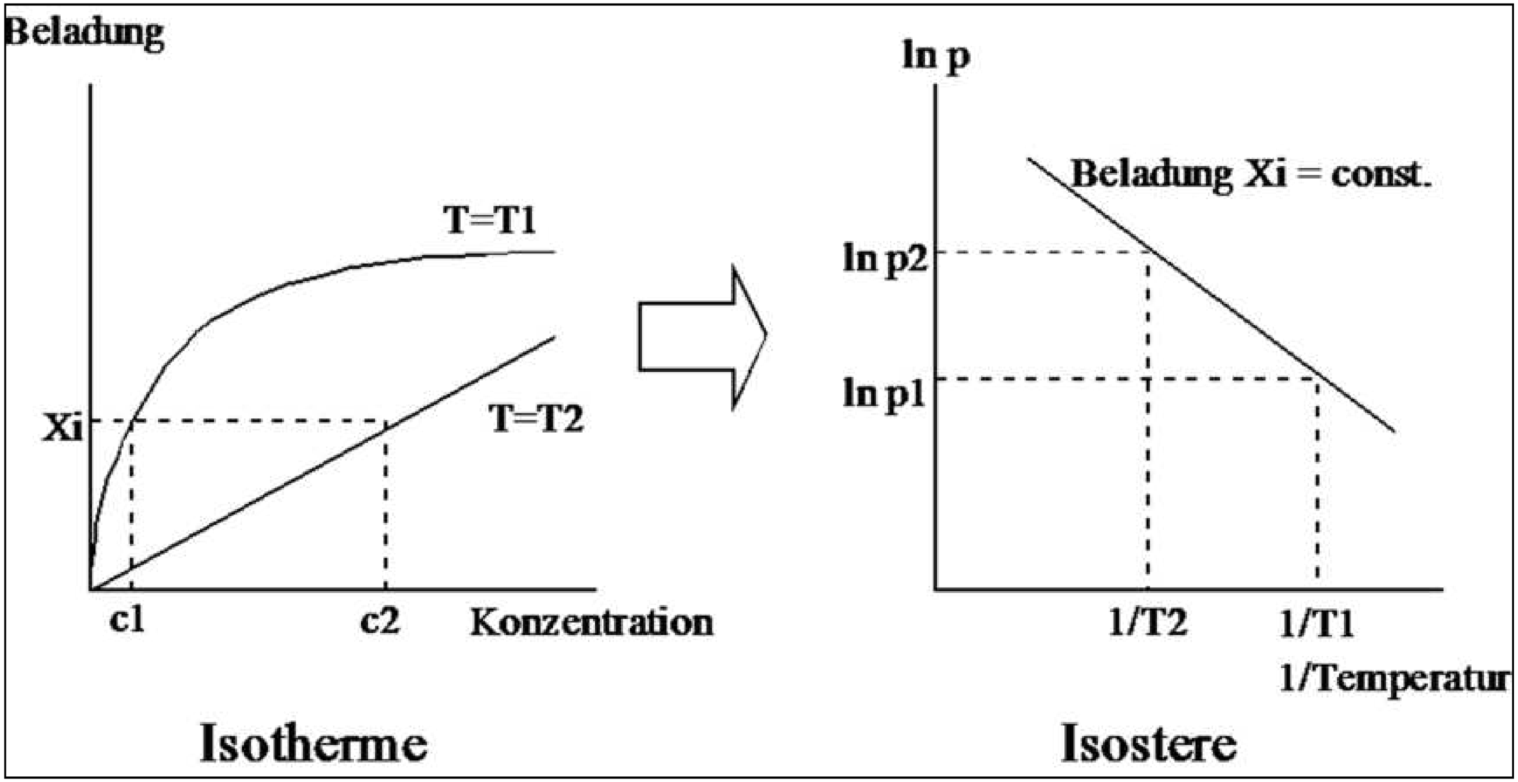


Heat of Adsorption - Experiment



Quelle: Zimmermann/Keller Universität Siegen

Isosteric heat of adsorption

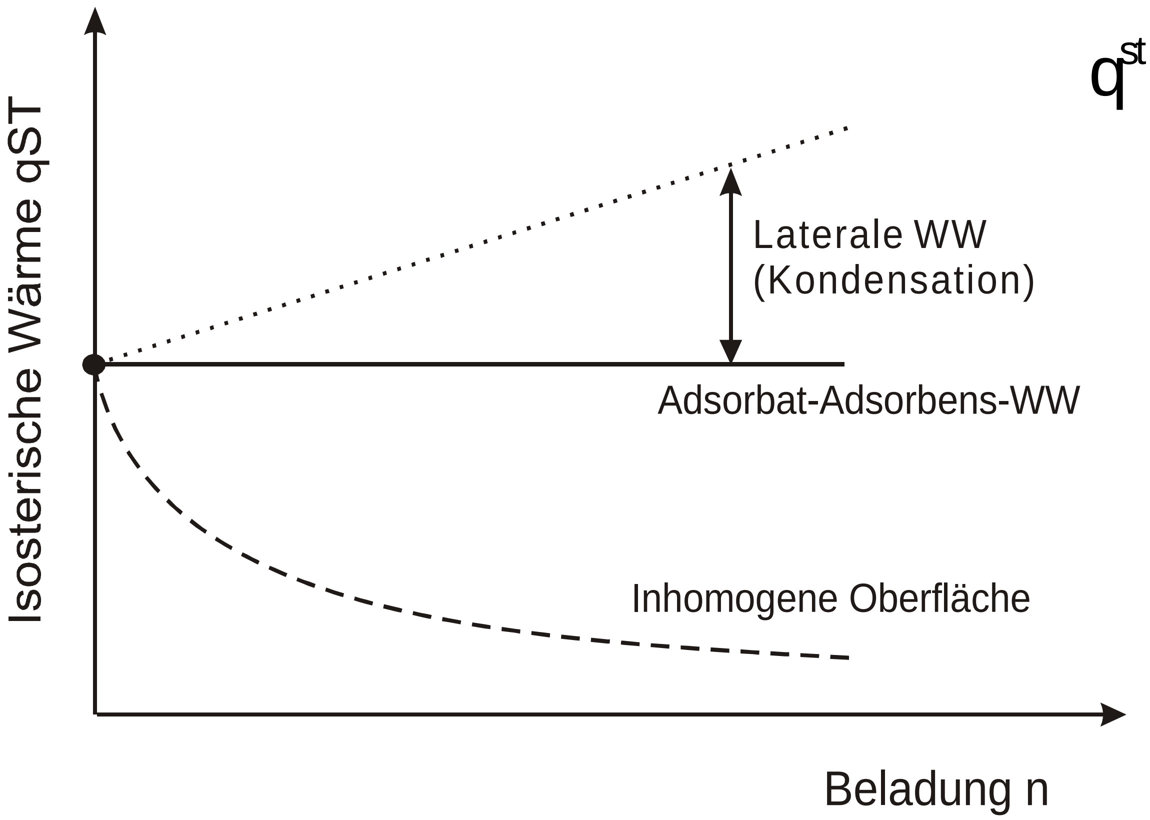


cp. Clausius Clapeyron

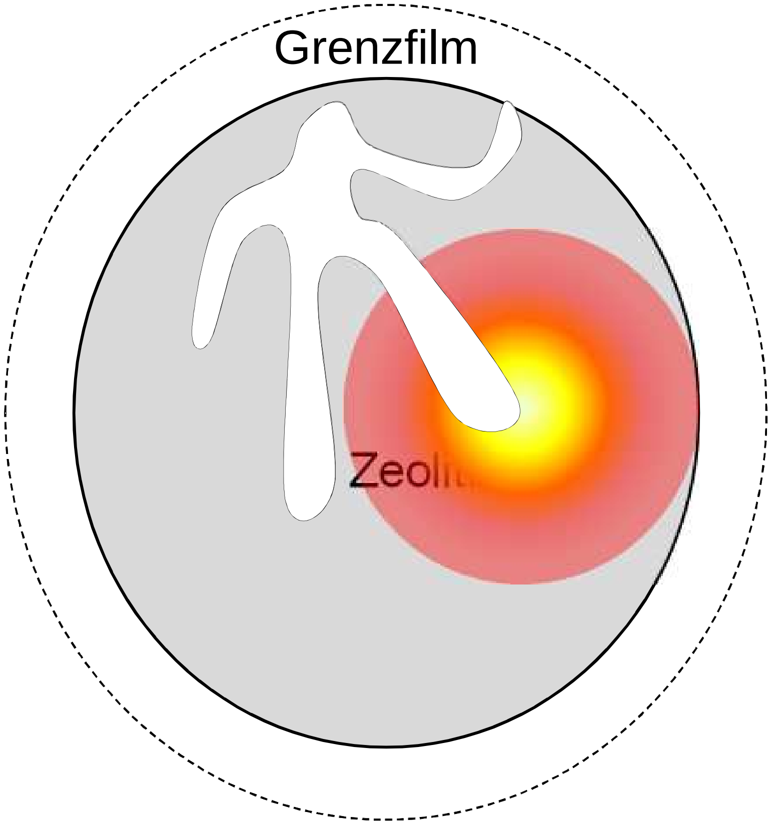
$$q^{st} = \frac{R\ T_1\ T_2}{T_2 - T_1}\left(\ln\frac{p_2(c_2)}{p_1(c_1)}\right)_{xi}$$

Heat of adsorption

$$q^{st} = \frac{R\ T_1\ T_2}{T_2 - T_1}\left(\ln\frac{p_2(c_2)}{p_1(c_1)}\right)_{xi}$$



Kinetics of Adsorption



Transportmechanismen:

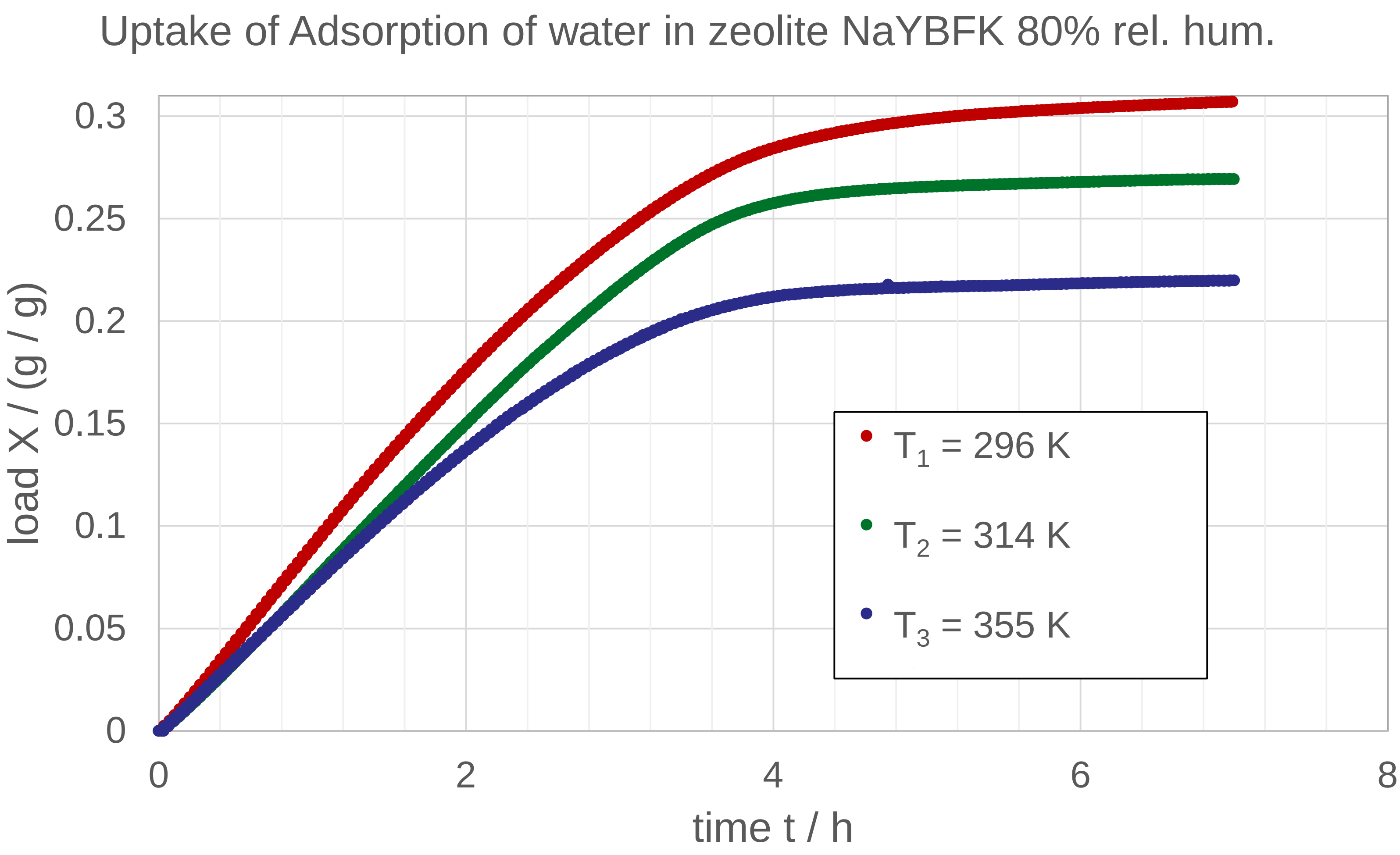
- Festbettdiffusion
- Grenzfilmdiffusion
- Porendiffusion

Linear Driving Force

Zusätzlich:

- Wärmetönung

Gravimetric experiment



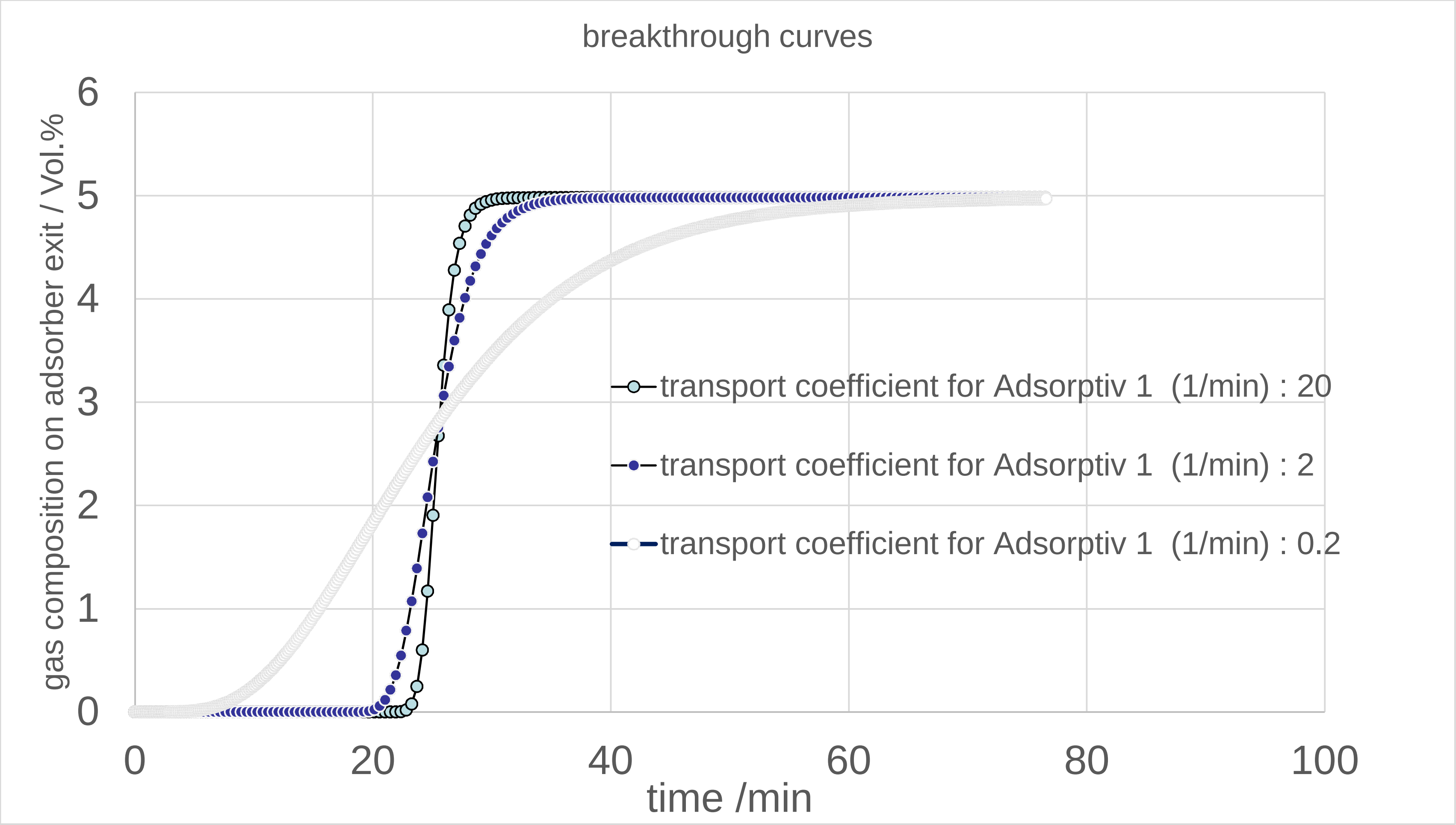
Kinetics - Linear Driving Force

$$\frac{dX}{dt} = k_{eff} \cdot \frac{A_{Partikel}}{\rho_P} \cdot (X_{GG} - X)$$

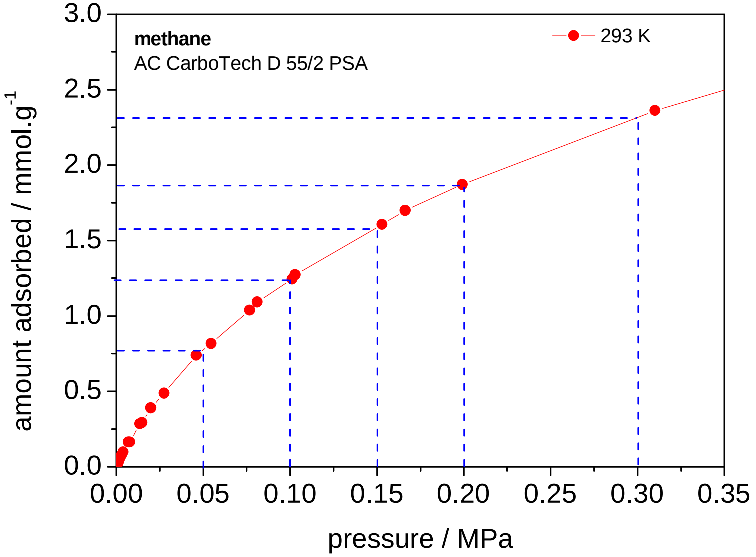
ΔX → concentration gradient

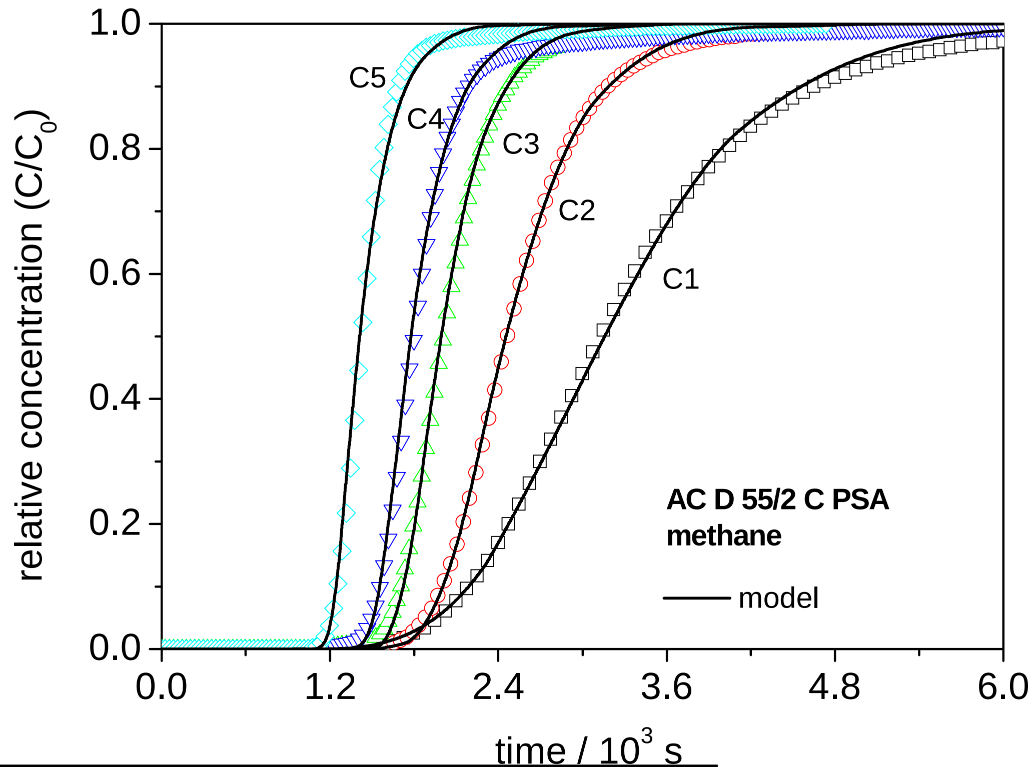
k_{eff} → effective transport coeffizient

Kinetics – Transport coefficient



Hydrogen Purification - Results for methane

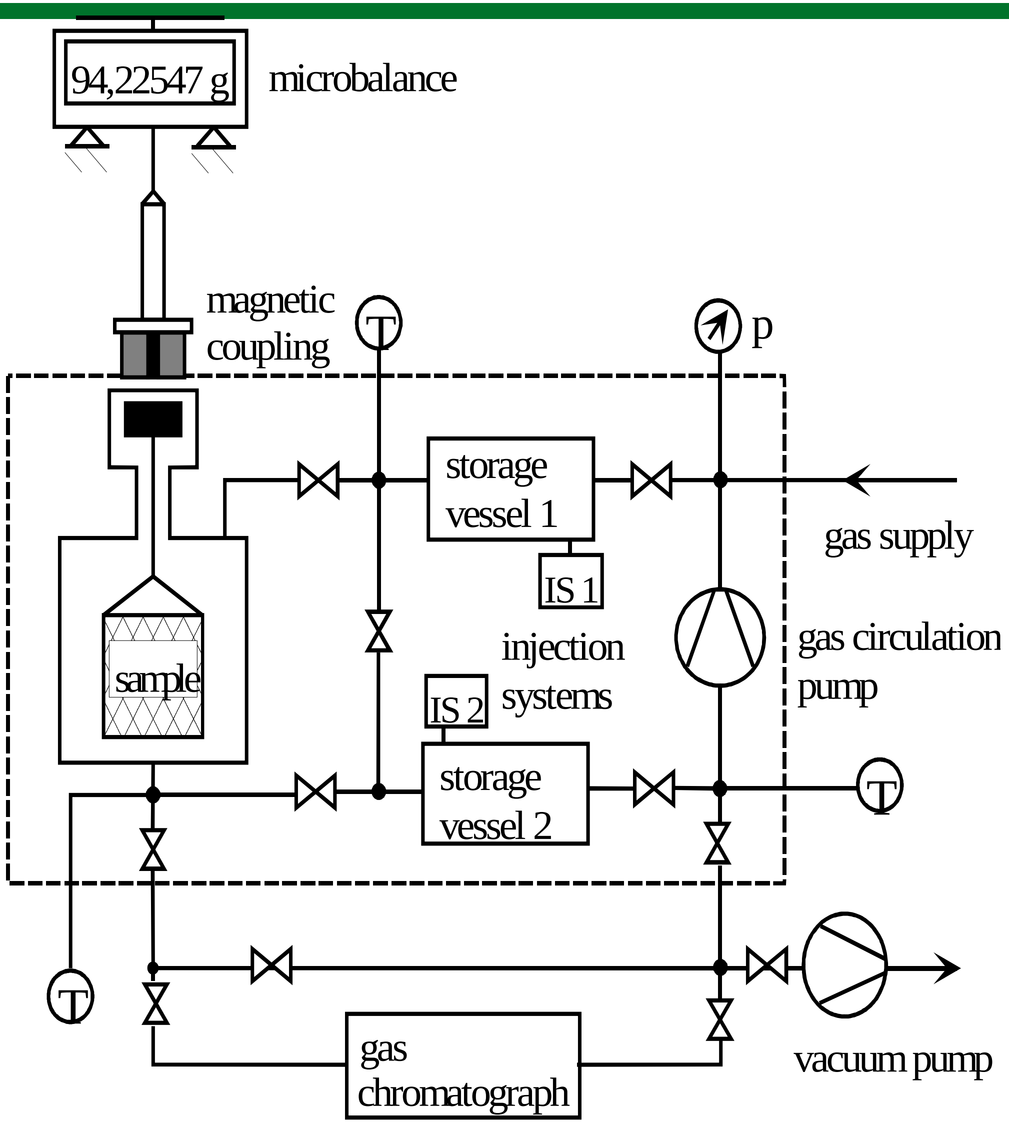




Feed	**Experimental run**				
v_{Feed} = const.	**C1**	**C2**	**C3**	**C4**	**C5**
Feed pressure / MPa	0.5	1.0	1.5	2.0	3.0
Feed molar fraction of CH_4 / %	16.5	17.0	17.2	17.2	17.3
Feed flow rate / $cm^3\ s^{-1}$ at SATP	0.74	1.49	2.23	2.98	4.47

* Bastos-Neto et al., *Chem. Ing. Tech.*, **83** (2011)

Volume-Gravimetry & Volumetry with GC



Calibration:
Volume of vessel & sample holder, GC ...

Volume-Gravimetry:

Measurement: p, T, m

Calculation:

m^{fl}_1, m^{fl}_2, m_1, m_2

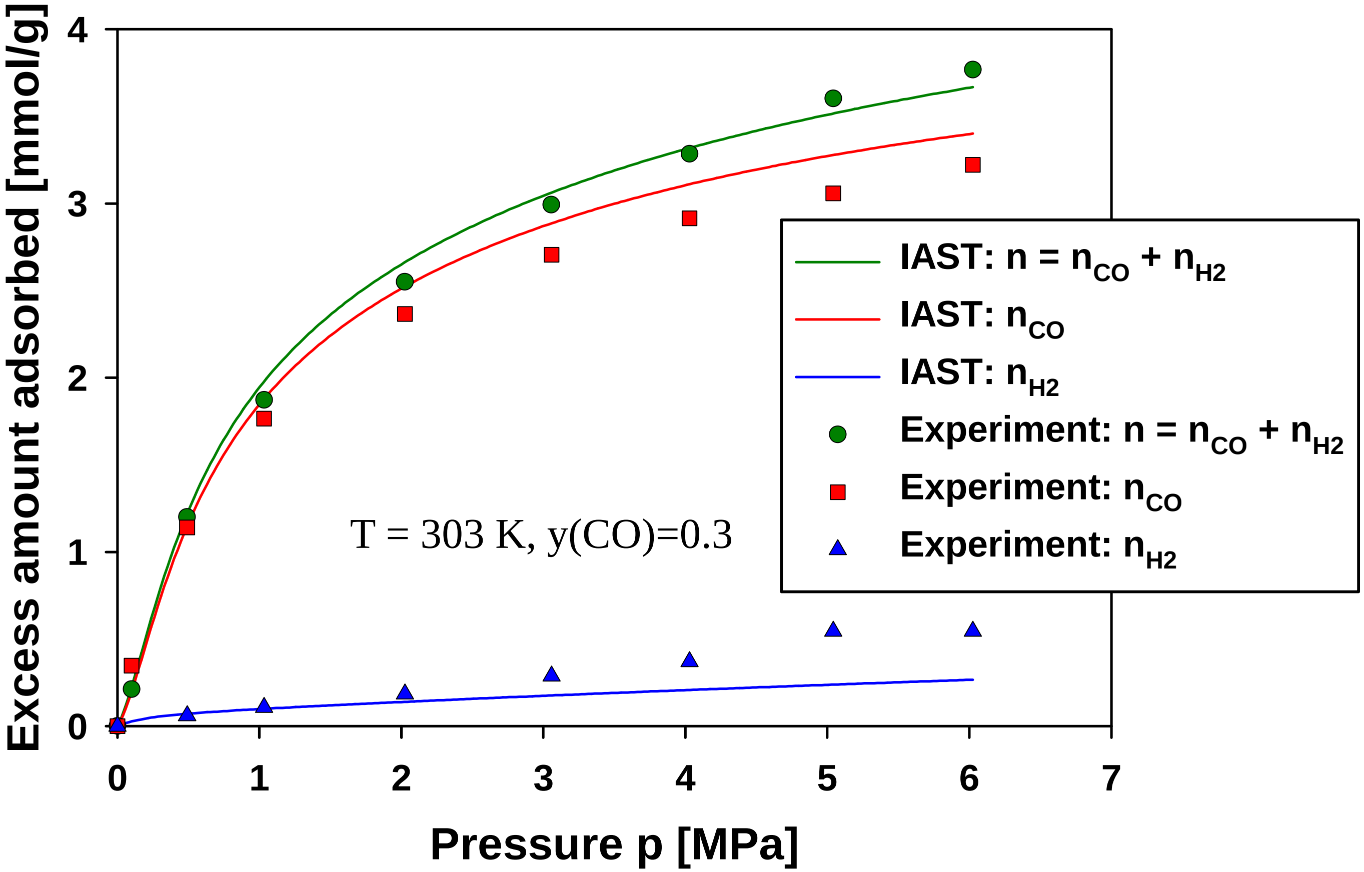
Volumetry with GC:

Measurement: p, T, c

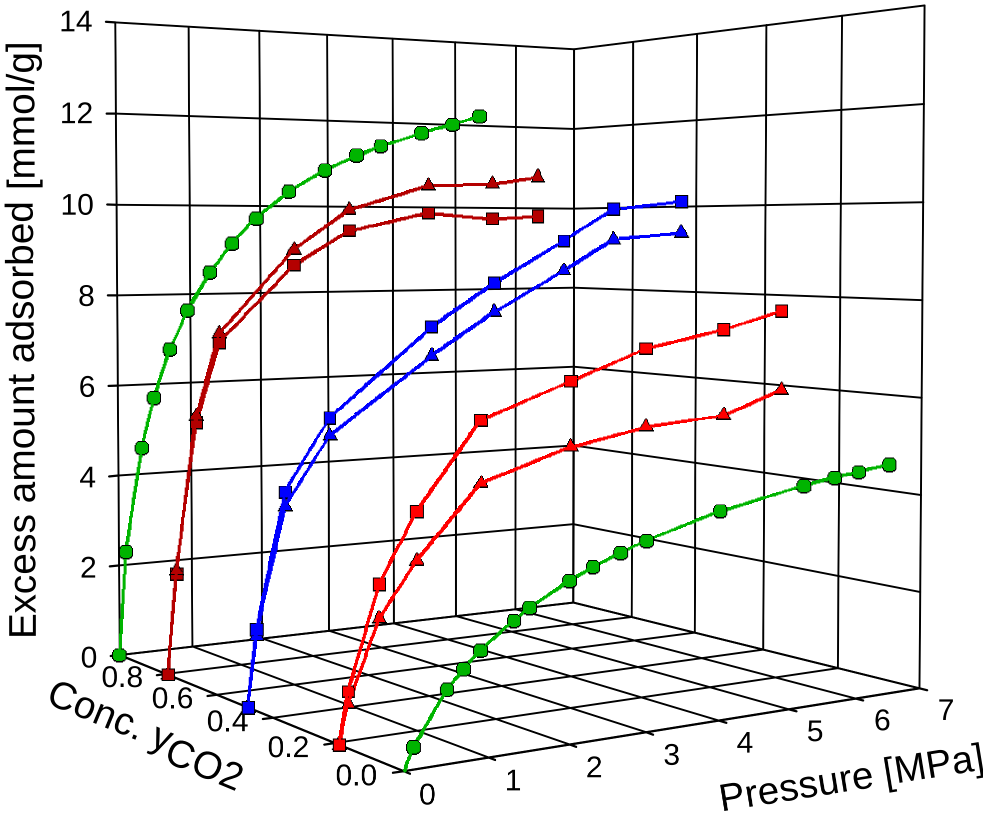
Calculation:

m^{fl}_1, m^{fl}_2, m_1, m_2

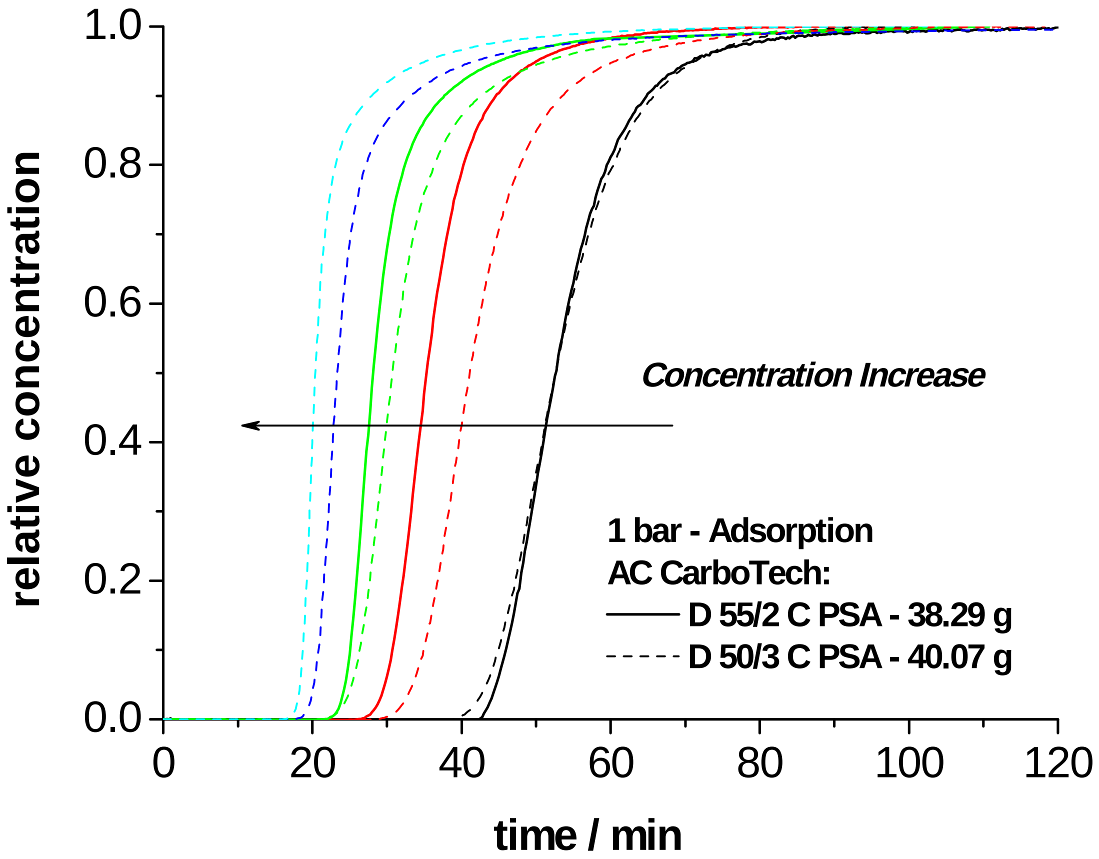
CO/H2 Mixture on 5A Zeolite



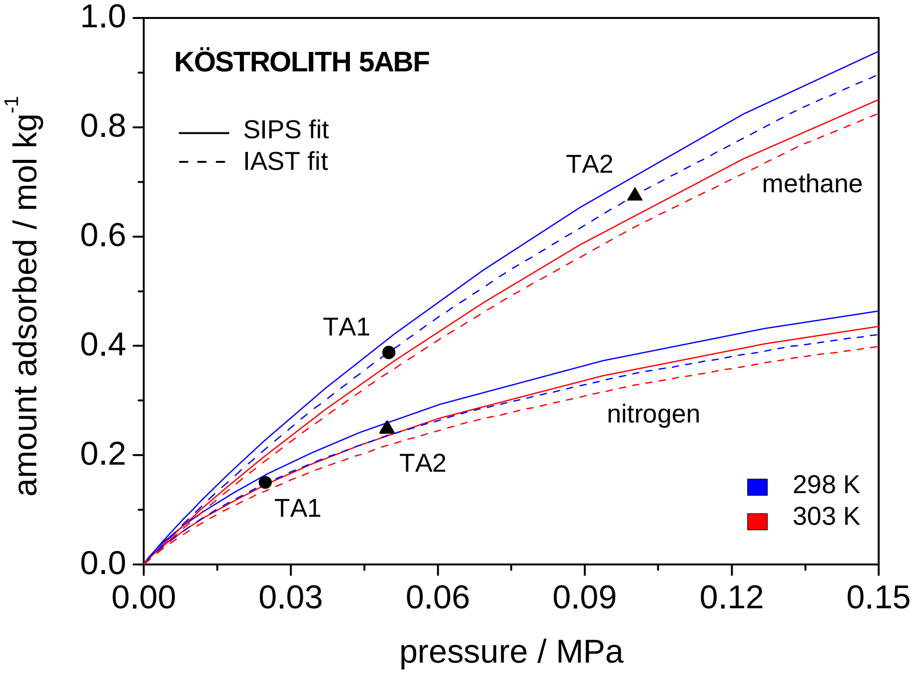
CO2/N2 an AK Norit R1, T = 298 K

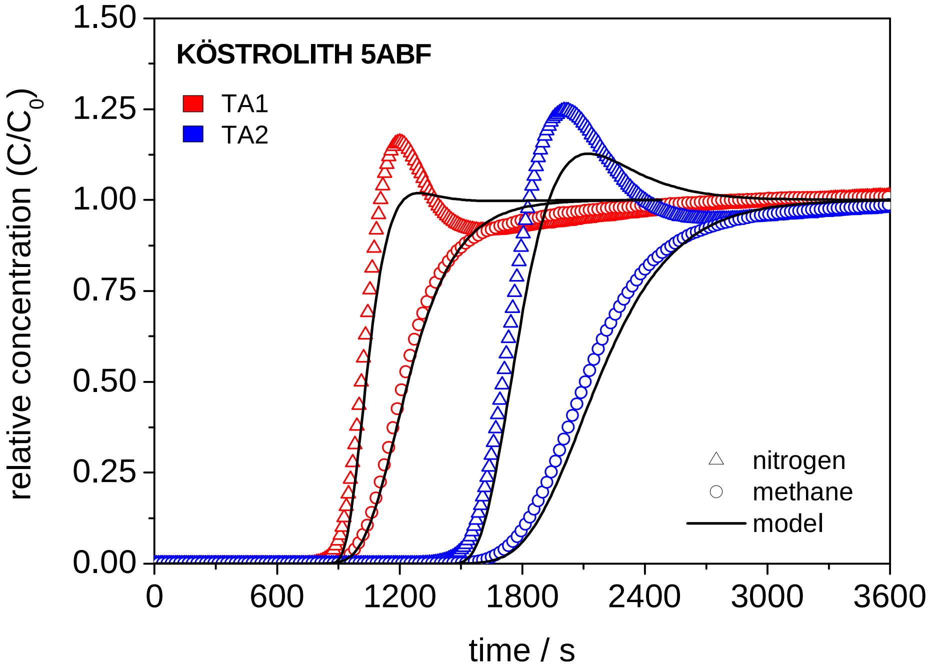


Results - Influence of the input concentration

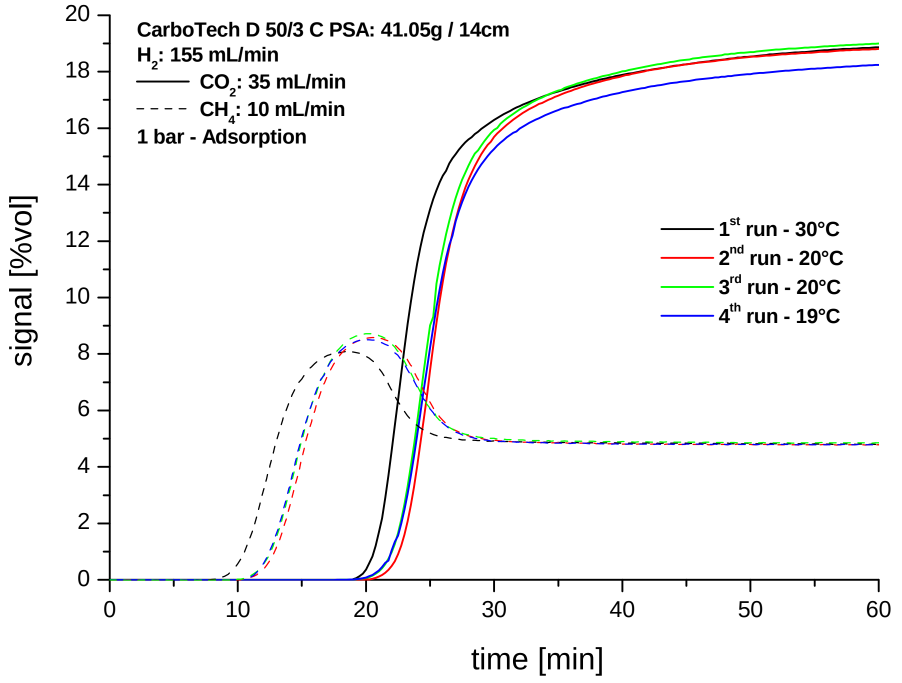


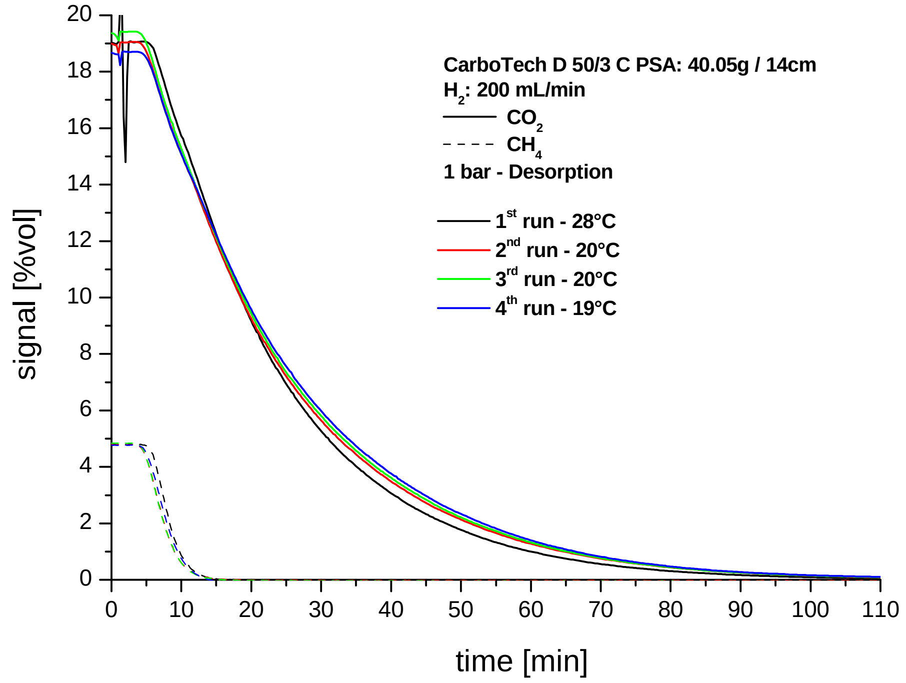
Results - Ternary Mixtures



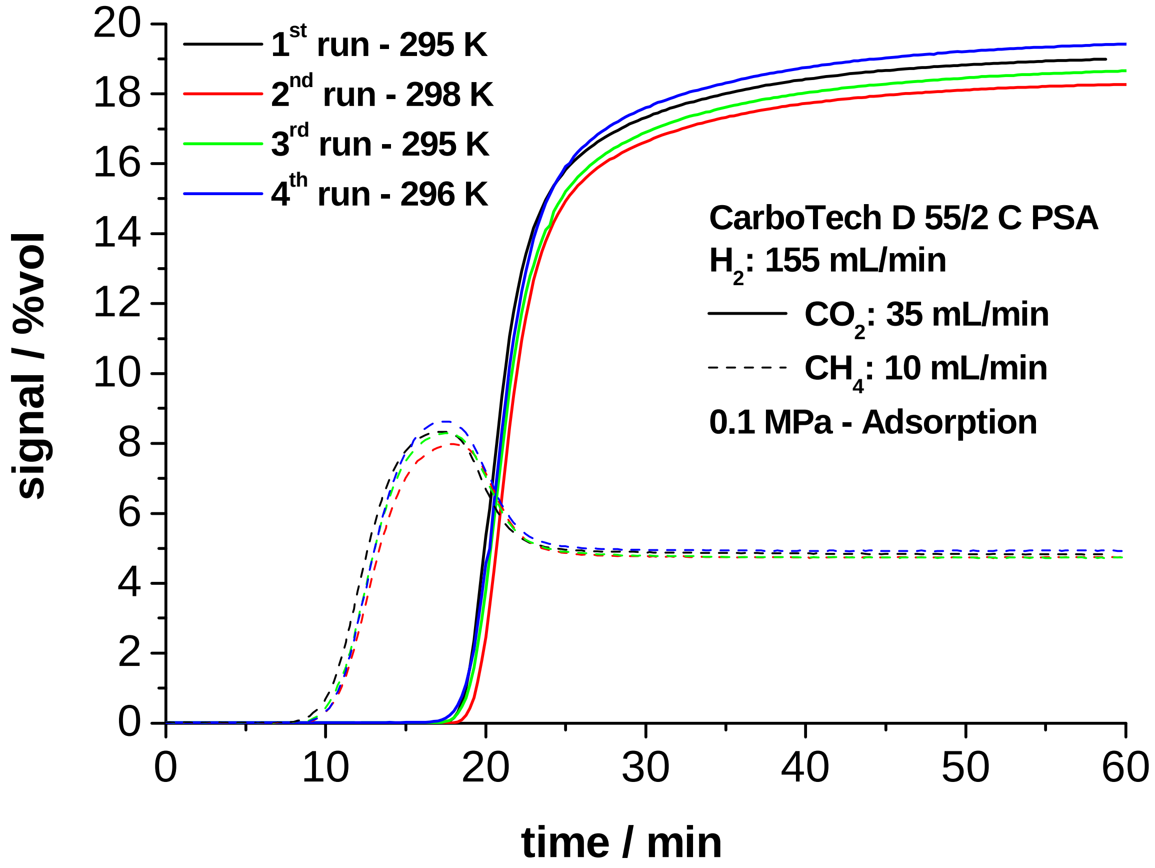


Ternary Mixture $CO_2/CH_4/H_2$ – AC CarboTech D 50/3 C PSA

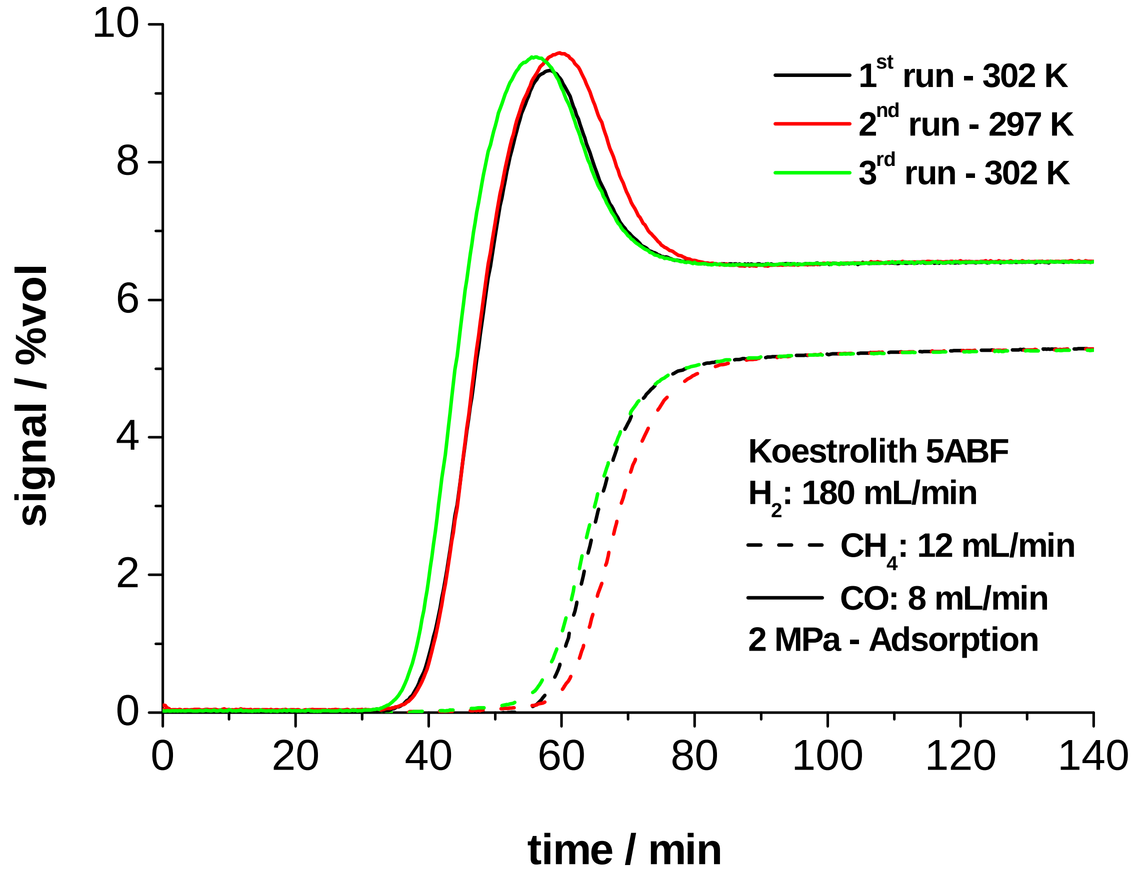




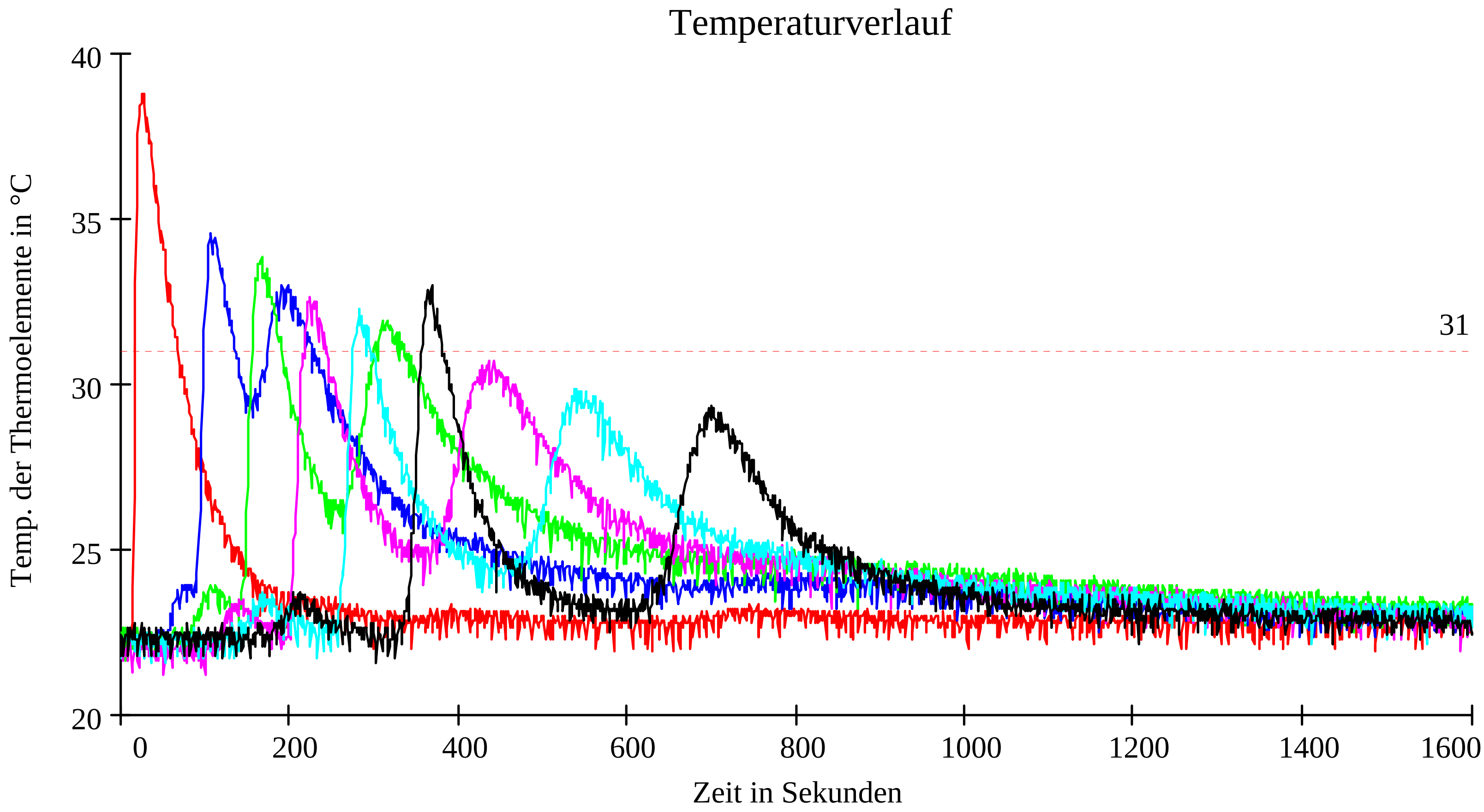
Results - Multicomponent system



Results - Multicomponent system



N_2 / CO_2 / CH_4 (10% / 40% / 50%) in AC Norit NR1 Extra



Mass AC = 75,9 g, p = 1,2 bar

Adsorption Isotherm Model

Dynamic equilibrium based on Langmuir theory

- Langmuir Adsorption Isotherm
- BET Isotherm
- Tòth Isotherm
- Sips Isotherm
- Freundlich Isotherm
- Virial equation

Thermodynamik in sense of Gibbs

Potential theory of Polanyi

Adsorption Isotherm Model

Dynamic equilibrium based on Langmuir theory

Thermodynamik in sense of Gibbs

- Gibbs'sche Adsorptionsisotherme
- Vacancy - Solution - Model (VSM)
- Associating Theory of Adsorption (ATA)
- Ideal Adsorbed Solution Theory (IAST) and modification

Potential theory of Polanyi

- Dubinin
- Myers – Prausnitz – Dubinin – Approach (MPD)

Experiment – accuracy

Pressure	Temperature	Mass	Volume of sample holder
Δp = 0.002 MPa	ΔT = 0.01 K	Δm = 0.01 mg	ΔV = 0.0002 cm^3

Volume of vessel	Concentration	Gas Flow	Time
ΔV = 0.02 cm^3	Δc = 0.1 %	ΔV^t =0.1 ml/min	Δt =0.01 s

Gravimetry	Volumetry	Breakthrough	Gravimetry dyn.
$\Delta m/m$ = 0.1 %	$\Delta m/m$ = 0.5 %	$\Delta m/m$ = 0.5 %	$\Delta m/m$ = 0.25 %

Choice of my experimental setup

Gravimetry

- Direct measurement of m, p, T
- Mass change during sample preparation
- Uptake curve
- Adsorption isotherm (Kinetics)

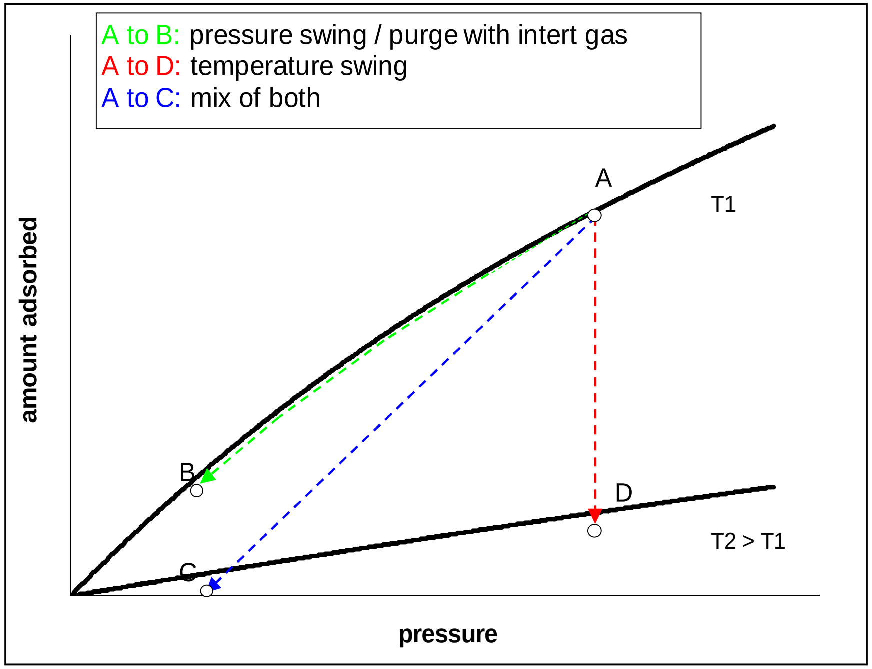
Volumetry

- Direct measurement of p, T
- “Simple” apparatus
- Adsorption isotherm
- Corrosive components

Breakthrough curve

- Direct measurement of c, p, T
- “Simple” apparatus
- Pure and Mixed gas components
- Adsorption isotherm
- Kinetics of process
- Small concentration
- Close to technical separation / regeneration

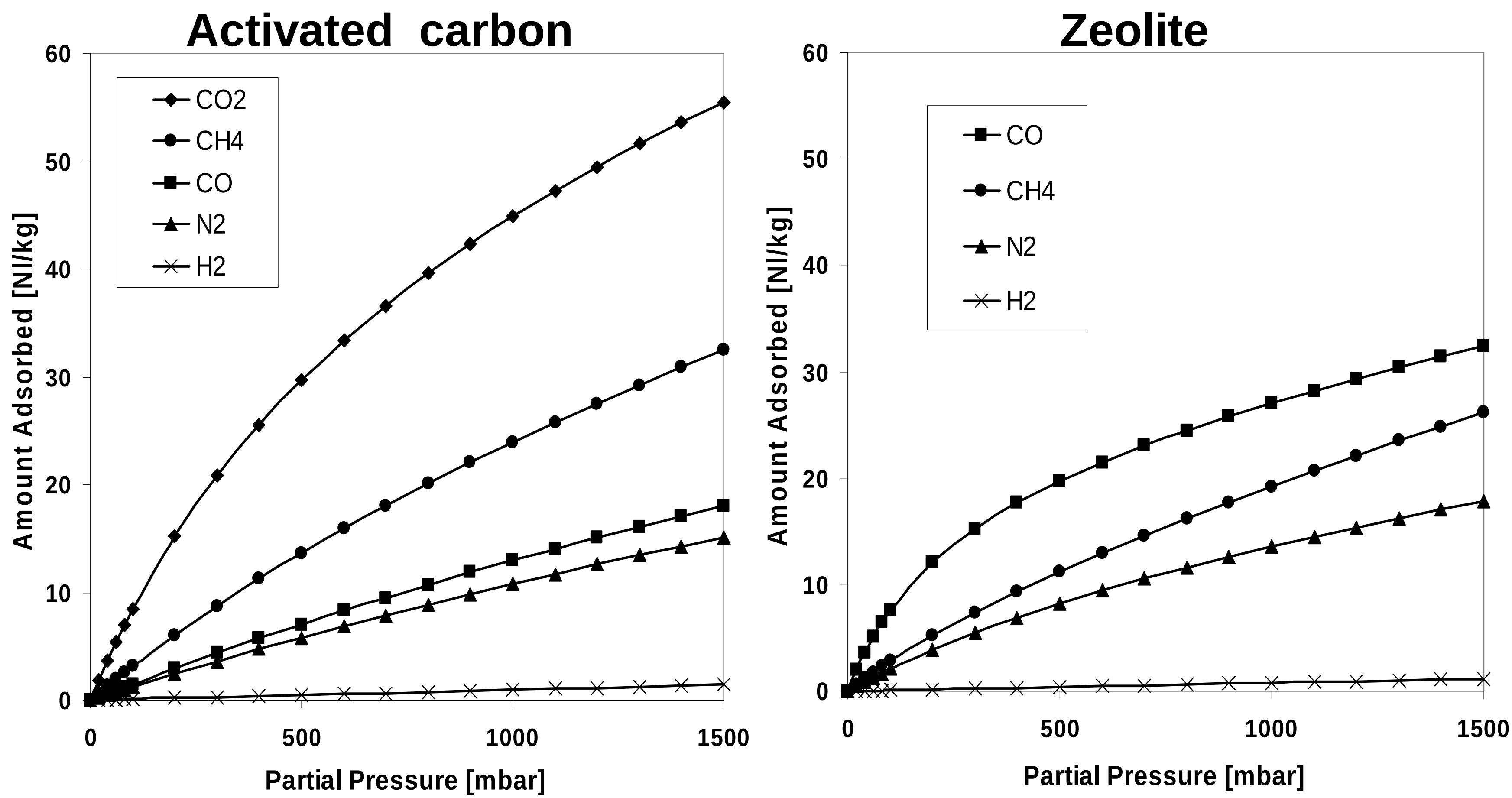
Basics of adsorption technique / processes



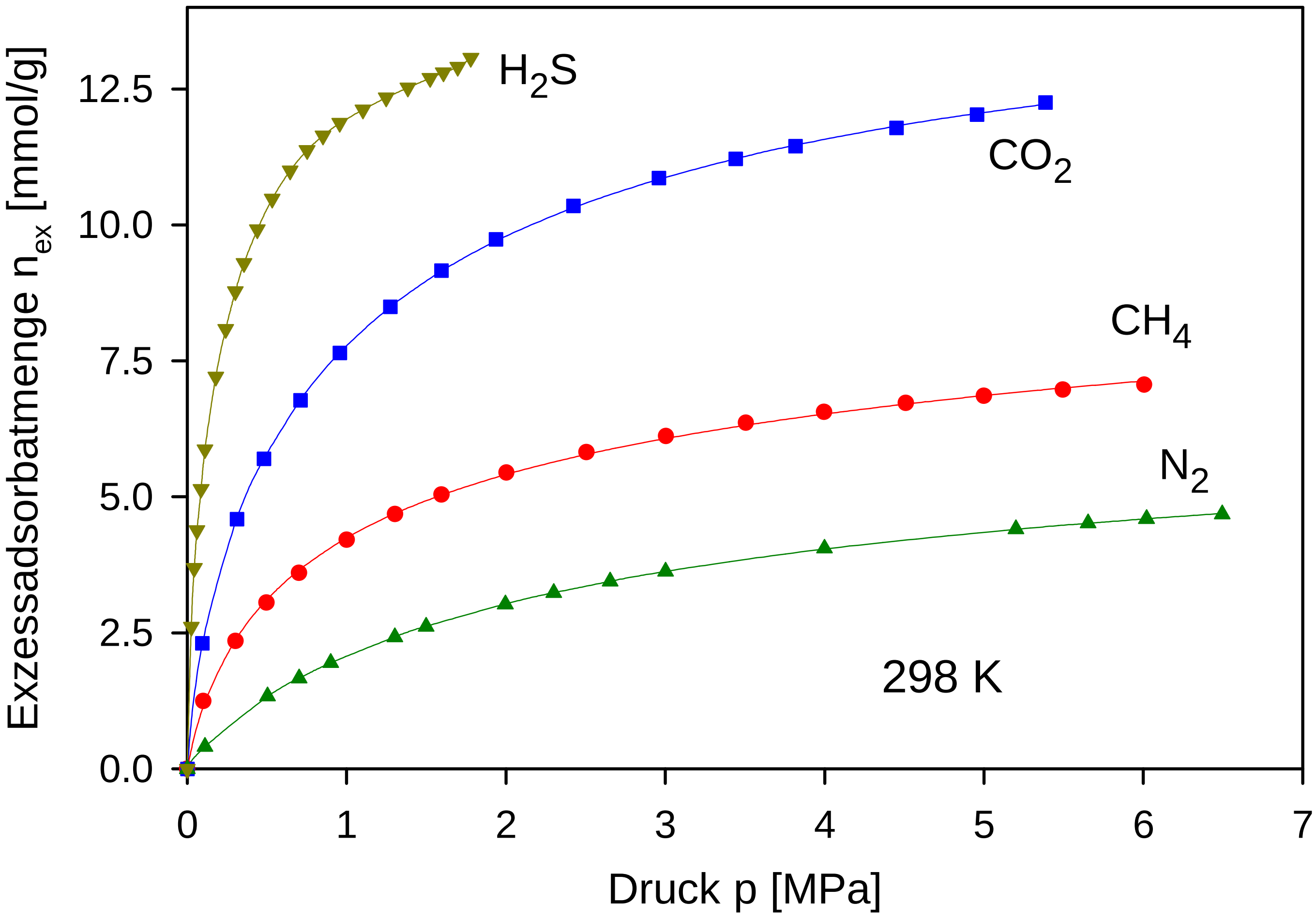
- *Temperature swing process (TSA)*
  - *Desorption by increase of T (A to D)*
    - *Hot inert gas, Water vapor, Electrical heating*
- *Pressure swing process (PSA/VPSA)*
  - *Desorption by decrease of p (A to B)*
    - *PSA adsorption at higher pressures; regeneration at atmospheric pressure*[1]
    - *VPSA adsorption at higher pressures; regeneration under vacuum* [1]
- *Combined TSA-PSA*
  - *Desorption by increase of T and decrease of p (A to C)*[1]

(1) D. Bathen, M.Breitbach, Adsorptionstechnik, Springerverlag, 2001

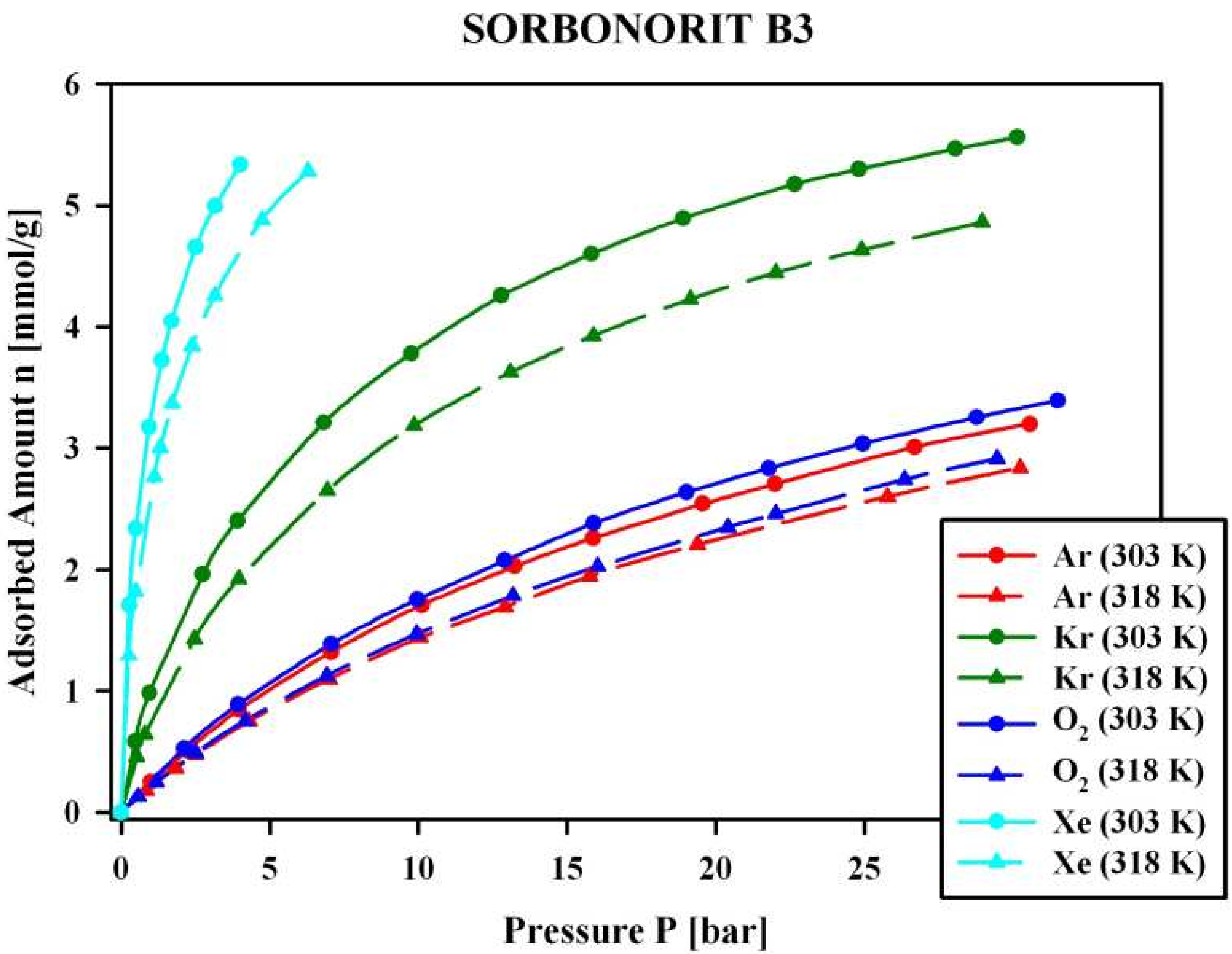
Adsorption isotherm @ 298 K, H_2, CO_2, CO, CH_4, N_2



Adsorptionsisothermen an AK

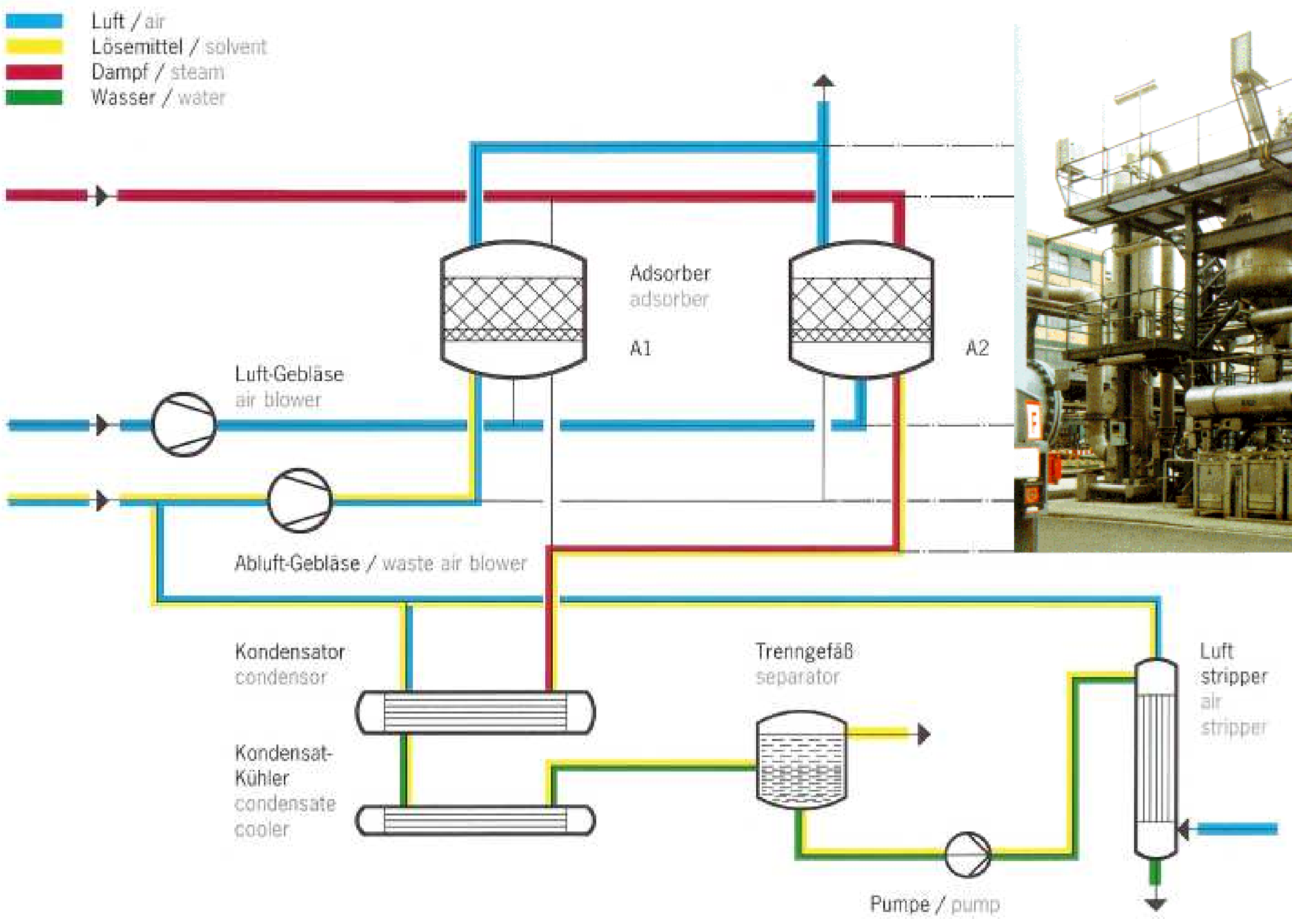


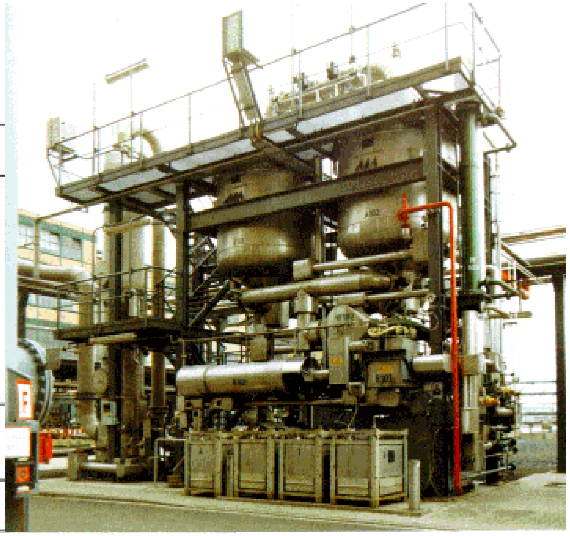
Adsorption Isotherms of Ar, Kr, O_2 and Xe



Adsorber zur Lösungsmittel-Rückgewinnung (TSA-CSA)

TSA-Festbett-Adsorber: Desorption mit Wasserdampf





Fließbild und Foto:
Silica VT GmbH

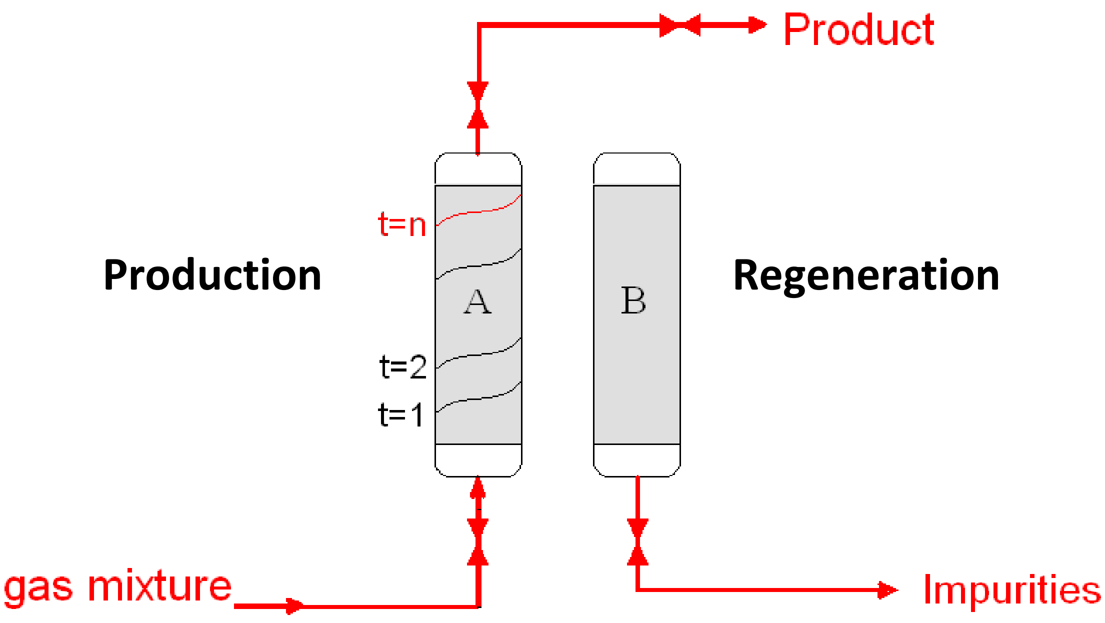
Pressure swing adsorption

- Air separation into N_2 (>99,9 %), O_2 (< 97 %) or Ar
- Production / Cleaning of H_2
- Separation of CO_2 from biogas
- Drying of compressed air

Hydrogen – Production by PSA

Use	**Purity Requirements**
Ammonia Synthesis	< 10 ppm CO_X, X = 1,2
Compressed Gas	< 10 ppm CO_X, 100 ppm CH_4, < 200 ppm N_2
Fuel Cells	< 30 ppm CO
Electronics (Semiconductors)	< 10 ppb N_2, O_2, CH_4, CO, C_xH_y
Food Industry	3.1 – 5.5 (% Vol. H_2)

Hydrogen Purification



Required Information

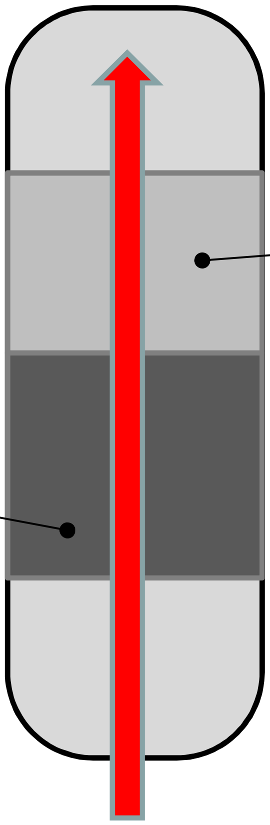
- Isotherms
- Heat of Adsorption
- Heat capacities
- Kinetics
- Co-adsorption

Hydrogen Purification – PSA Unit

Activated Carbons

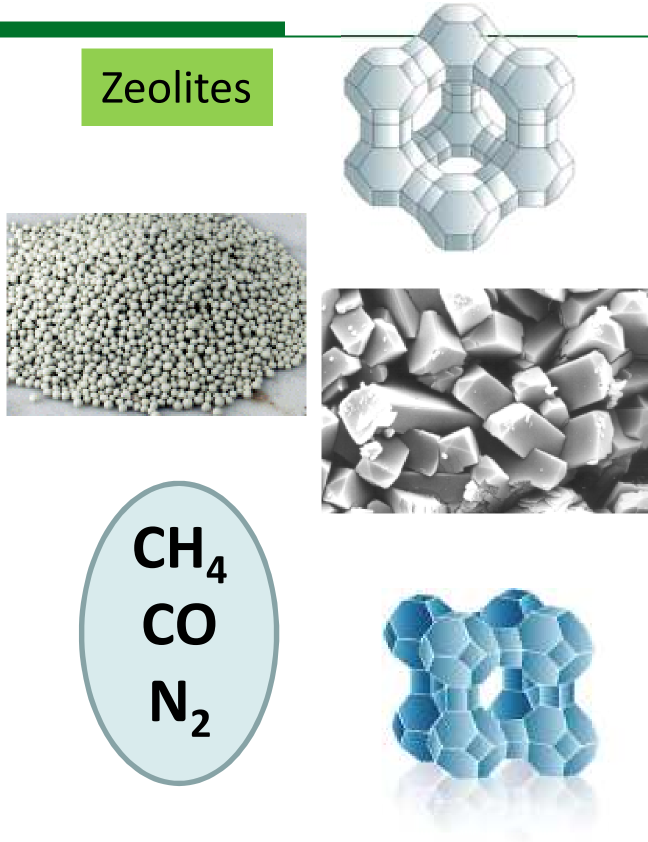
CO_2
CH_4
CO

Pure H_2



H_2-rich mixture

Zeolites

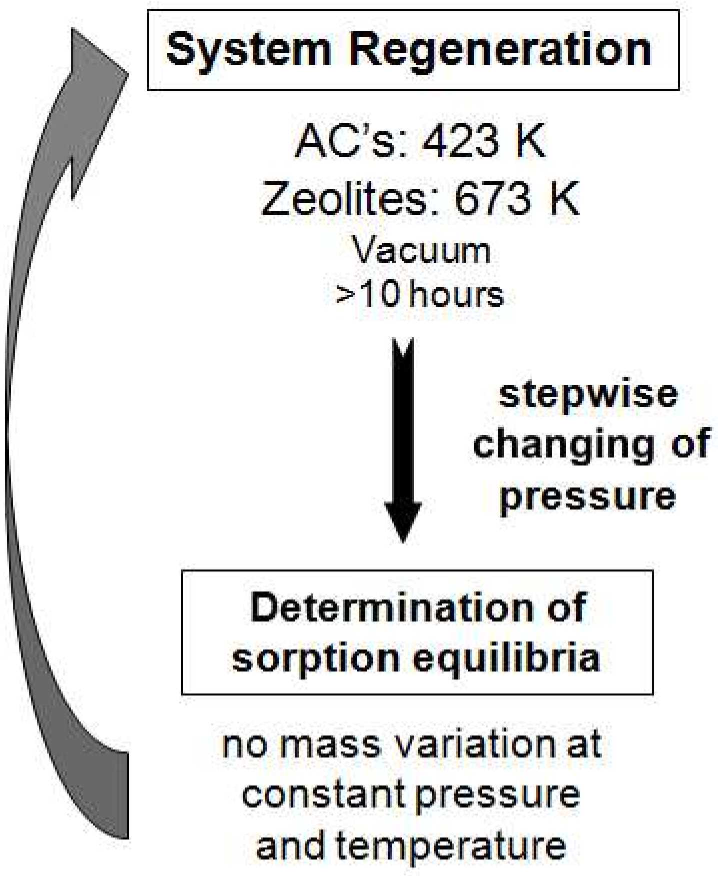


CH_4
CO
N_2

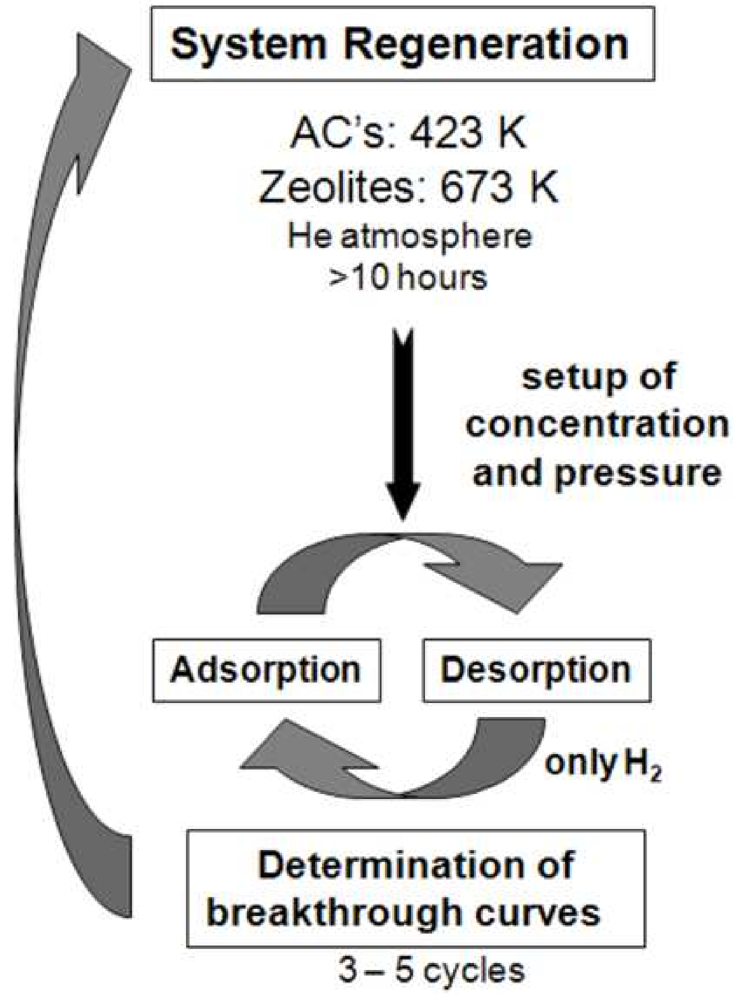
Studied Samples
2 Activated Carbons
3 Zeolites 5A

Hydrogen Purification

Measurement of Isotherms

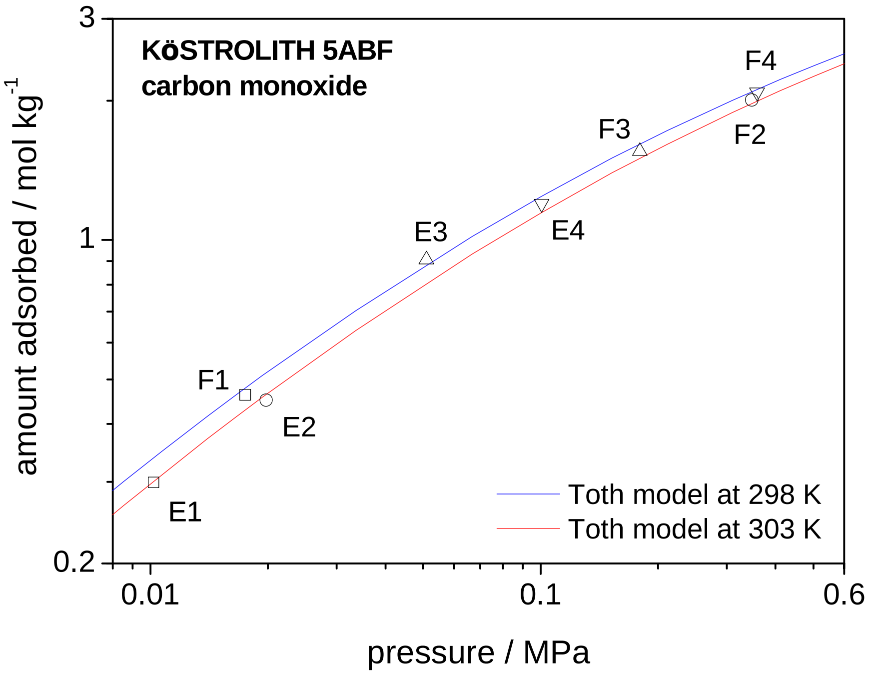


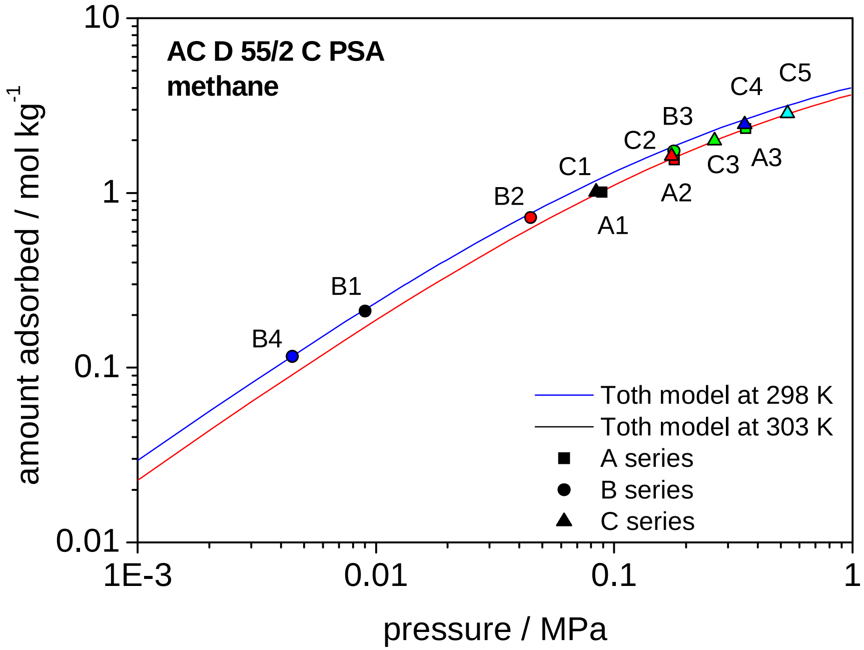
Measurement of Breakthrough Curves



Hydrogen Purification

Validation of the Experimental Breakthrough Curves





Lines are Toth fit based on gravimetrically measured results

Points correspond to measured breakthrough curves

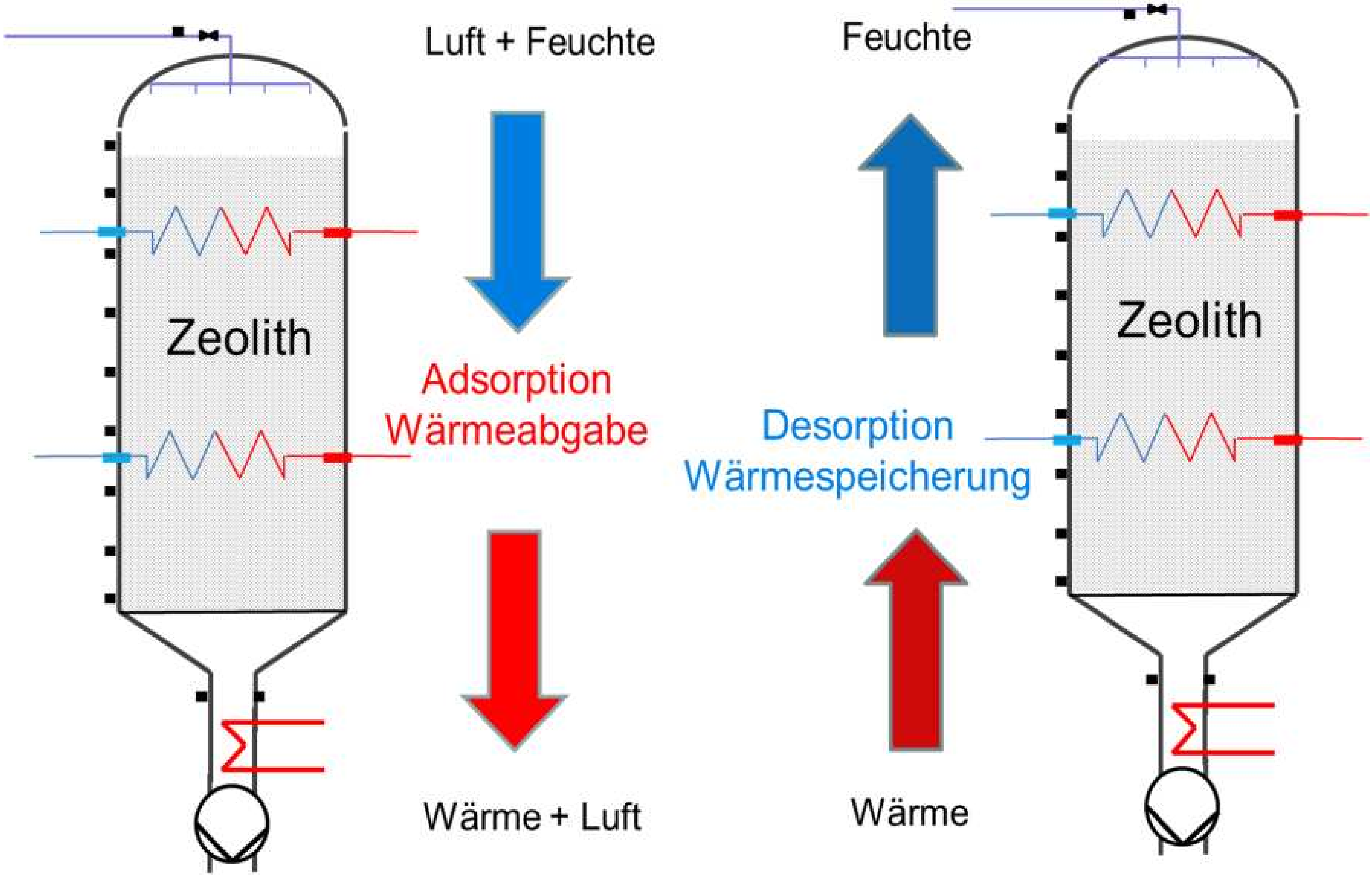
Adsorption based gas separation processes (I)

Process	**Feed**	**Product(s)**
Air separation	Air, dry, clean	Nitrogen (N_2) Oxygen
Pressure swing adsorption (PSA)]		Oxygen, Methan, Hydrogen
Air conditioning	Air loaded with exhaust gases from industry, traffic, resi-dential heating etc. N_2, O_2, H_2O, CO_2, H_2S, aromatics etc.	Clean air N_2, O_2, (H_2O)
Temperature swing adsorption (TSA) Air purification Solvent recovery	Air loaded with VOC (Volatile Organic Compounds), BTX (Benzole, Toluene, Xylole), Smells, odors	Clean air (N_2, O_2, Ar) VOC, BTX

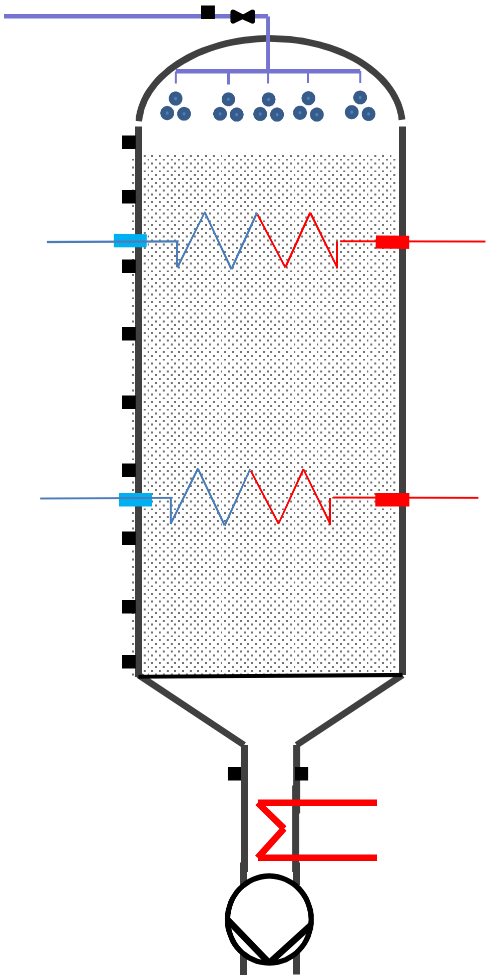
Adsorption based gas separation processes (II)

Process	**Feed**	**Product(s)**
Carbon dioxide removal	Blast-furnace gas CO_2, CO, H_2, H_2O	Syngas (H_2, CO)
Drying of air prior to pressurization	Humid air	Dry air
Flue-gas purification	Exhaust gases of power stations N_2, O_2, CO_2, SO_2,NO_x, etc. Hg from crematories, Isotopes nuclear	"Clean flue gases" N_2, O_2, H_2O, CO_2
Hydrogen separation	Reforming gas, Blast-furnace gas H_2, CO, CO_2, CH_4, H_2O	Hydrogen rich gas (Syngas: H_2, CO)
Natural gas enrichment of methane content	Raw gas from well CH_4, CO_2, N_2, H_2S, CO, etc.	Town gas CH_4, H_2, CO

Wärmespeicher



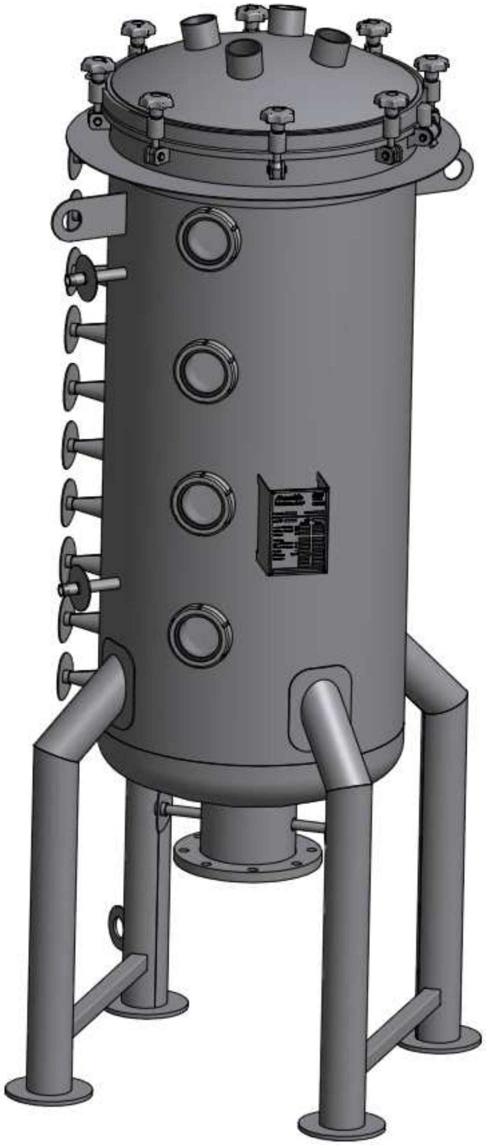
Pilotanlage zur Wärmespeicherung



Möschle GmbH, Behälterbau, Ortenberg,

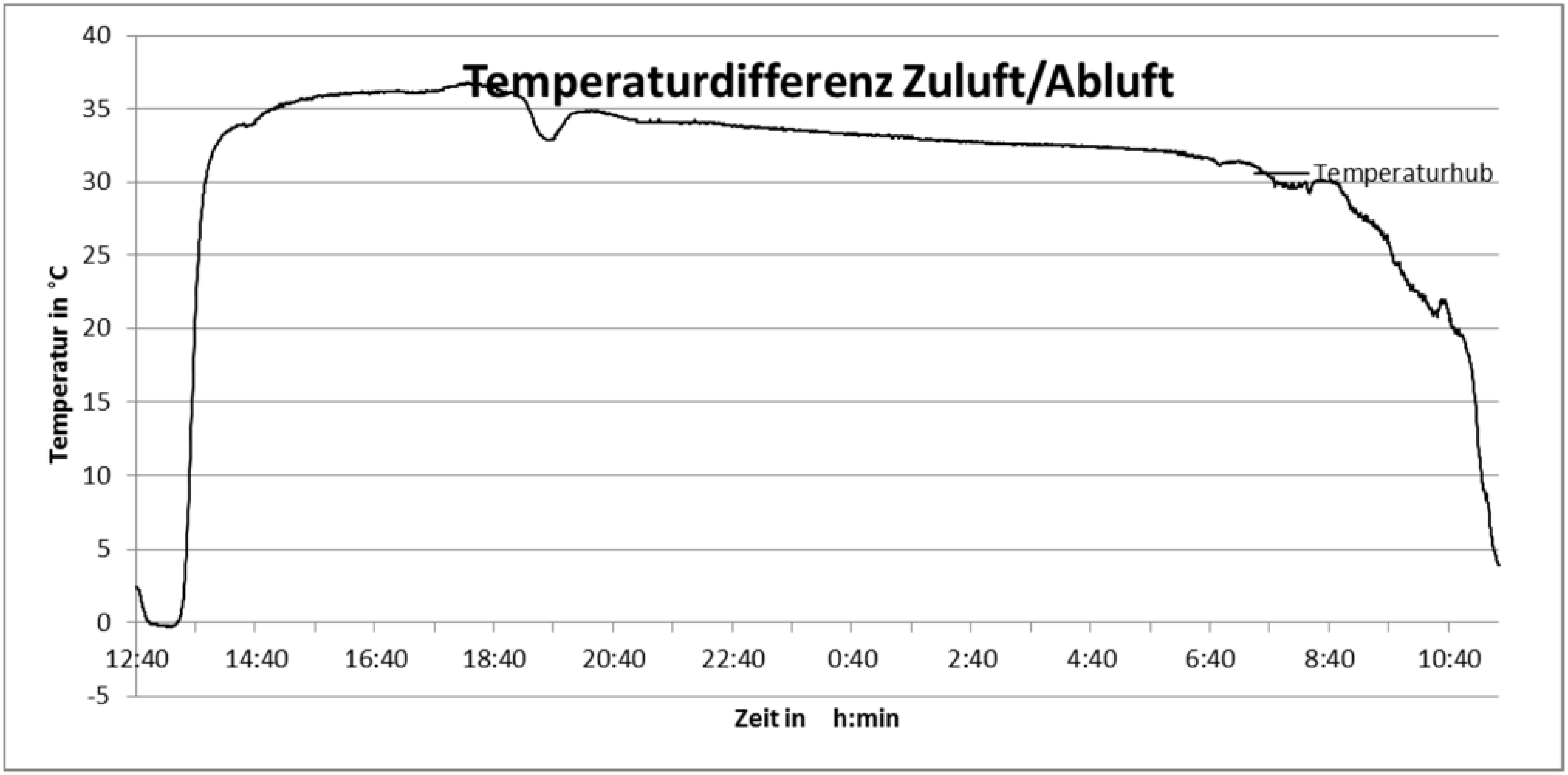
Pilotanlage

Befeuchtungssystem:

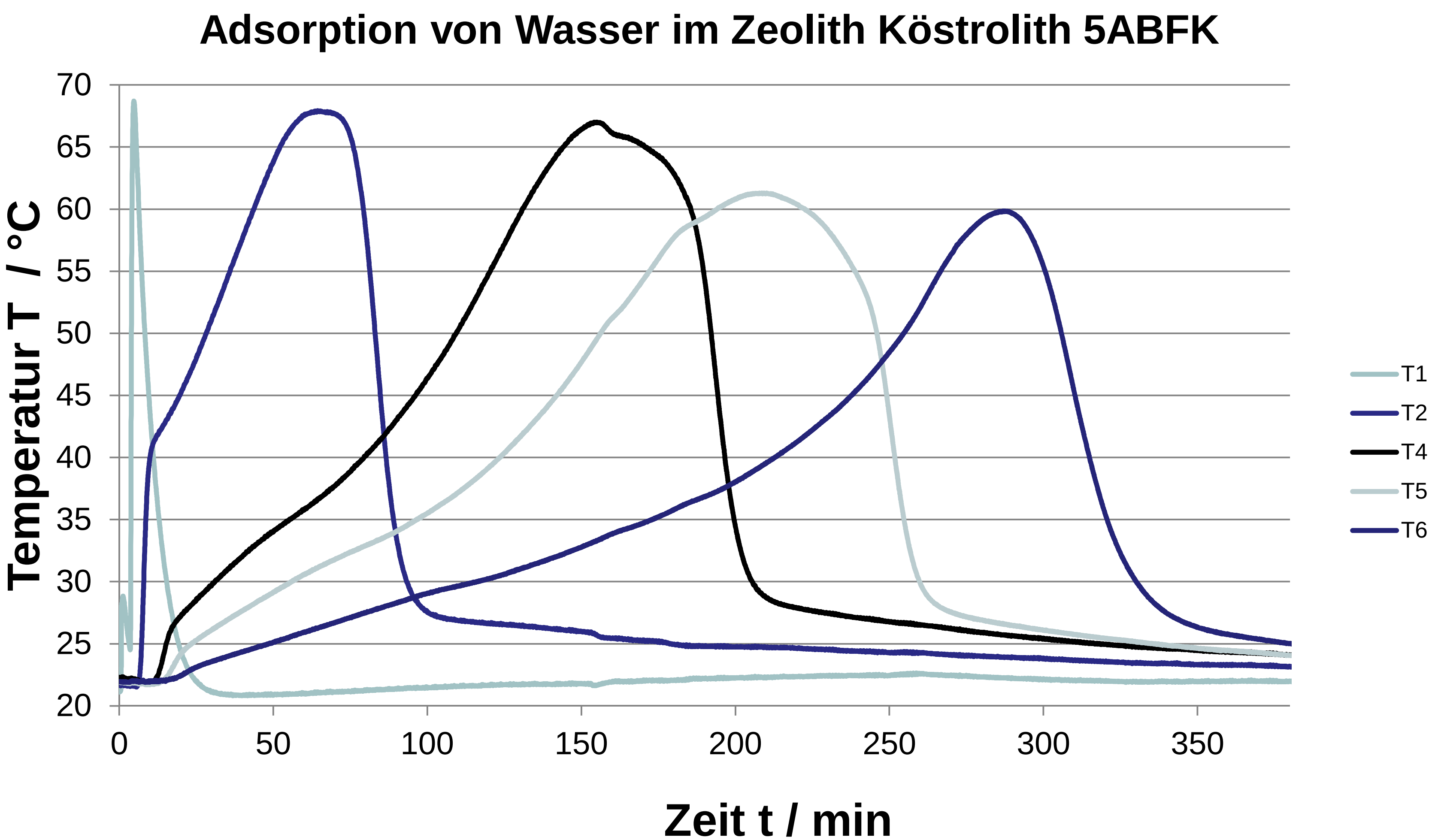


Möschle GmbH, Behälterbau, Ortenberg,

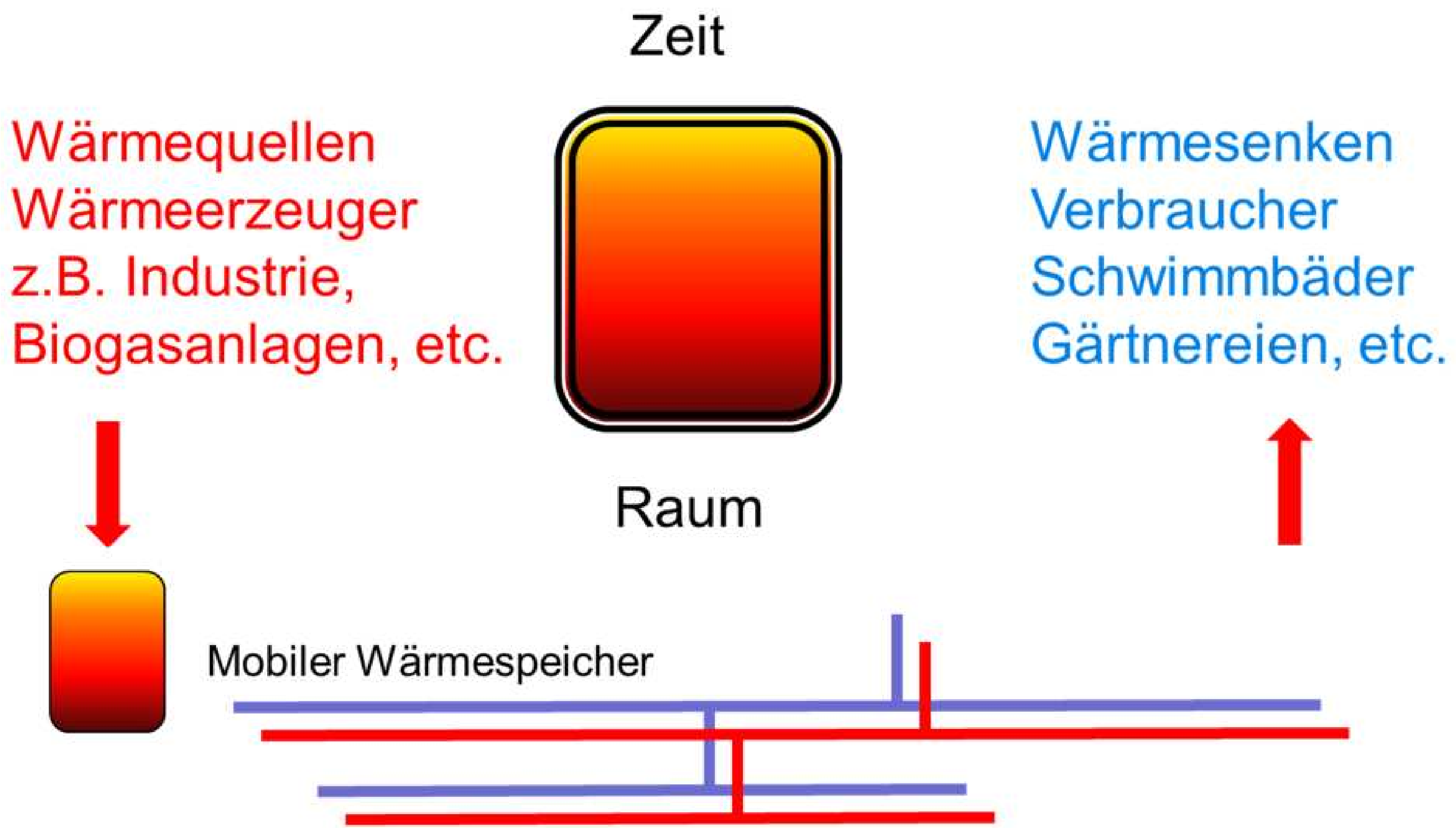
Heizen im Winter



Temperaturanstieg durch Adsorption von Wasser



Mobiler Wärmespeicher



My Conclusion

Dynamic characterisation of adsorption process delivers:

1. Adsorption Isotherm
2. Transport coefficient
3. Heat production / Temperature change during process

Dynamic measurements are applicable for

1. Experimental simulation of real technical adsorption process
2. Wide range of pressure and temperature
3. Low concentrations, multicomponent gas,…

Simple and robust apparatus

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