

Gas - Adsorption

Measurement Methods and Separation Processes

J.U.Keller

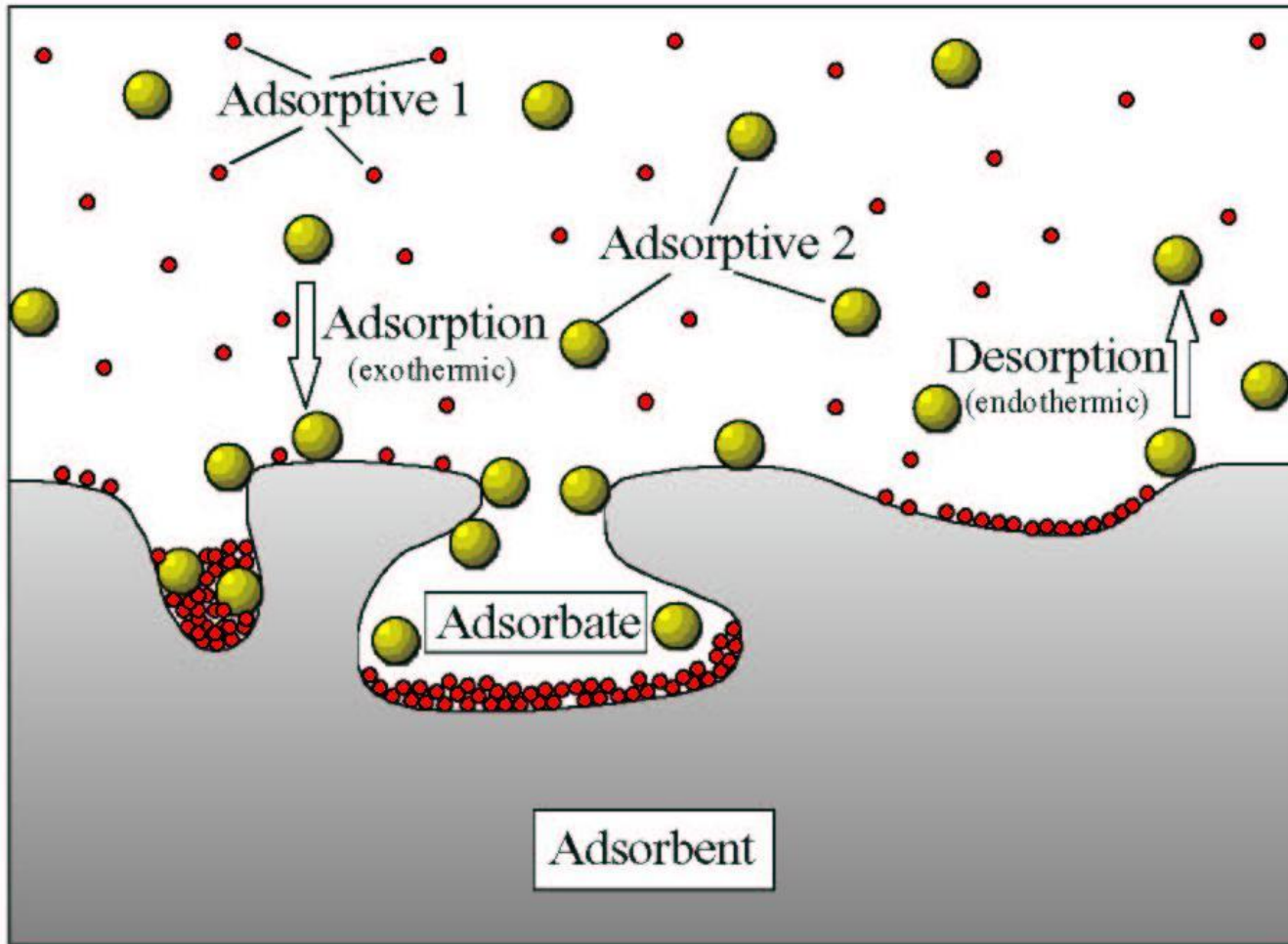
Inst.Fluid- and Thermodynamics

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1. Basic Concepts
2. Sorbent Materials
3. Measurement Methods
Equilibria, Heats of Adsorption,
Kinetics, Diffusion
4. Hydrogen: Production and Purification
5. Engineering Adsorption Cycles
6. Literature
7. Conclusions

Basic Concepts of Gas - Adsorption

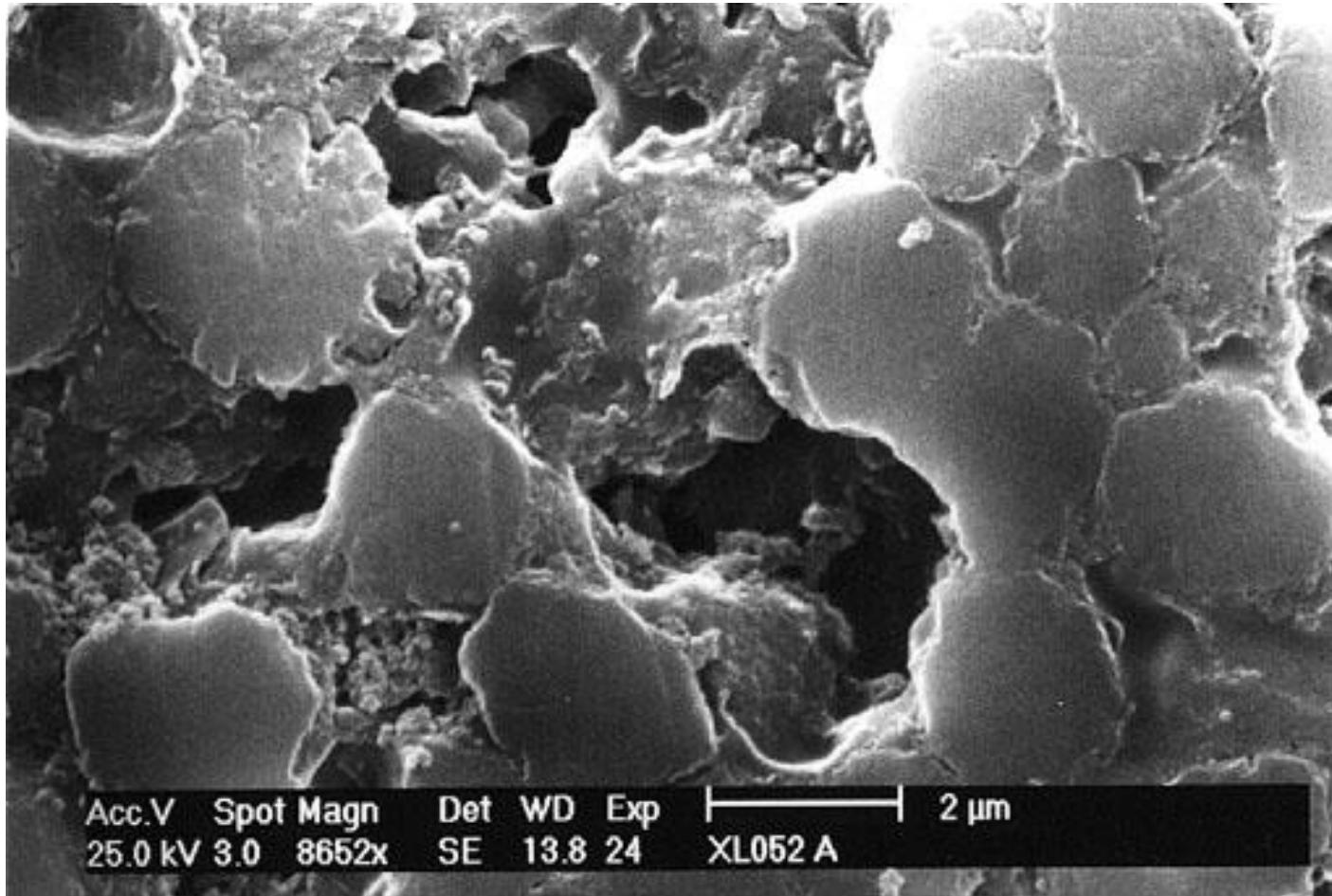


Gas / Vapor
Phase

Adsorbed Phase
Adsorbate (~L)

Inert Solid Phase
Sorbent

Surface Structure of Zeolite Molecular Sieve UOP/Linde 13X



Capillaries and macropores supporting transport of gas molecules to and from meso - and micropores can be recognized.

Sorbens Materials (Selection 2006)

Material's Name
BET Area (m² / g)

Main Technical Use
Desorption Enthalpy (kJ / mol)

Alumina, activated

Al (OH)_x x<3

300 - 400

Air separation

Dehydration agent

20 - 60

Biopolymers from starch etc.

300 – 800

Water, organic vapors, odorants

30 -60

Carbon, activated

C(H_x)(O_y) x>0, y>0

600 – 3500

Removal of organic substances
 (VOCs) from air, technical gases etc.

Hydrogen purification

10 – 60

Polymeric sorbents, resins

300 – 1100

Waste water treatment (ion exchange)

10 - 50

Material's Name**BET Area (m² / g)**

Silica gel
 (Si O₄)₄- amorphous
 100 – 800

Mesoporous silica (MCM41)
 600

Silica aerogels

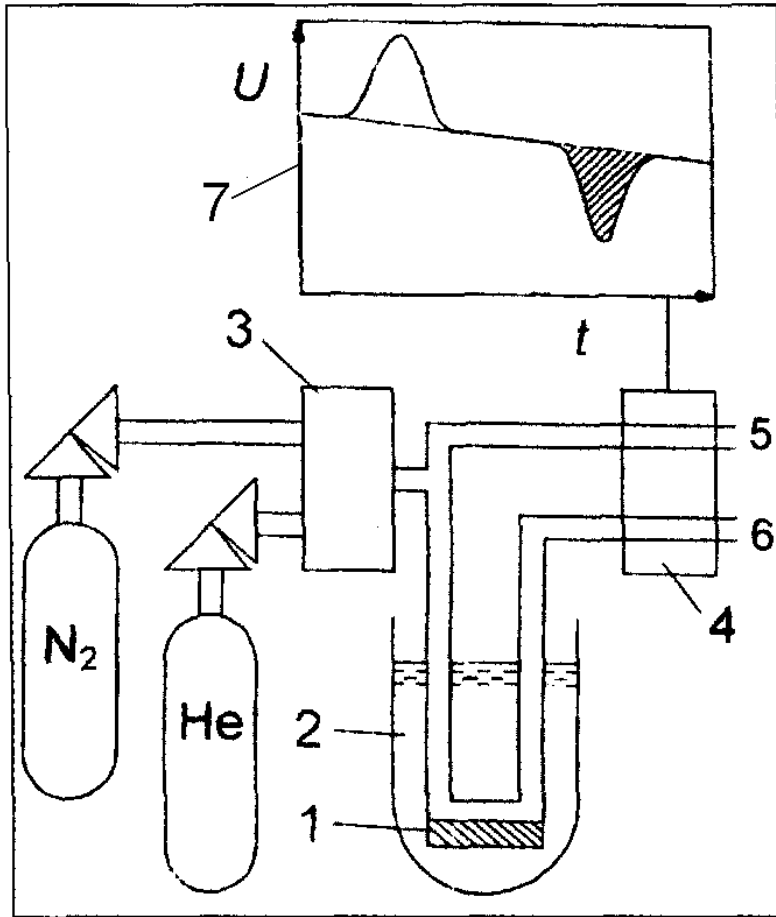
Zeolites, Type A, X, Y
 ca. 500
 hydrophylic

Main Technical Use**Desorption Enthalpy (kJ / mol)**

Drying of air and technical gases
 Removal of VOCs
 Air separation, Gas storage
 20 -40

Air separation, Drying of natural gas
 Removal of CO₂ from exhaust gases
 Separation of paraffines Tolefines etc.
 40 -80

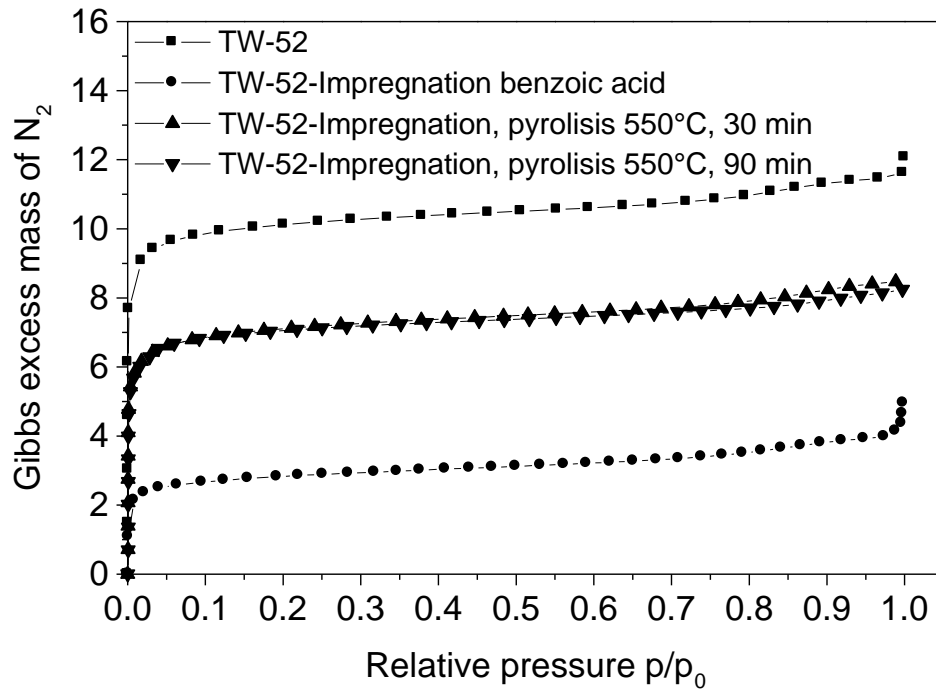
Gas Flow Porosimeter (He, N₂, BET, 77 K)



- 1 Sample / Sorbent
- 2 Dewar vessel (N₂, 77 K)
- 3 Mixing chamber
- 4 Thermal diffusivity detector (Δa)
- 5 Sorptive gas flow (original)
- 6 Reduced gas flow (changed)
- 7 Data display system ($\Delta U \cong \Delta a$)

Ref.: Rouquerol F., Rouquerol J.,
Sing K.S.W., Adsorption...

Academic Press, San Diego, 99

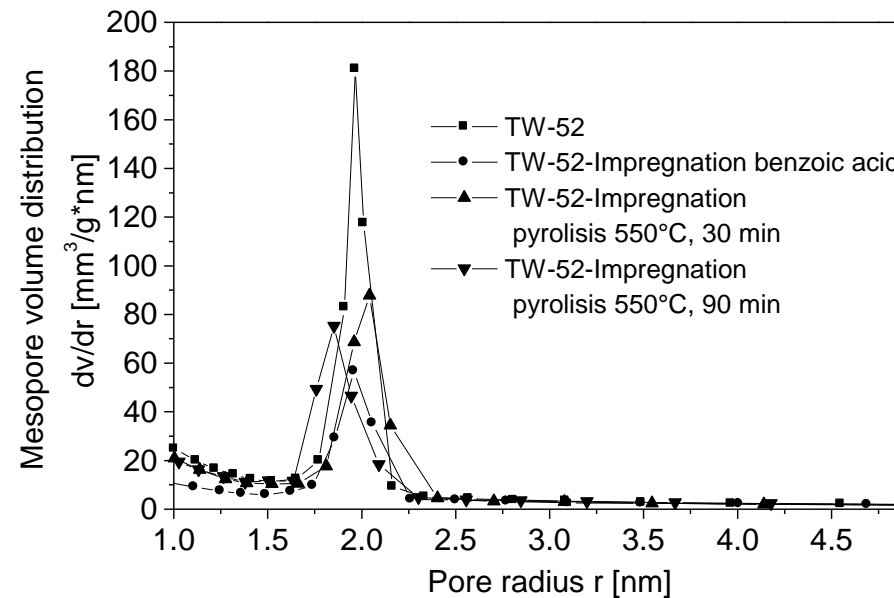


N₂ – Isotherms of ACTW 52 and modifications by < impregnation with benzoic acid (30 min.,90min.), 77K.

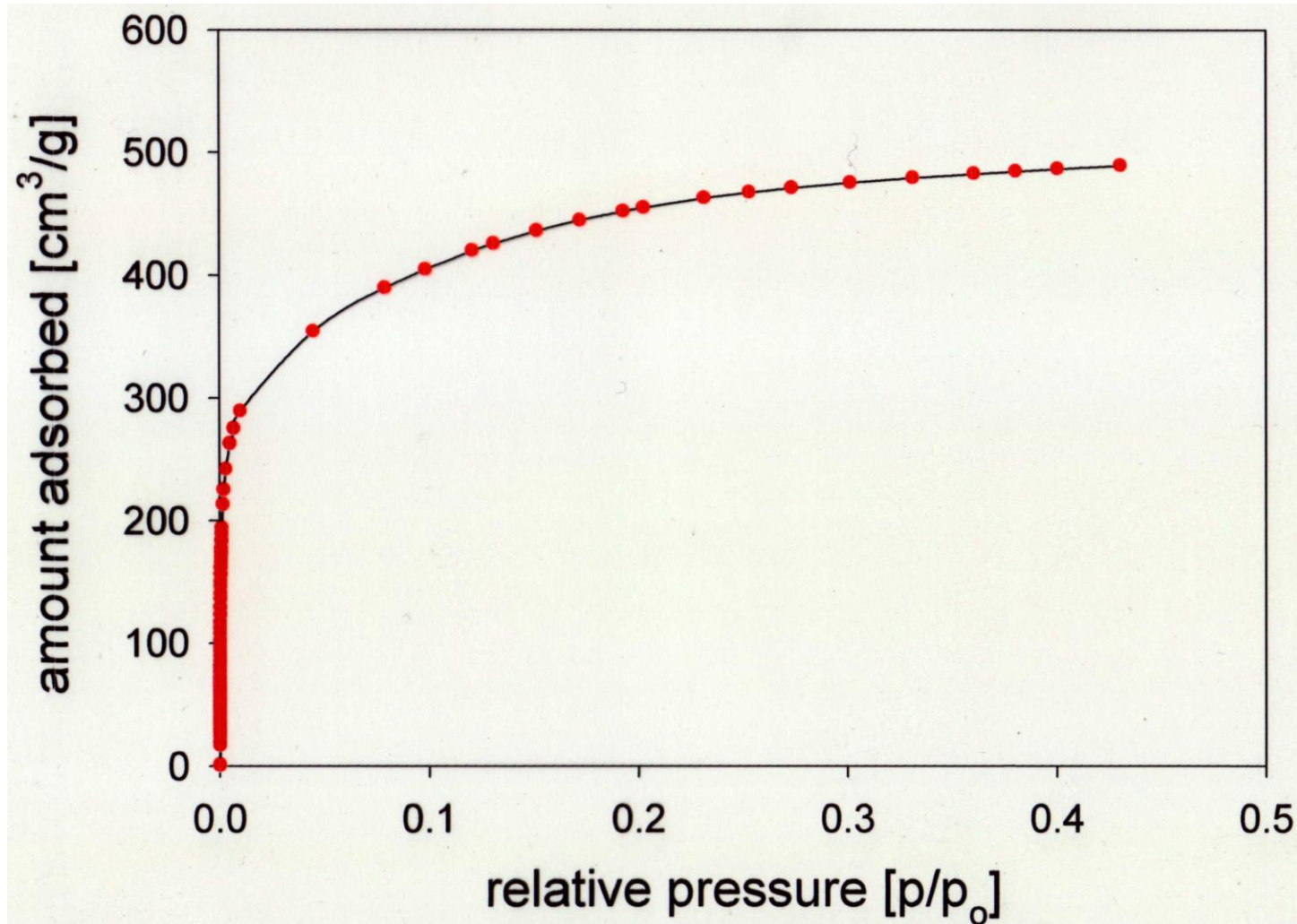
Distribution of mesopore volume of ACTW 52 and modifications calculated from N₂-isotherms by the BJH-method



IUPAC Classification, K.S.W.Sing
 0 < 2nm < 50nm < ∞
 Micro- Meso- Macropores

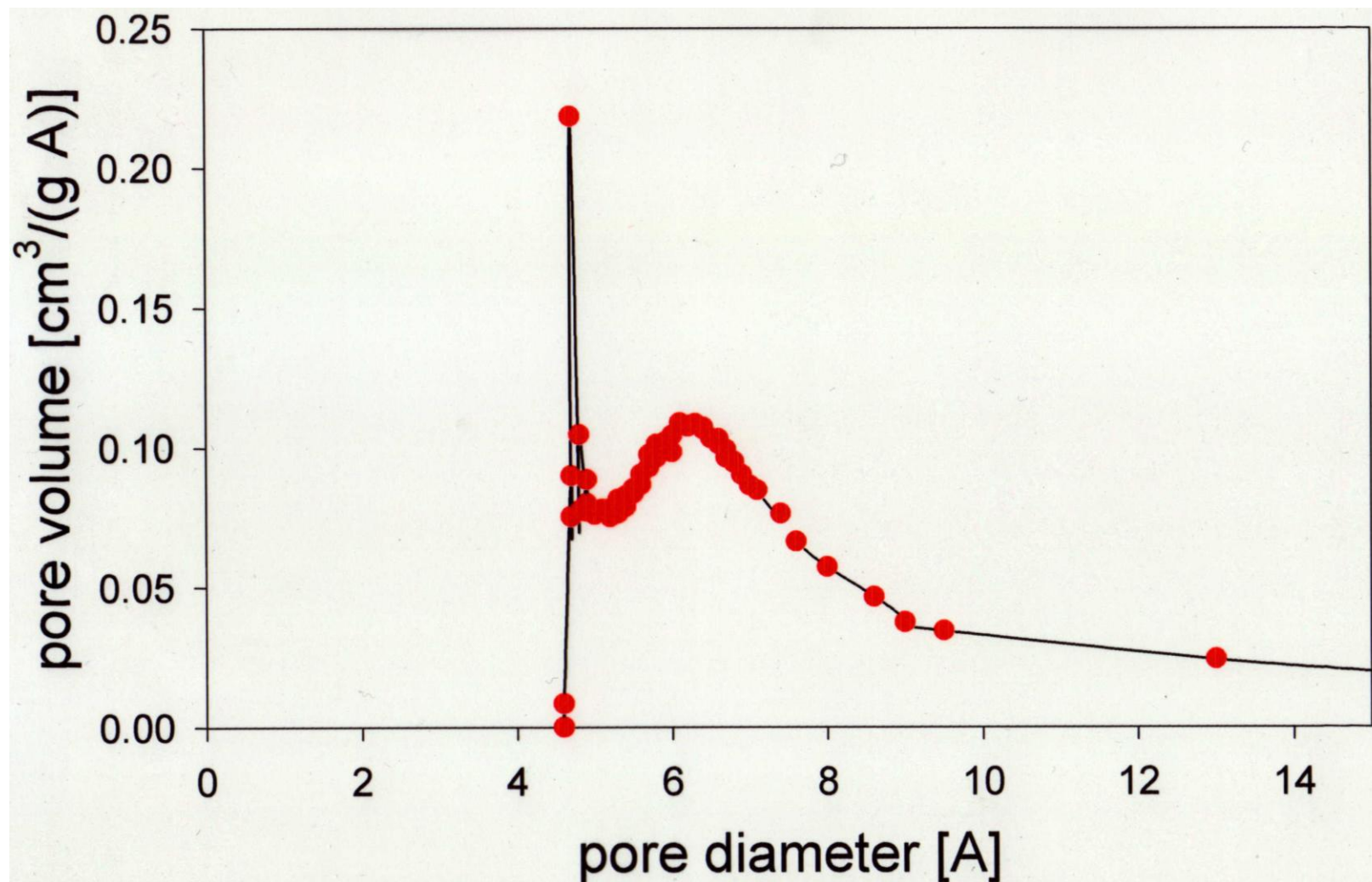


Characterization of Activated Carbon by Ar -Adsorption



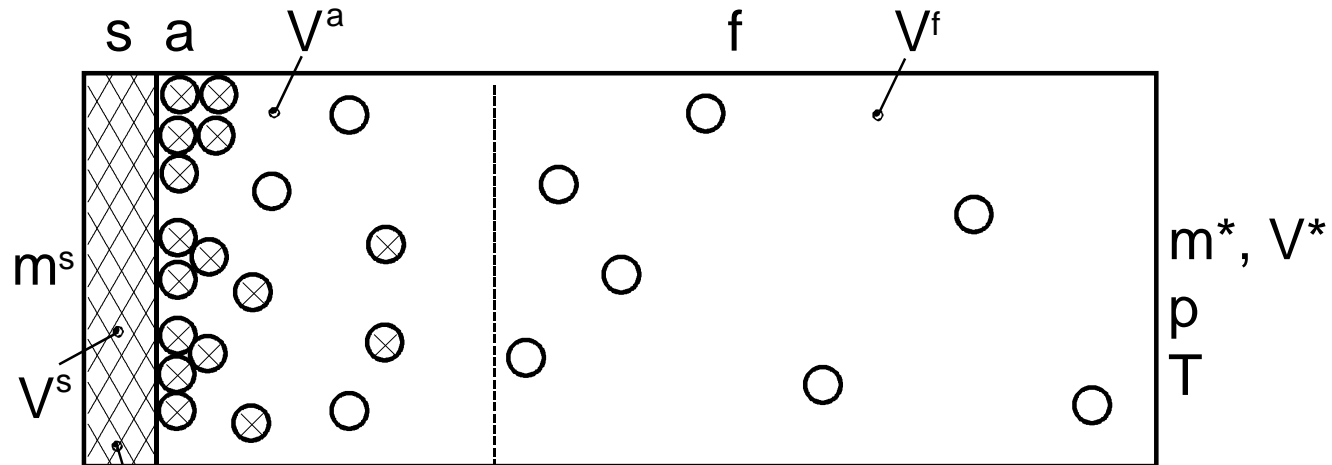
Adsorption of Ar on AC Norit R1 Extra at $T_s(1 \text{ atm}) = 87 \text{ K}$.

Pore Specrum of AC Norit R1 Extra by Ar - Adsorption



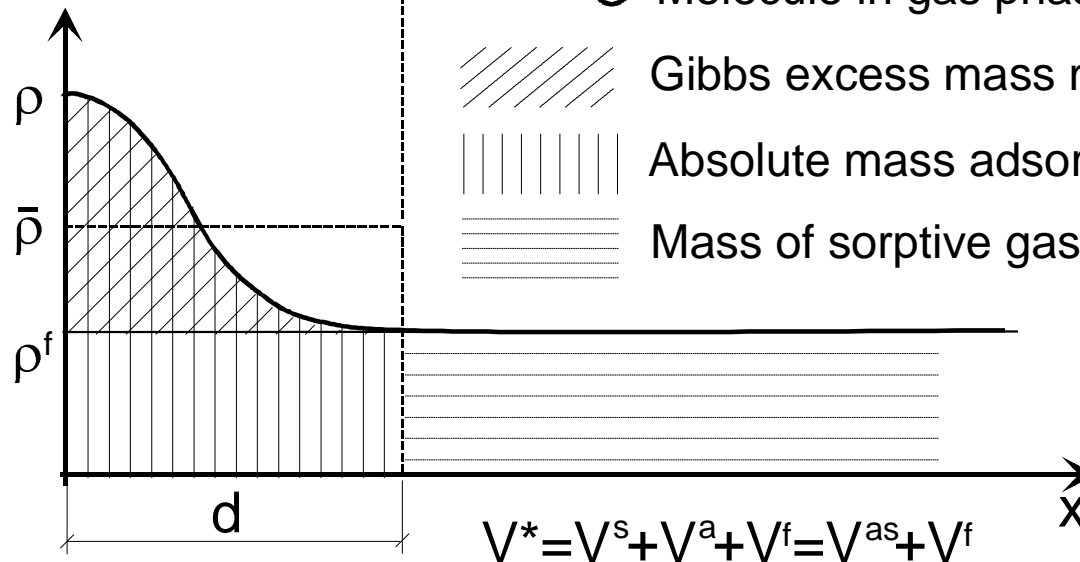
Horvath-Kawazoe Differential Pore Volume of activated carbon Norit R1 Extra.

Plane Surface Sorption System: Absolute/Excess Mass



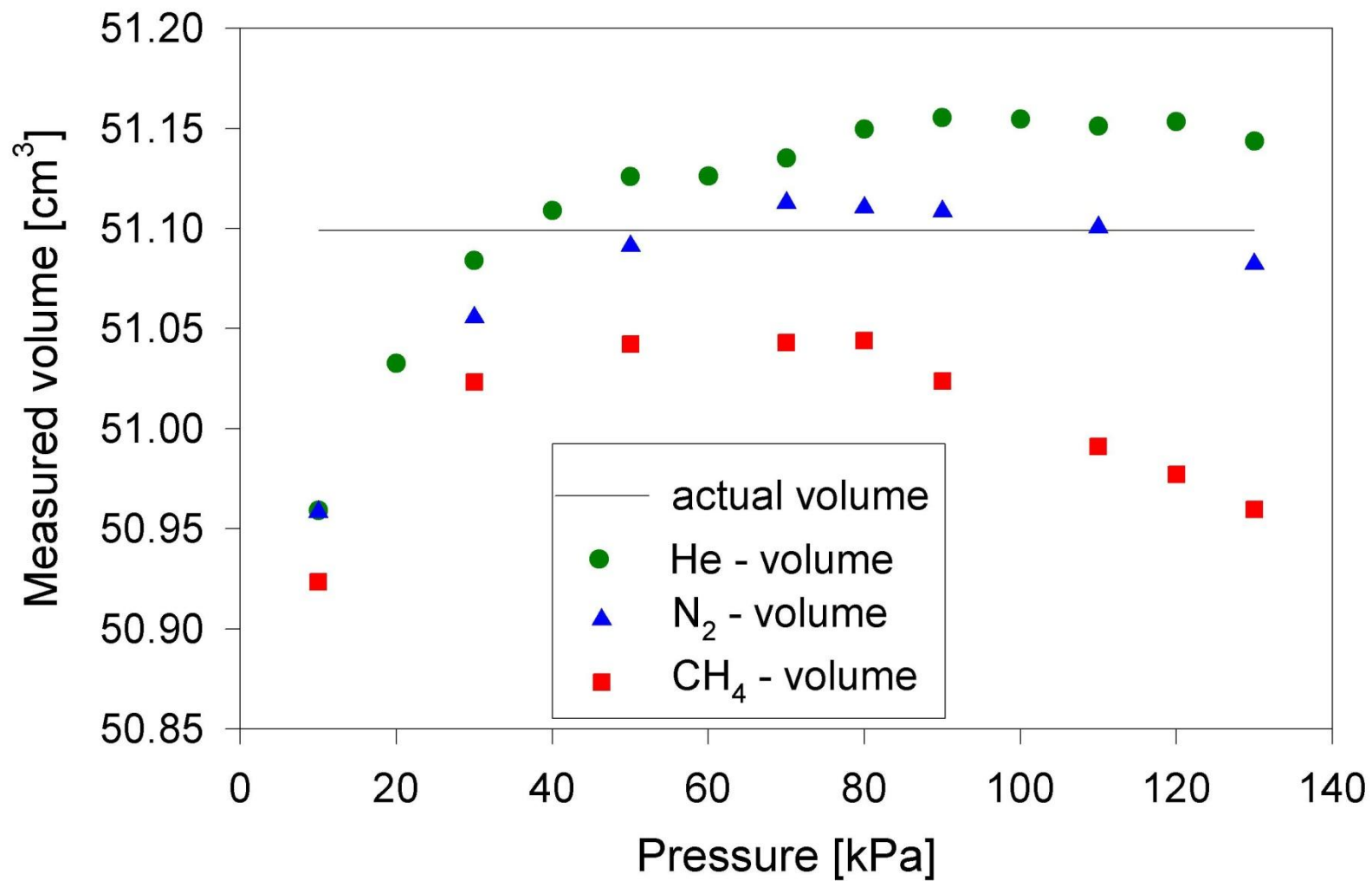
Sorbent material(s)

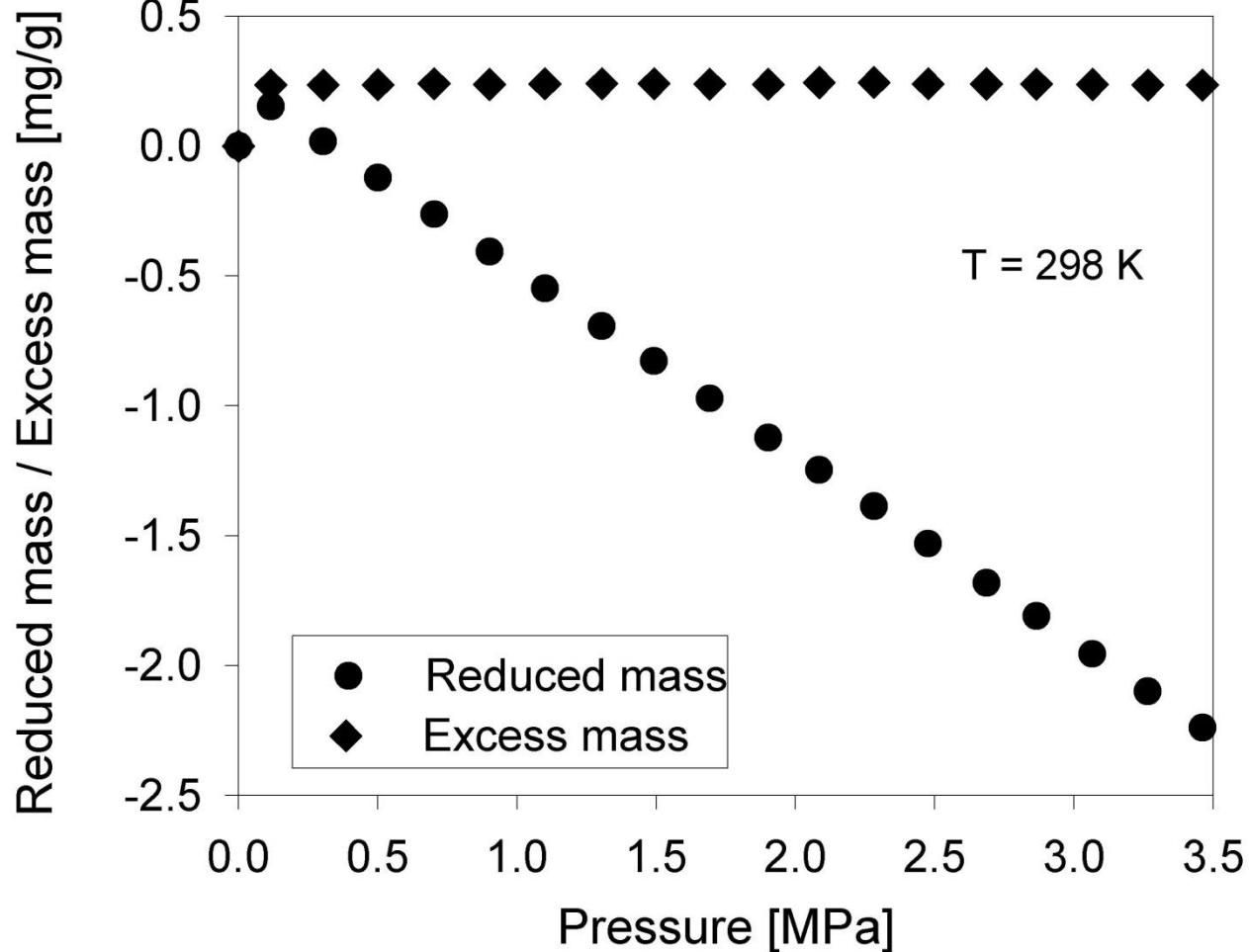
- ⊗ Molecule adsorbed
- Molecule in gas phase



- Gibbs excess mass m_{GE}^a
- Absolute mass adsorbed m^a
- Mass of sorptive gas m^f

$$V^* = V^s + V^a + V^f = V^{as} + V^f$$





Adsorption isotherm of helium on activated carbon (AC) Norit R1 Extra at 293 K. Full circles present data of the reduced mass (Ω) defined by Eq. (1.5). As these can be correlated linearly as function of the helium gas density $\rho^f = p/R_{\text{He}}T$, the volume of the AC impenetrable to the helium molecules can be calculated from Eq. (1.6). From Eq. (1.5) the mass of helium initially adsorbed at low pressures can be calculated (via Eq. (1.7)) leading to $m^a = 0.25 \text{ mg/g} = \text{const.}$

Adsorption of Helium on Porous Solids Theory

Reduced mass to be measured by a helium pycnometer

$$\Omega = m^a - \rho^f V^{\text{as}} \quad (1.5)$$

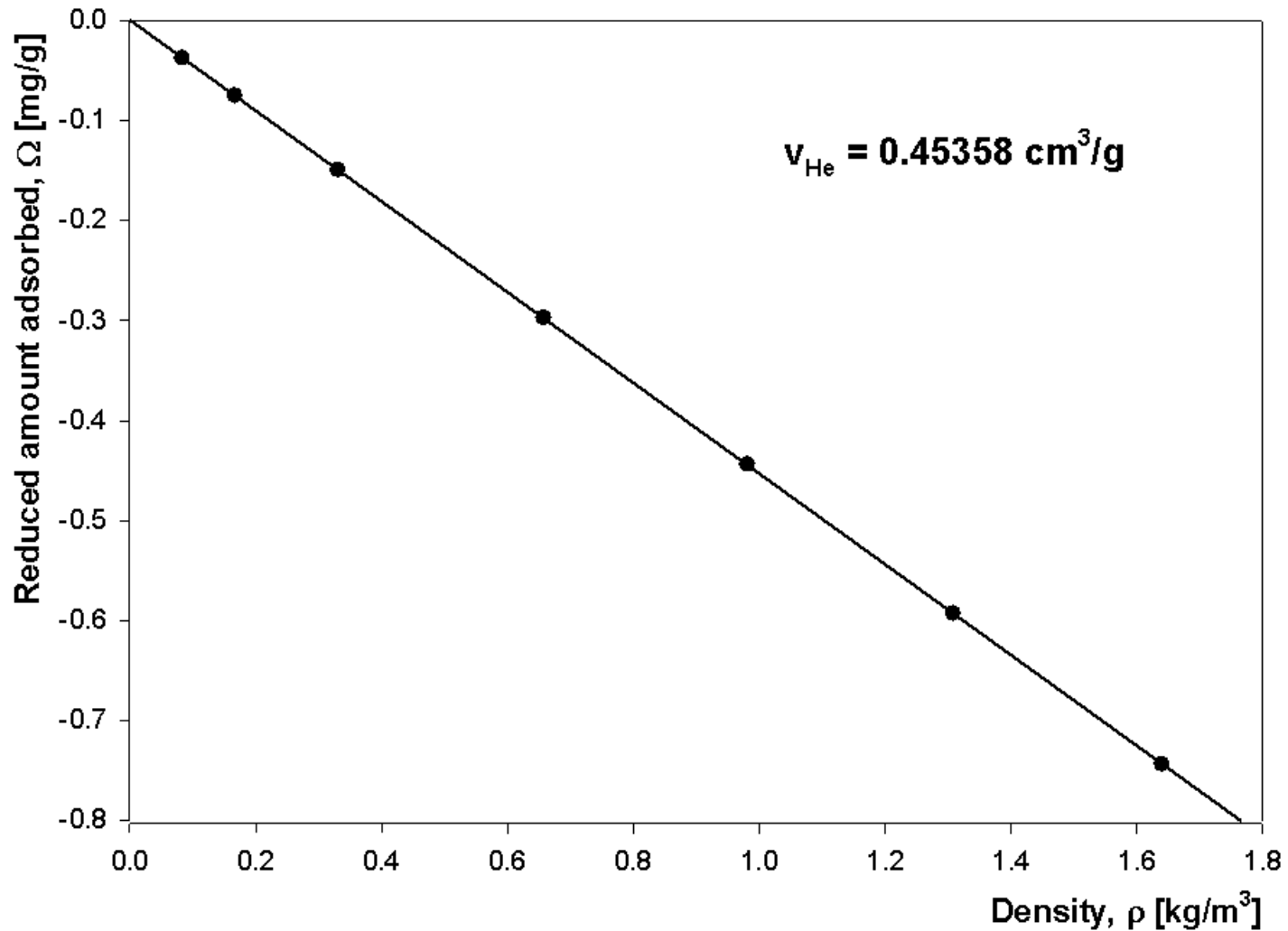
Volume of adsorbent (s) - Adsorbate (a) system:

$$(1.5) \quad p \rightarrow \infty: \quad V^{\text{as}} = - \left(\frac{\partial \Omega}{\partial \rho^f} \right)_{T, \infty} = - \left(\frac{\partial \Omega}{\partial p} \right)_{T, \infty} R_{\text{He}} T \quad (1.6)$$

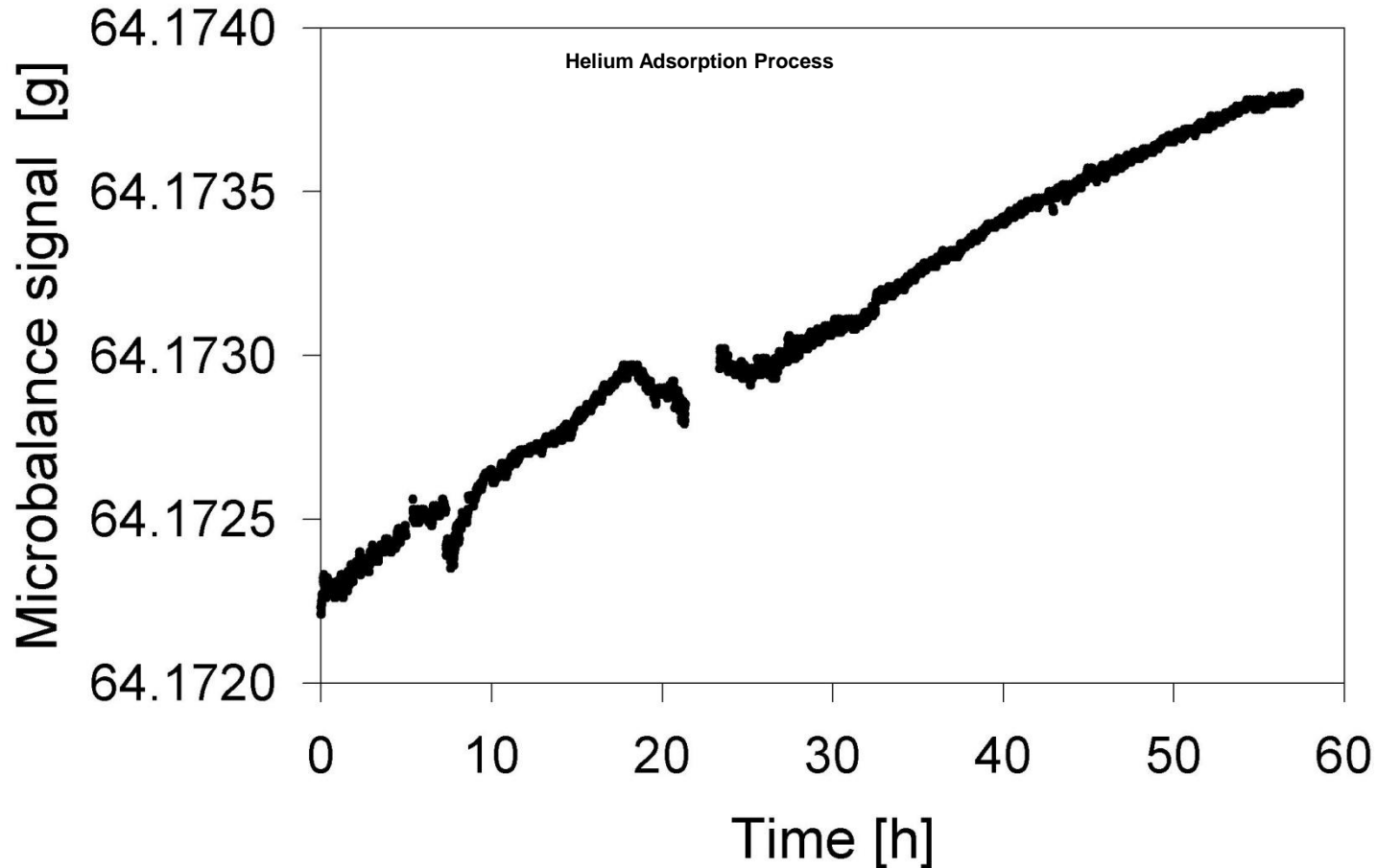
Absolute mass adsorbed

$$(1.5), (1.6): \quad m^a = \Omega - \rho^f \left(\frac{\partial \Omega}{\partial \rho^f} \right)_{T, \infty} \quad (1.7)$$

ρ^f	...	density of helium gas
R_{He}	...	specific gas constant of helium
T	...	absolute temperature



Adsorption isotherm of helium (He) on industrial activated carbon (ACAL) at 293K.



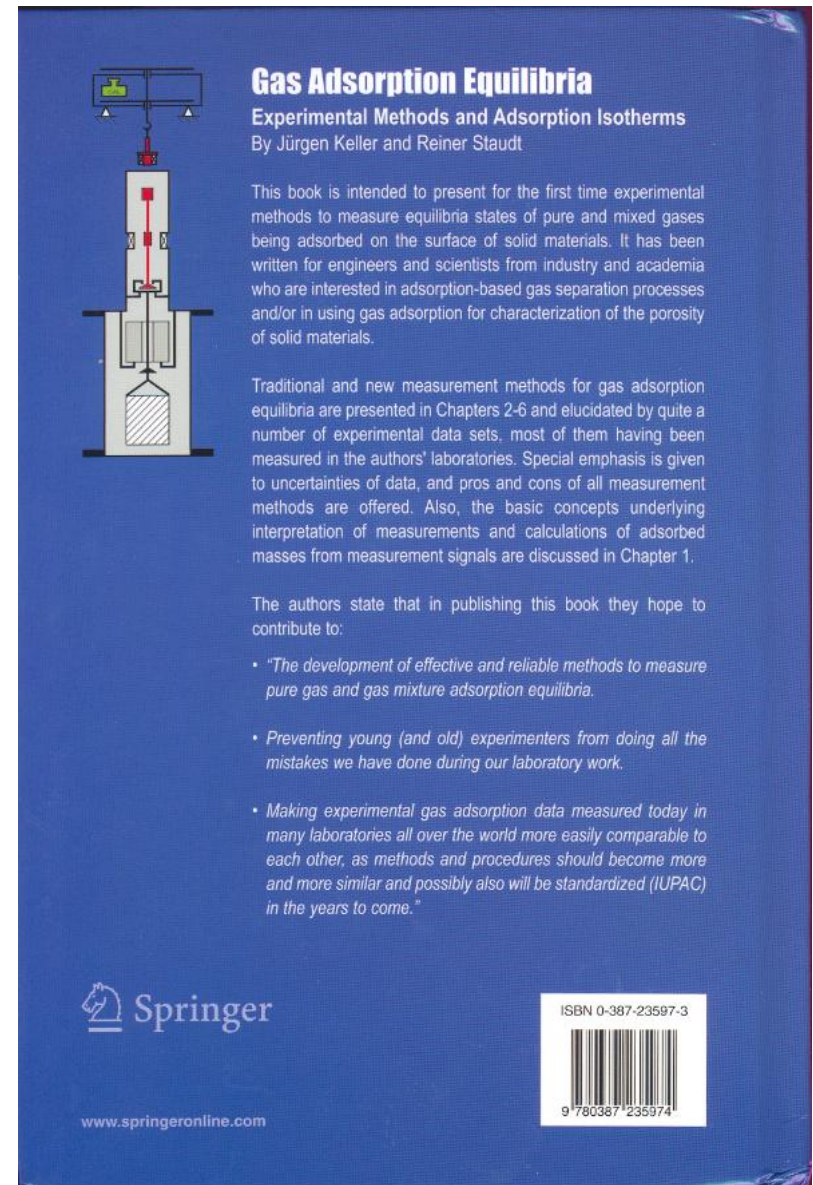
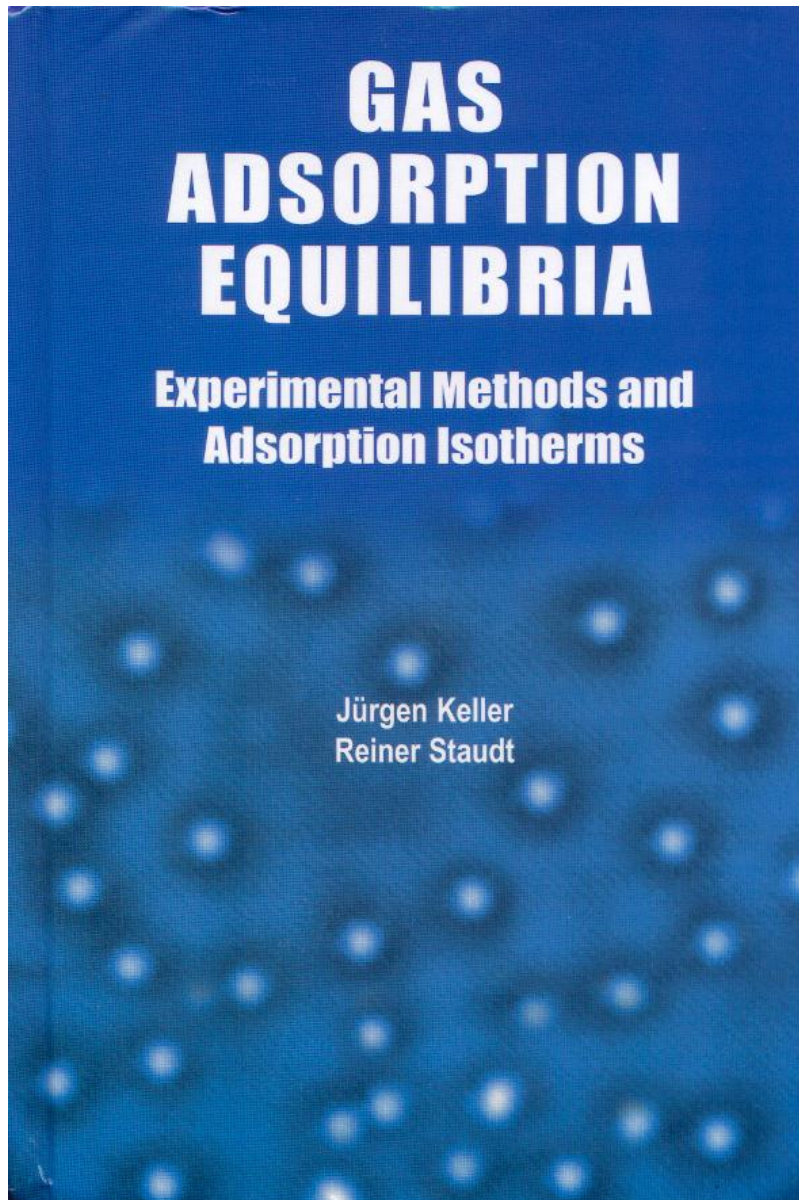
Adsorption process of helium (He(5.0)) on AC Norit R1 Extra at $T=298.17\text{K}$ during 58 hours measured gravimetrically (magnetic suspension balance, Rubotherm). The interruption of measurement data at about 24 h is due to limitations in data storage capacity, i. e. an overflow of data, which made a change of the data storage device necessary.

References

Characterization Porous solids

- [1] **Keller J.U., Staudt R.**
Gas Adsorption Equilibria, Experimental Methods and Adsorption Isotherms, p. 420, Kluwer/Springer, to be published 2004.
- [2] **Rouquerol F., Rouquerol J., Sing K.S.W.**
Adsorption by Powders and Porous Solids, Principles, Methodology and Applications, Academic Press, London, 1999.
- [3] **Kaneko K., Setoyama N., Suzuki T.**
Ultramicropore characterization by the adsorption, Proceedings Conference on Porous Solids 3, Marseille, May 1993, J. Rouquerol, Ed. Elsevier, Amsterdam, 1994, p. 593-602.
- [4] **Robens E., Keller J.U., Massen C.H., Staudt R.**
Sources of Error in Sorption and Density Measurements, J. of Thermal Analysis and Calorimetry, 55 (1999), 383-387.

Ref: J.U. Keller, R. Staudt, *Gas Adsorption Equilibria*, Springer, New York, 2004.



Gas Separation by Physical Adsorption

1. Thermodynamic coadsorption equilibria
Equilibria load: component, pressure, temperature 80%
2. Kinetic separation processes
Diffusion coefficient: component, temperature 30%
Chromatography, Molecular traffic
3. Molecular sieve effects 30%
Pore size, molecules' sizes, exclusion effects
4. Quantum effects 5%
Anomalous diffusion (de Broglie wave effect)
Ortho- ,Parahydrogen separation

Technical processes: Combined effects! (Ref.: Ruthven, Yang, Sircar..)

Measurement Methods for Gas Adsorption Equilibria

Pure Gas Method

Volumetry/Manometry

Gravimetry

Oscillometry

Dielectric Permittivity

Purpose

Characterization of porous solids

Equilibria, Kinetics, Gas Density, Process Cont.

Swelling Material

Industrial Process Control

Gas Mixtures (N=2)

Volumetric-Densimetric M.
(2-sites Magnetic Balance)

Equilibria, Process Control

Gas Mixtures (N>2)

Volumetric/Gas Phase Analysis Process Design

Ref: J.U. Keller, R. Staudt, *Gas Adsorption Equilibria*, Springer, New York, 2004.

Measurement Methods of Masses of Adsorbed Phases

1. Volumetry / Manometry

Result of measurements:

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

Approximations:

1. Gibbs excess mass

$$V^{as} \cong V_{He}^s, \quad V^a = 0$$

$$m_{GE}^a = \Omega + \rho^f V_{He}^s$$

2. Gravimetry

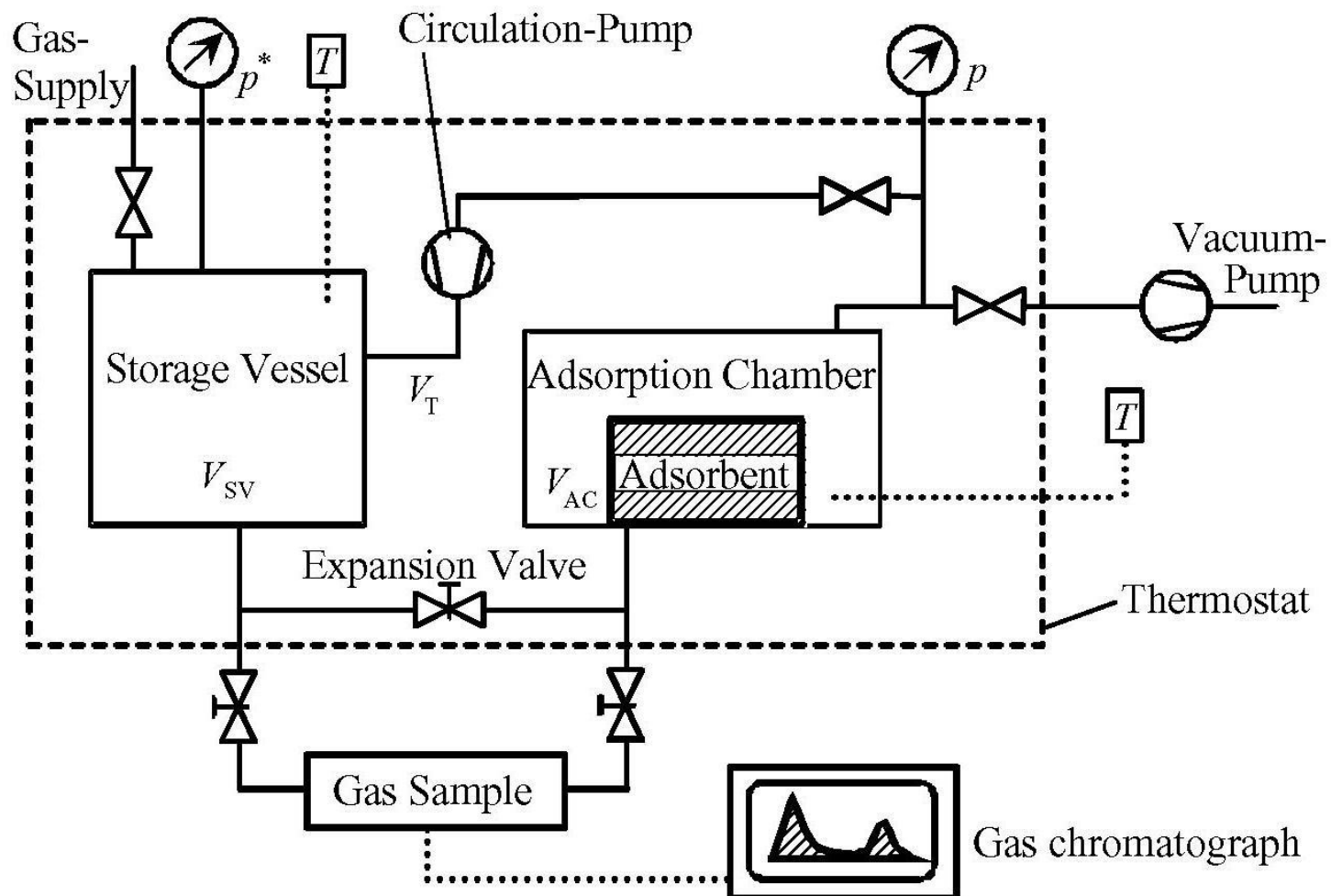
Volume of Gas Adsorption System

$$V^* = V^f + V^{as}$$

2. Absolute mass adsorbed

$$V^{as} \cong V_{He}^s + (m^a / \rho_0^L)$$

$$m^a = \frac{m_{GE}^a}{1 - (\rho^f / \rho_0^L)} \geq m_{GE}^a$$



Experimental Setup for Volumetric- Chromatographic Measurements of Gas Adsorption Equilibria

Mass balances $m_i^* = m_i^f + m_i \quad i = 1 \dots N \quad (1)$

Total mass (i) $m_i^* = w_i^* \rho_i^f(T, p^*, w_1^* \dots w_N^*) V_{SV} \quad (2)$

Adsorptive's mass (i) $m_i^f = \rho_i^f V_{SV} + V_{AC} - V^S \quad (3)$

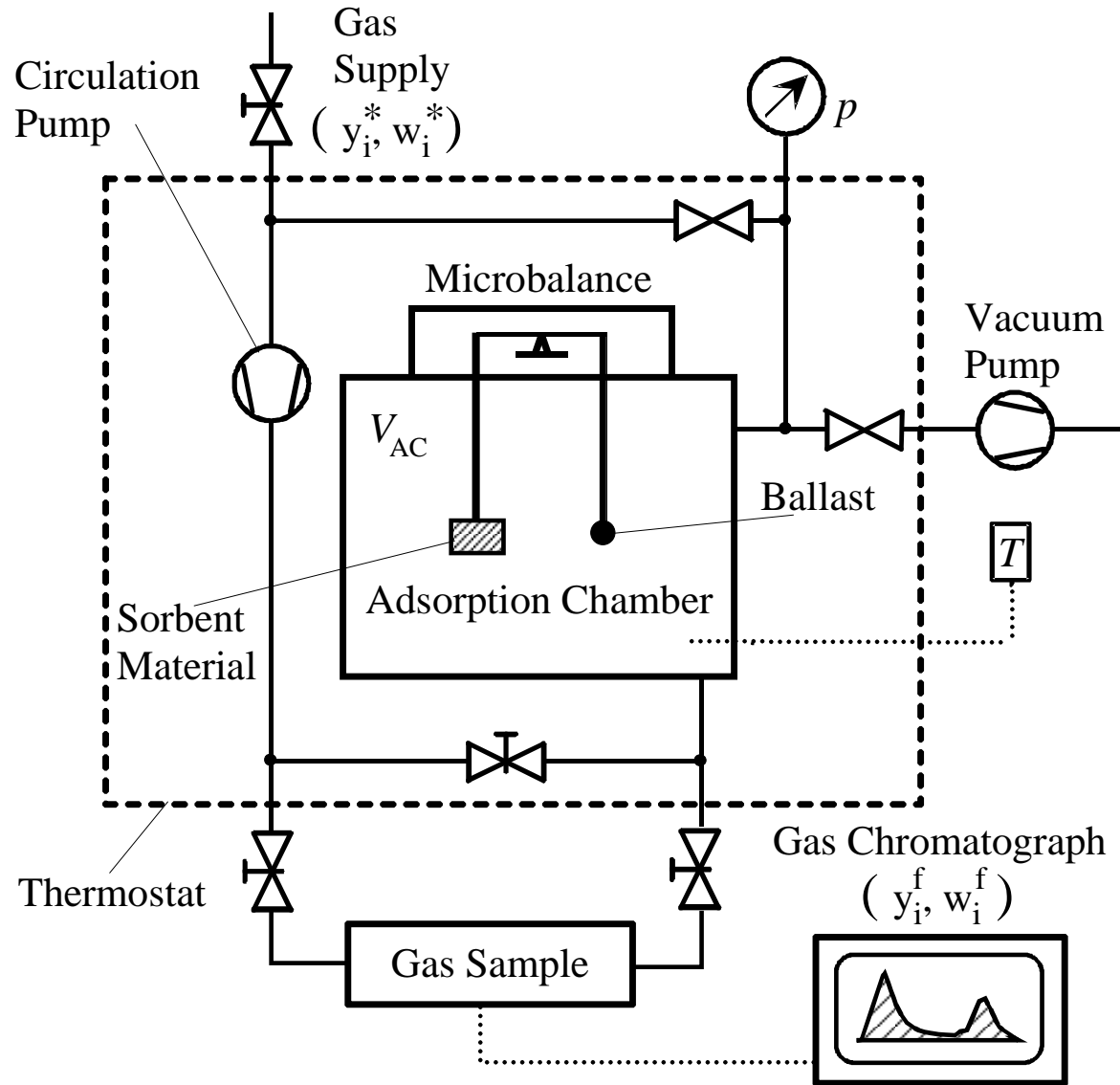
$$(1-3) : \underline{\Omega_i = m_i - \rho_i^f V^S} \quad (4)$$

$$\Omega_i = \rho_i^* - \rho_i V_{SV} - \rho_i V_{AC}$$

$$\rho_i^f = w_i \rho_i^f(T, p, w, \dots w_N), \quad w_i : \text{GC}$$

$$V^S \cong V_{\text{He}}^S \quad m_i \dots \text{Gibbs excess mass}$$

Volumetry / Chromatography (N>=1) (Closed Systems)



Experimental setup for gravimetric-chromatographic measurements of multicomponent gas adsorption equilibria

Total mass of gas supplied to system:

$$m^* = m^f + m^a \quad 1$$

Microbalance:

$$\Omega = m^a - \rho^f V_{He}^s \quad 4$$

Sorptive mass / mole number:

$$m^f = M^f n^f = \left(\sum_i^N y_i^f M_i \right) n^f \quad 2$$

$$m^a = \Omega + \frac{m^f}{V_{AC} - V_{He}^s} V_{He}^s \quad 4A$$

$$n^f = \frac{p V_{AC} - V_{He}^s}{RTZ \ p, T, y_1^f \dots y_N^f} \quad 3$$

Mass of component $i=1 \dots N$ adsorbed:

$$m_i^a = w_i^* m^* - w_i^f m^f$$

$$1-4 : m_i^a = w_i^* \left[\frac{p V_{AC} - V_{He}^s}{RTZ} M^f + \Omega \right] - w_i^f \frac{p (V_{AC} - V_{He}^s)}{RTZ} M^f$$

Gravimetry / Chromatography ($N \geq 1$)

Data Correlation and Prediction of Mixture Adsorption: Generalized two-site (Dual-Place) AI (2LAI)

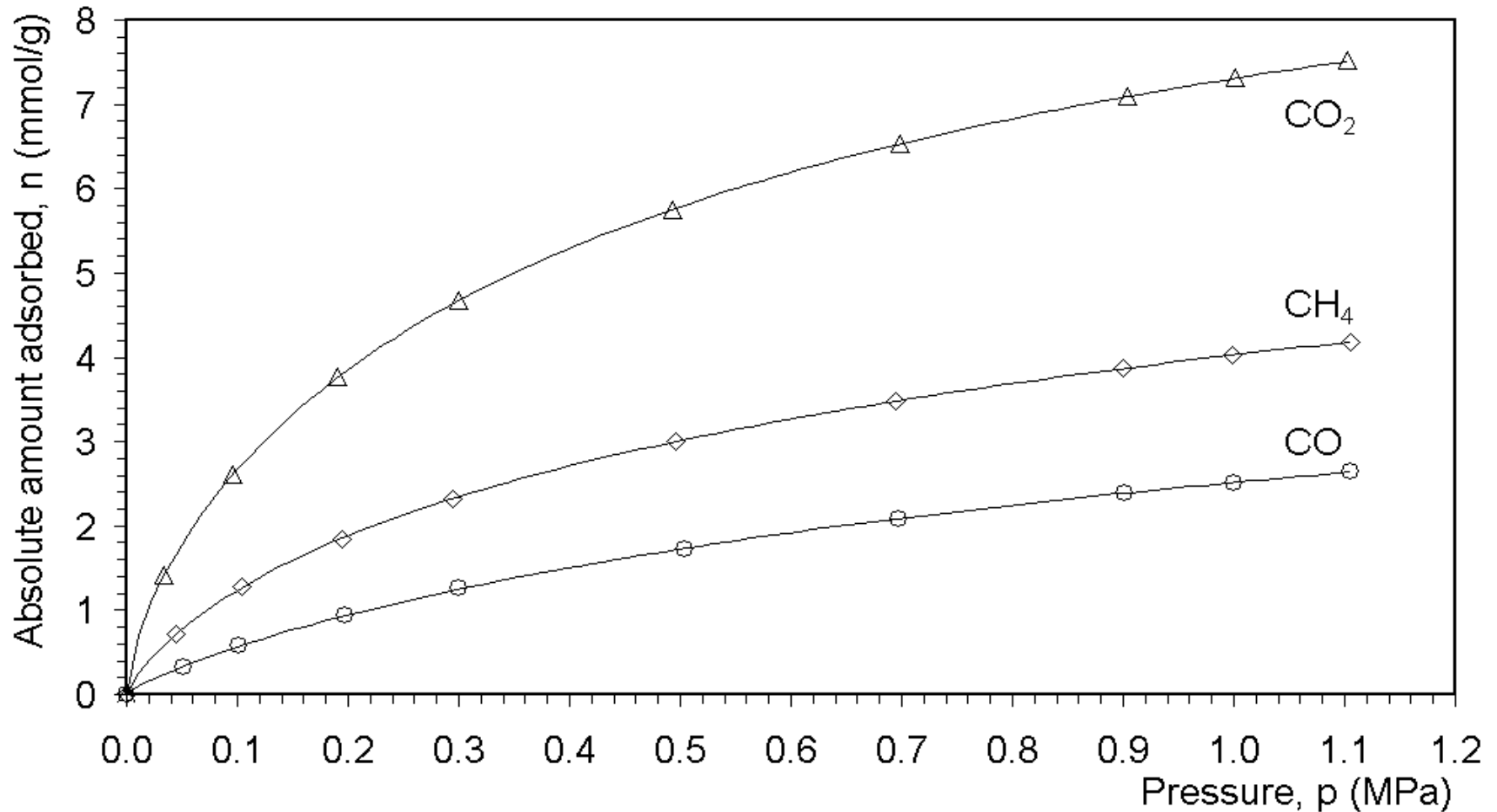
For pure gases:

$$n(p, T) = n_{\infty}^P(T) \cdot \alpha^P \cdot \frac{(b^P(T) \cdot p)^{\alpha^P}}{1 + (b^P(T) \cdot p)^{\alpha^P}} + n_{\infty}^S(T) \cdot \alpha^S \cdot \frac{(b^S(T) \cdot p)^{\alpha^S}}{1 + (b^S(T) \cdot p)^{\alpha^S}}$$

For mixtures:

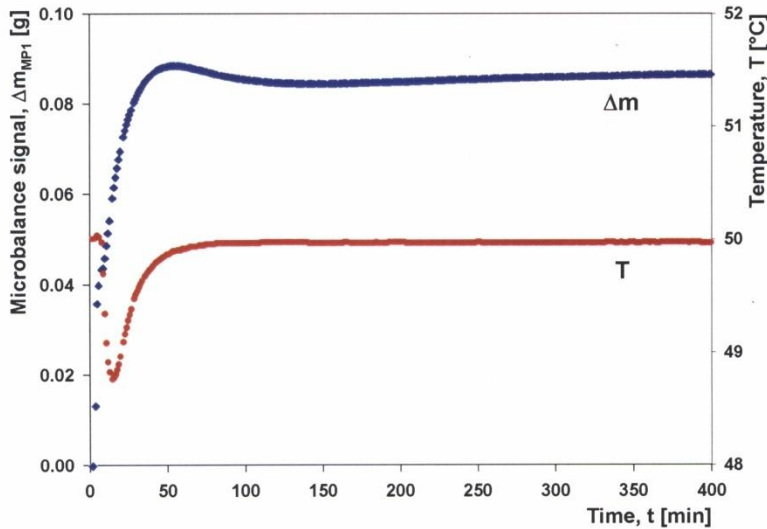
$$n_i(p, T) = n_{\infty, i}^P(T) \cdot \alpha_i^P \cdot \frac{(b_i^P(T) \cdot p_i)^{\alpha_i^P}}{1 + \sum_i (b_i^P(T) \cdot p_i)^{\alpha_i^P}} +$$

$$n_{\infty, i}^S(T) \cdot \alpha_i^S \cdot \frac{(b_i^S(T) \cdot p_i)^{\alpha_i^S}}{1 + \sum_i (b_i^S(T) \cdot p_i)^{\alpha_i^S}}, \quad i = 1, 2, 3.$$



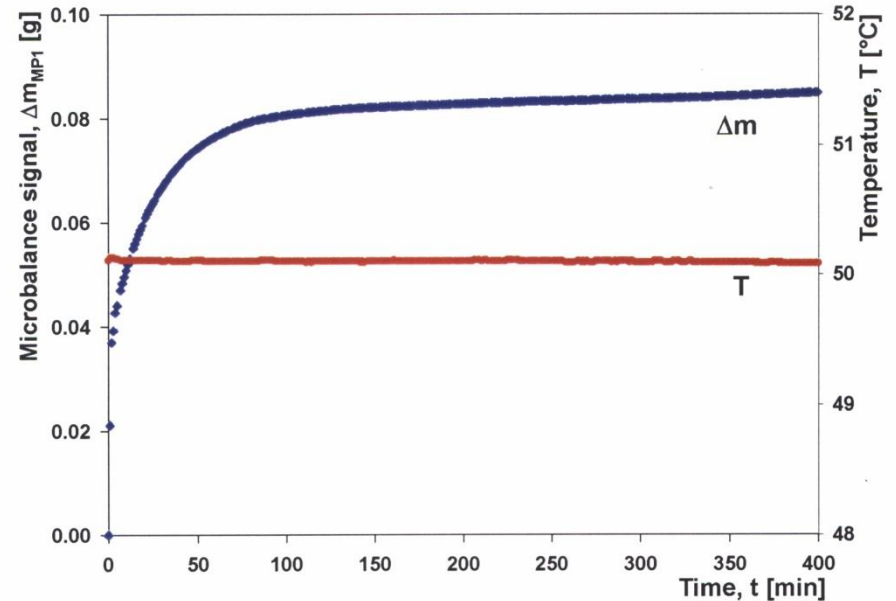
Adsorption equilibria of pure gases CO (\circ), CH₄ (\diamond) and CO₂(Δ) at 293K on industrial activated carbon (ACAL). Datafit: 2LAI ($\bar{}$).

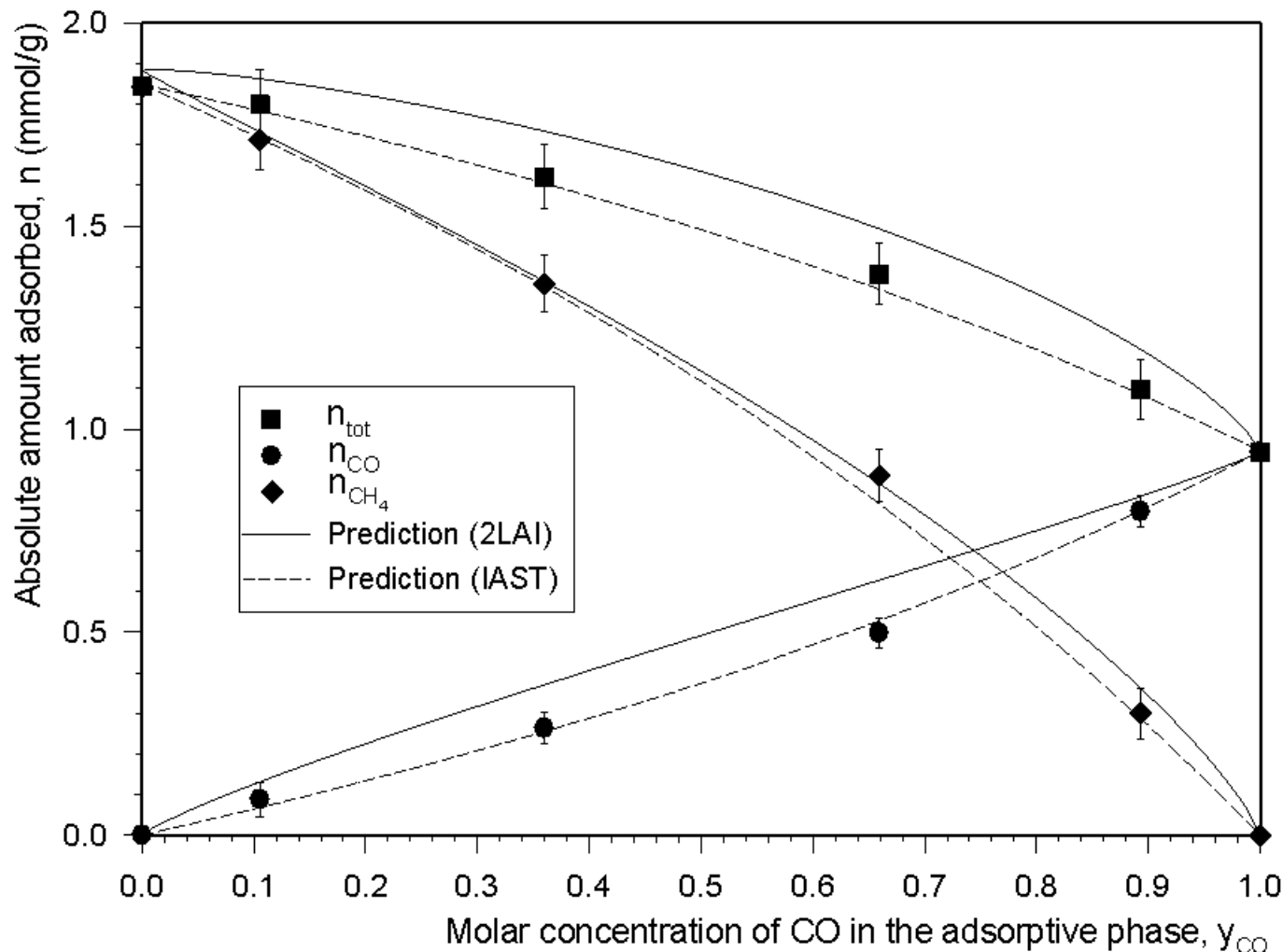
Kinetics of Adsorption of CO₂ on MS Na 13X



< Zeolite dry
 $p: 0.5 > 0.6$ MPa, $T = 50$ °C

Zeolite with preadsorbed water >
 (3.2 mmol H₂O/ g)
 $P: 0.5 > 0.6$ MPa, $T = 50$ °C





Adsorption equilibria of binary gas mixture CO/CH₄ (n_{tot} (■), partial amount of CO (●), partial amount of CH₄ (◆)) at 293K and 0.2MPa on ACAL. Prediction: 2LAI (—) and IAST (.....).

CO/CH ₄ T=293K ACAL		f _m , σ %			
		x _{CO} (adsorbed phase)	n _{CH4} (partial load)	n _{CO} (partial load)	n _{tot} = n _{CO} + n _{CH4}
0.2MPa	2LAI	f _m =24.5 σ =29.0	6.11 10.5	30.6 35.2	6.91 7.22
	IAST	8.46 11.6	3.16 4.39	7.86 11.5	1.39 1.58
1.0MPa	2LAI	52.0 76.3	5.01 7.31	62.1 83.3	8.21 8.75
	IAST	3.55 4.07	3.33 3.64	3.82 4.51	2.67 2.86

- Relative mean deviation (f_m)

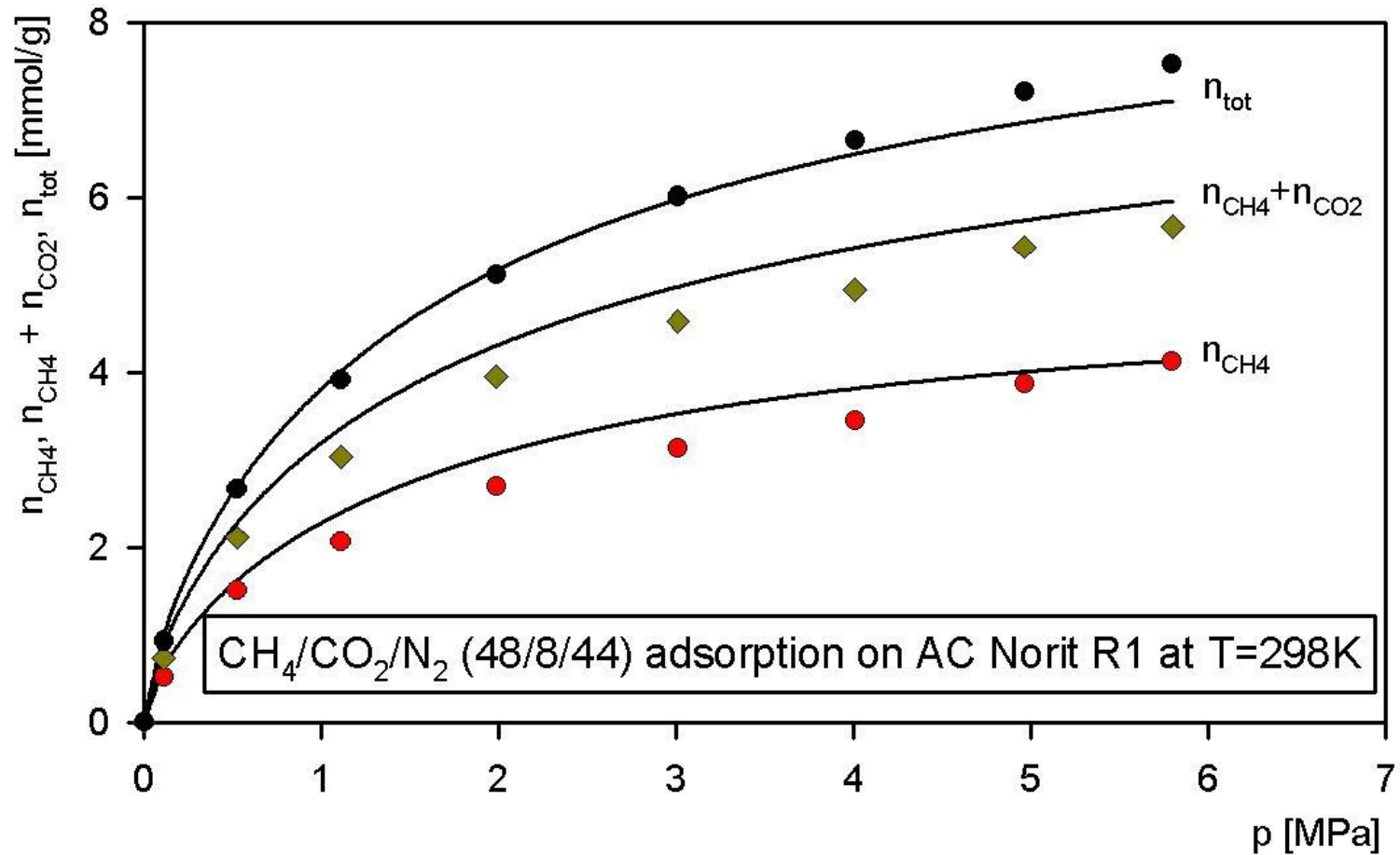
$$f_m = \frac{1}{N} \sum_{i=1}^N \left(\frac{|n_{PRE} - n_{EXP}|}{n_{EXP}} \right)_i$$

- Relative dispersion (σ)

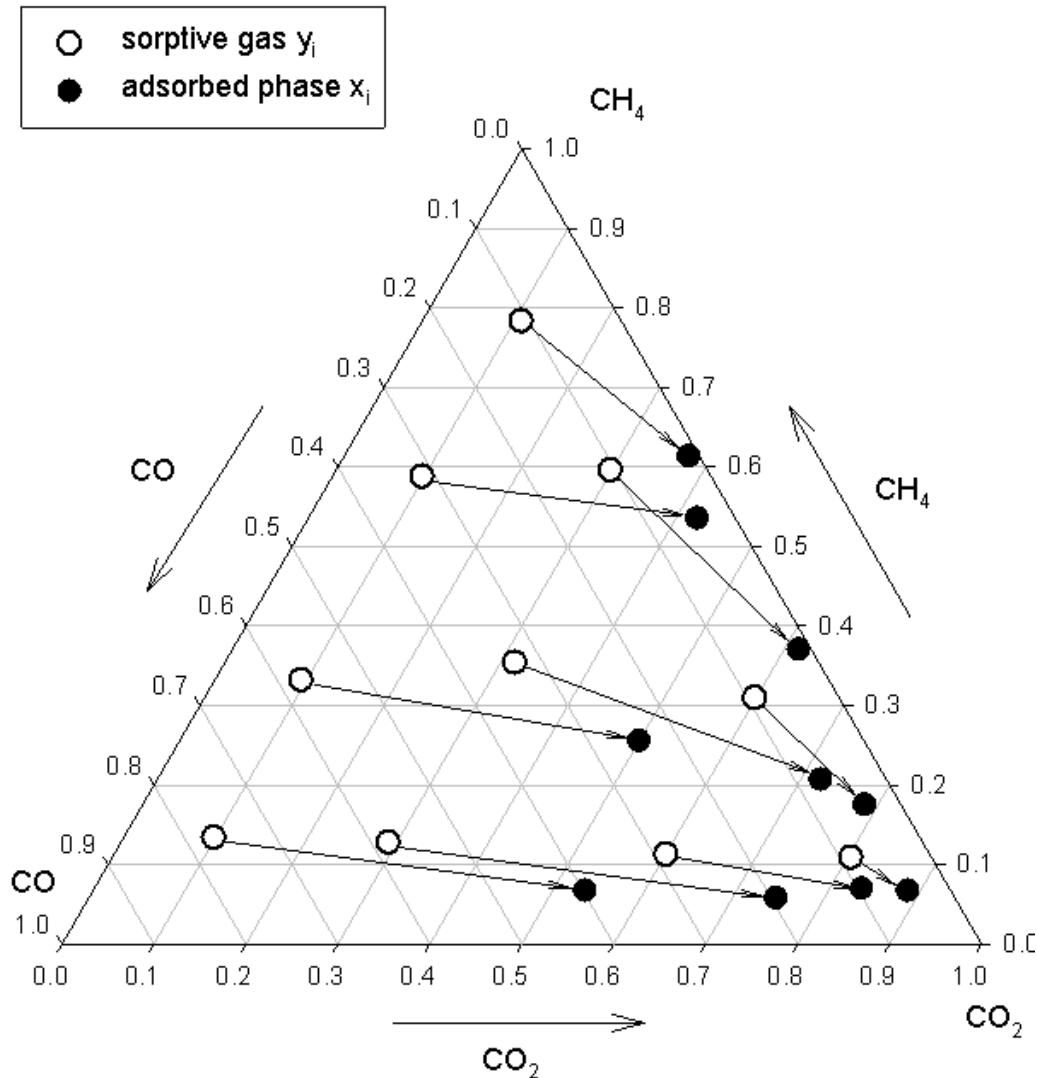
$$\sigma^2 = \frac{1}{N} \sum_{i=1}^N \left(\frac{n_{PRE} - n_{EXP}}{n_{EXP}^2} \right)_i^2$$

N = 1...4

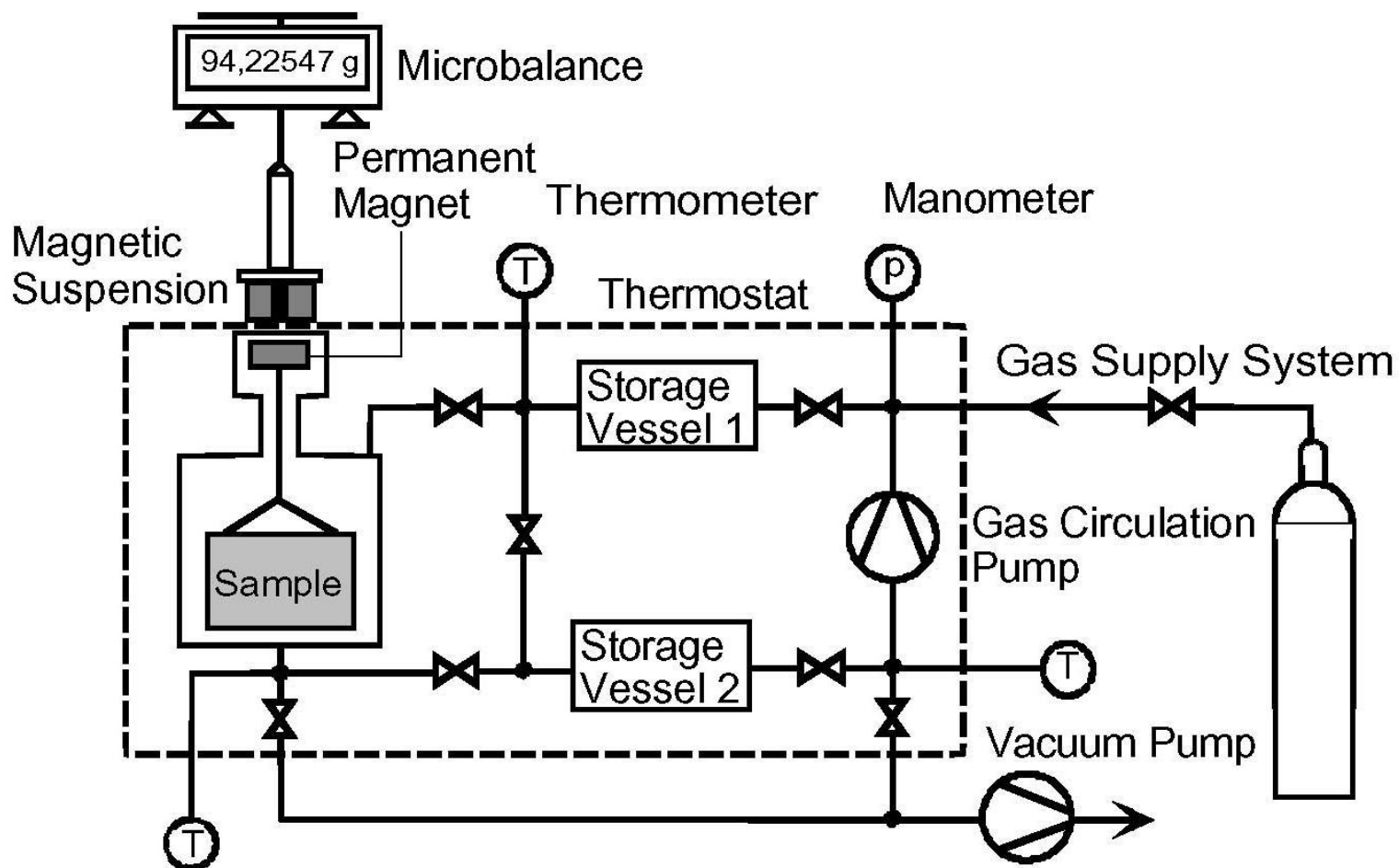
Statistical uncertainties (f_m, σ) of coadsorption data CO/CH₄ on ACAL at 293K and 0.2MPa, 1.0MPa predicted from pure adsorption data by two isotherms.



Prediction of ternary adsorption data with the 2-sites AI



Adsorption equilibria of ternary gas mixture CO₂/CH₄/CO (molar concentrations of the sorptive gases y (○), molar concentrations of the adsorbed phases x (●)) at 293K and 0.2MPa on ACAL.



Experimental Setup for volumetric-gravimetric measurements

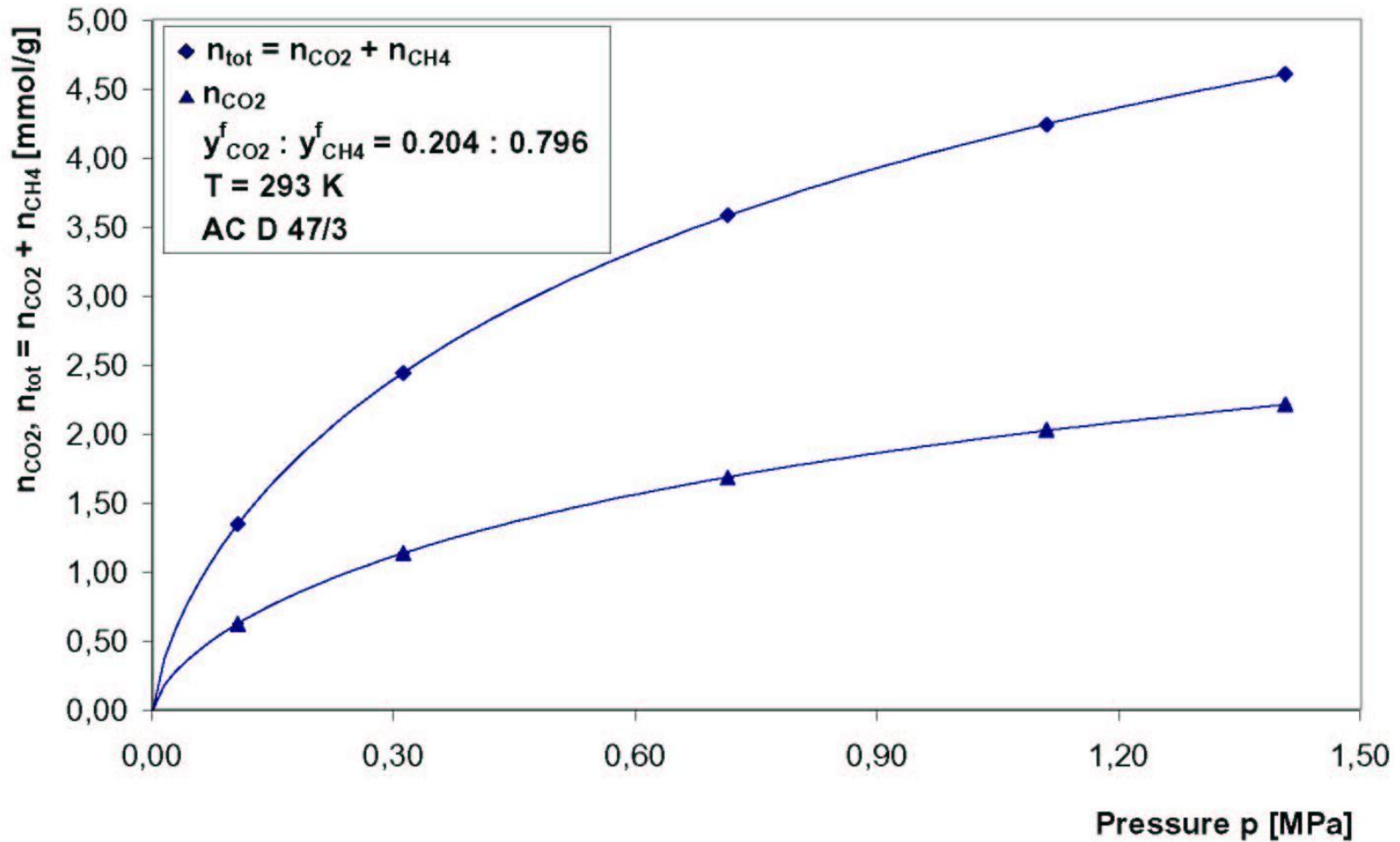
Mass balances $m_i^* = m_i^f + \left(1 + \frac{m_0^s}{m^s}\right) m_i \quad i = 1, 2$

Micro-balance equation $\Omega = m_1 + m_2 - V^{as} \frac{m_1^f + m_2^f}{V^* + V^f}$

Adsorptive's equation of state $\frac{m_1^f}{M_1} + \frac{m_2^f}{M_2} = \frac{p}{ZRT} (V^* + V^f)$

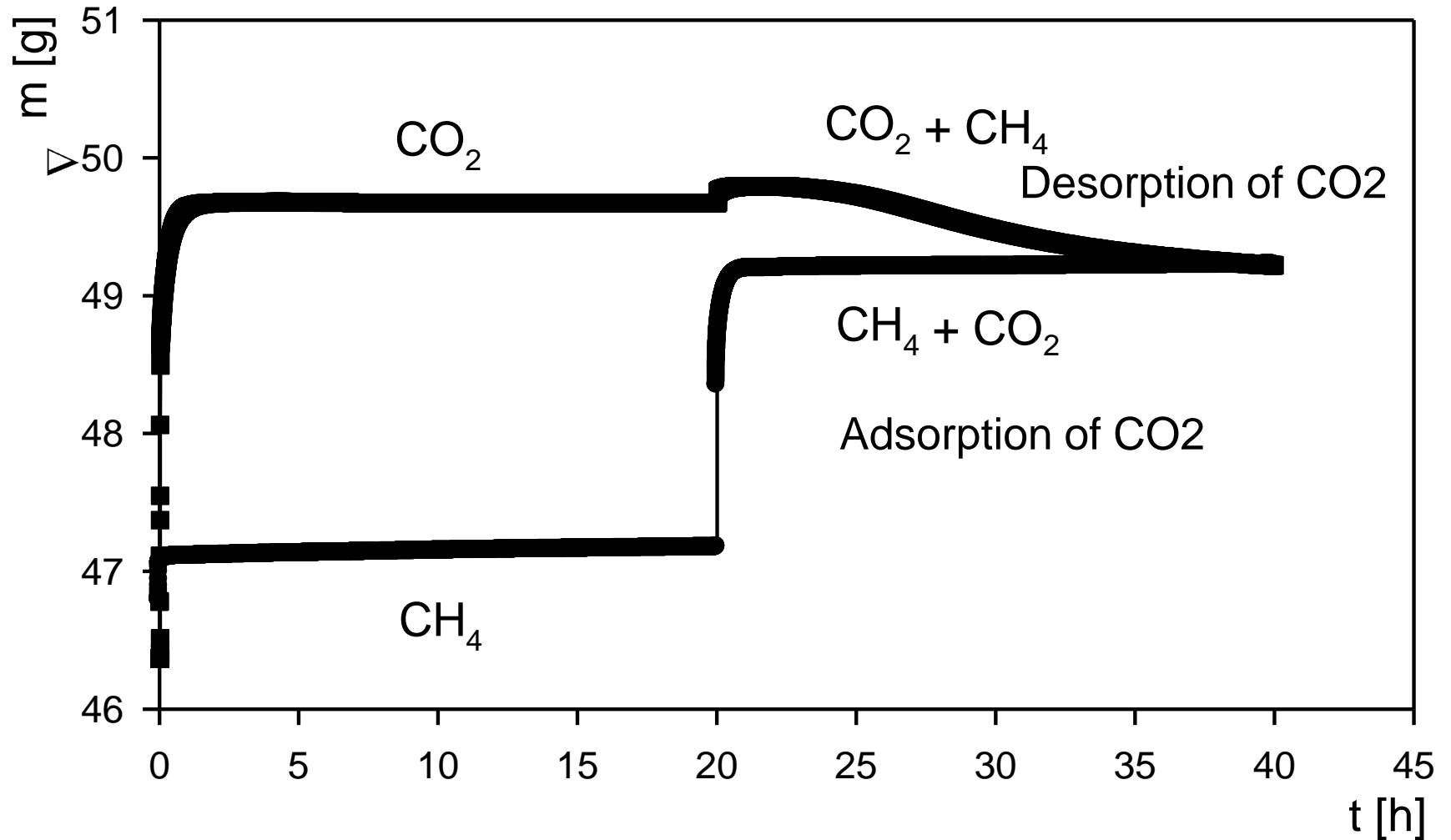
$\rightarrow m_1, m_2, m_1^f, m_2^f \dots V^f = V - \left(1 + \frac{m_0^s}{m^s}\right) V^{as} \quad \text{if } M_1 \neq M_2$

Volumetric-Gravimetric Measurements of Binary Coadsorption Equilibria

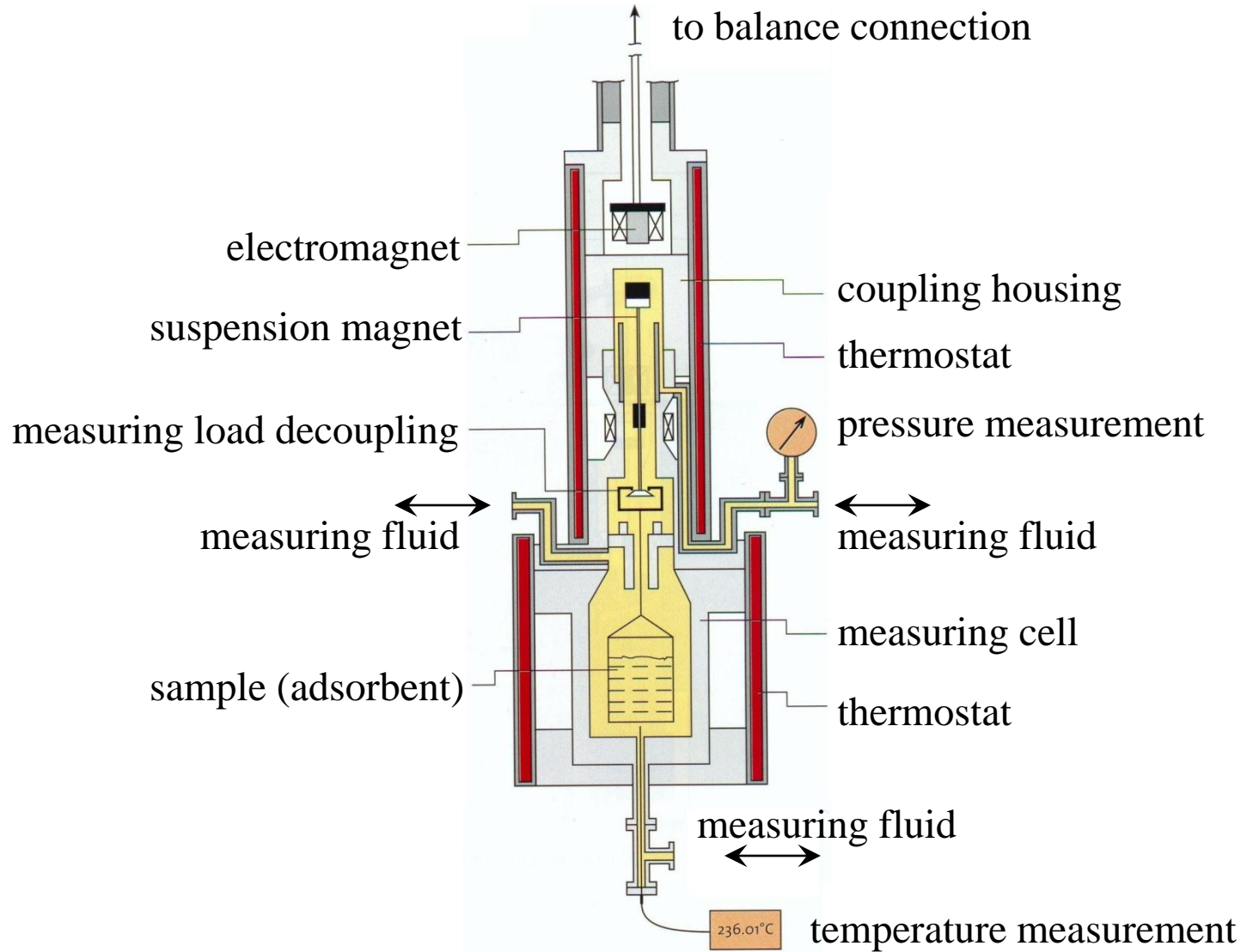


Coadsorption equilibria of $\text{CO}_2 / \text{CH}_4$ at $T = 293\text{K}$, $y_{\text{CO}_2} = 20.4\% \text{ mol}$, $y_{\text{CH}_4} = 79.6\% \text{ mol}$ on AC D47/3. Correlation by GAI: $n_i = n_{i_\infty} (bp)^{\alpha_i} / [1 + (bp)^{\alpha_i}]$, $i = \text{CO}_2, \text{CH}_4$

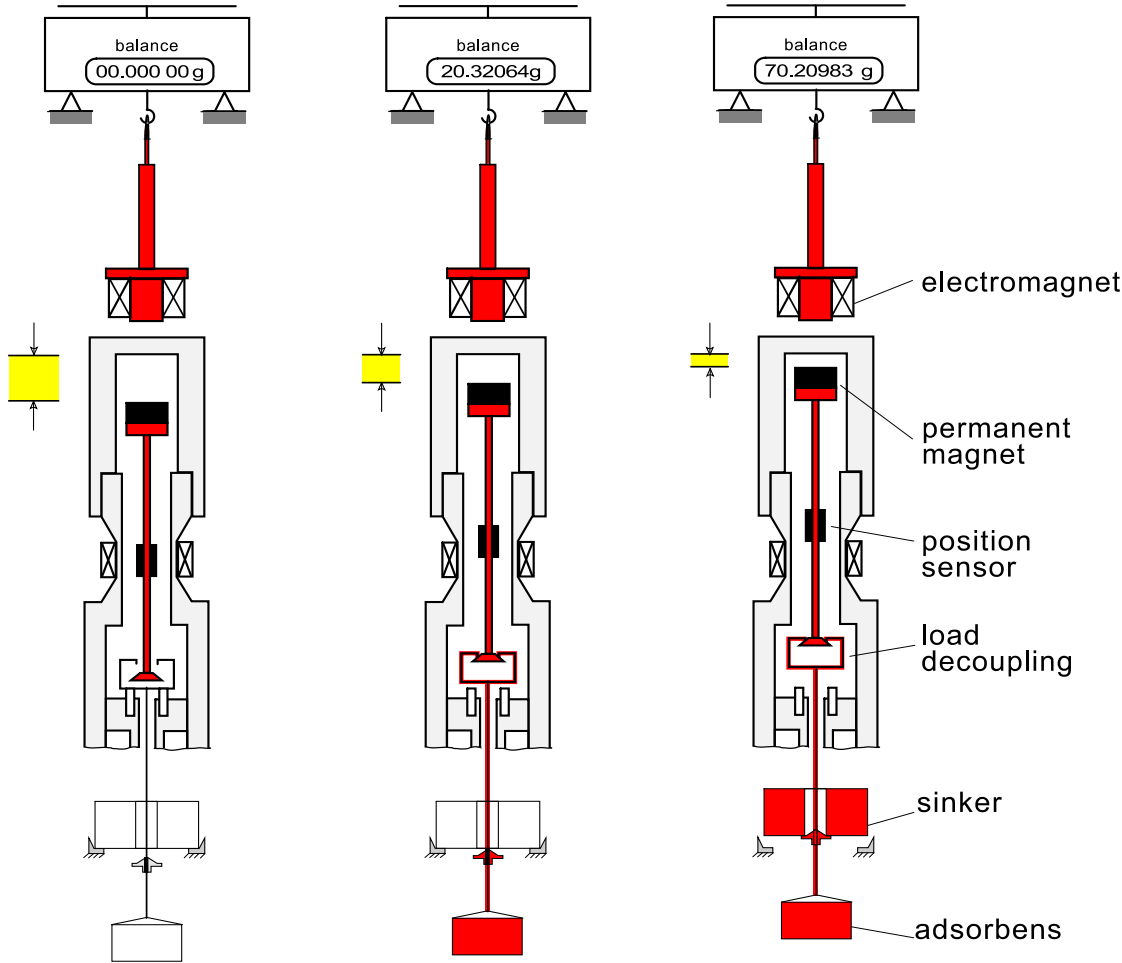
Kinetics of Coadsorption Experiments



Consecutive adsorption of CO₂, CH₄ on AC Norit R1, T= 298K, p=0.11 MPa



Sorption measurement (Rubotherm)



Simultaneous Sorption and Density Measurement (Rubotherm, Bochum, Germany)

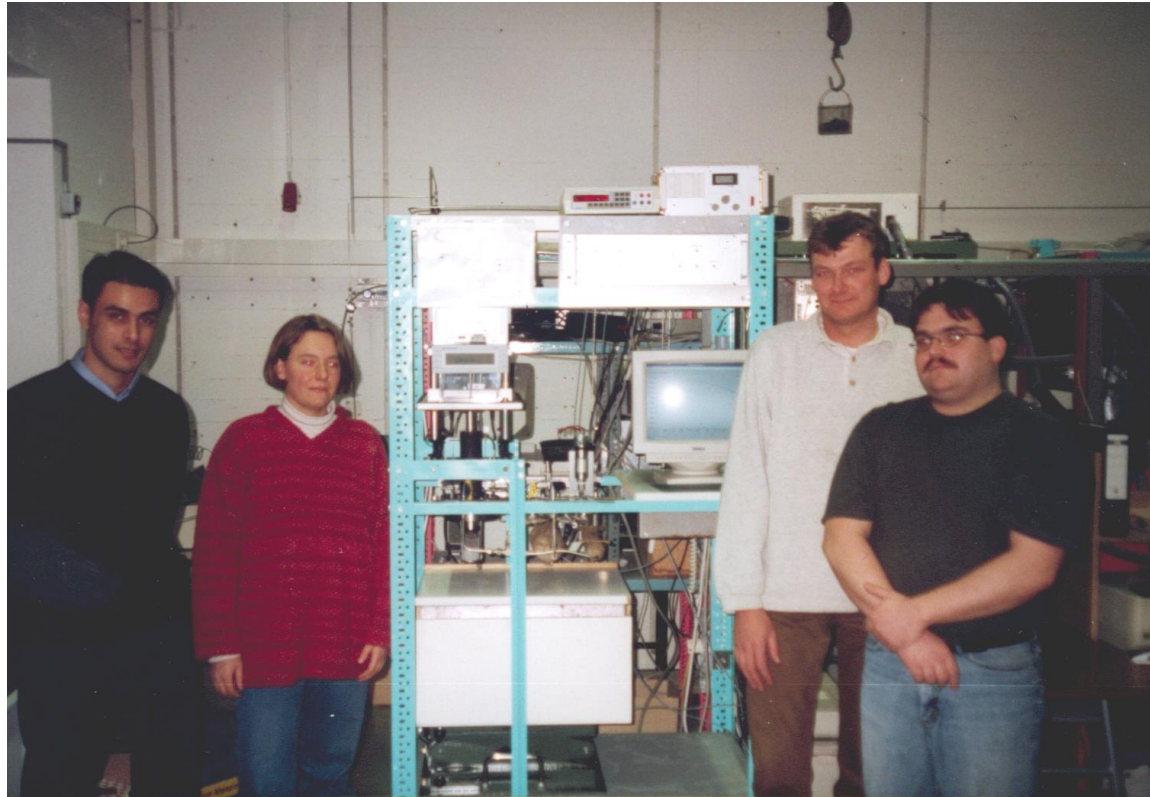
zero point
(tare)

measuring
point I
(sorption)

measuring
point II
(density)



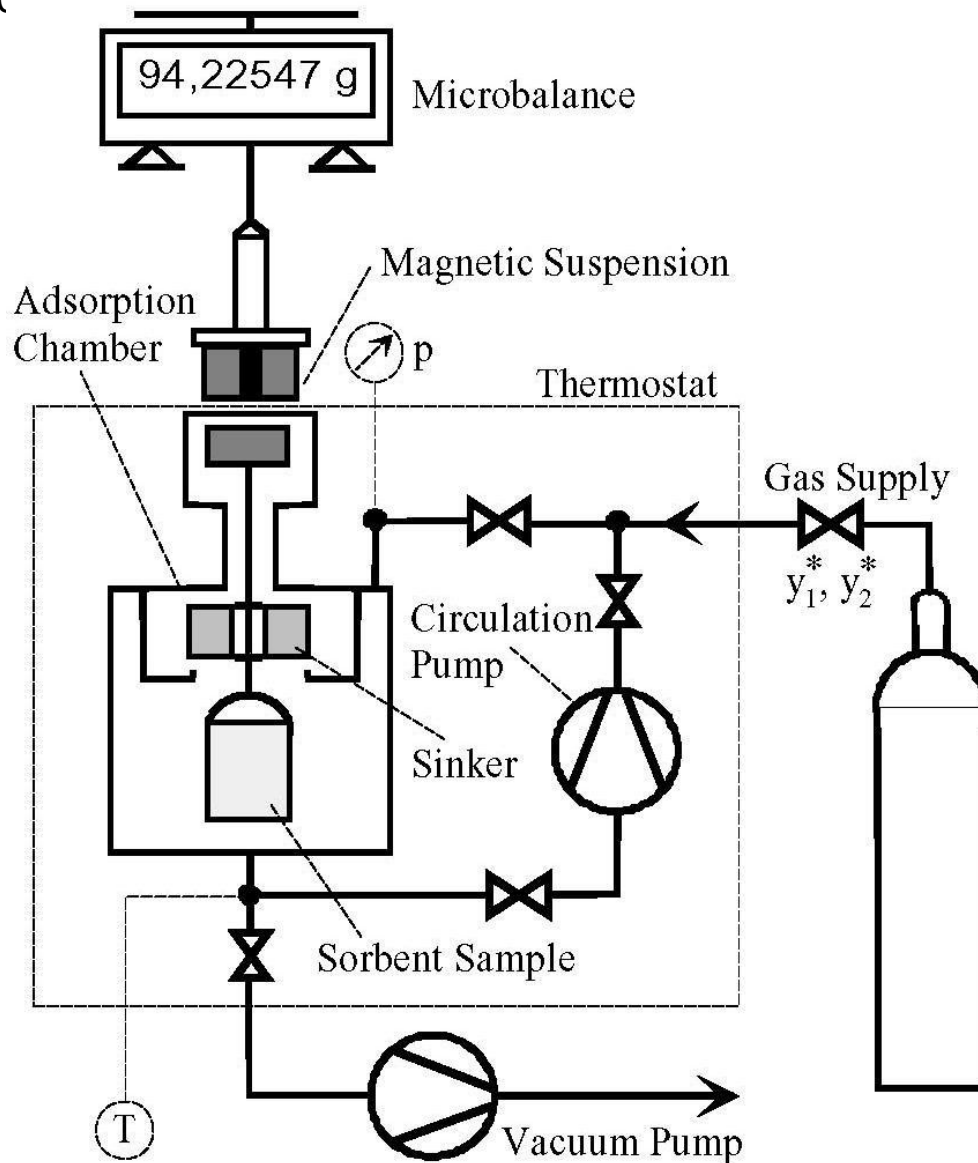
**Magnetic-Suspension-Balance
Instrument (12/96)
Inst. Fluid- and Thermodynamics
University of Siegen**



**First performance of DGMs using a MSB (3)
on 1998-02-11 in Lab PB-A0126 of IFT/USI**



**CO2 Adsorption Instrument
BEL-Rubotherm, IFT, 2001**



Installation for Densimetric-Gravimetric Measurements (DGMs) of Gas Adsorption Equilibria

$$\text{Mass balances} \quad m_i^a = m_i^* - m_i^f \quad i = 1, 2 \quad (1)$$

$$\text{Total gas mass supplied} \quad m^* = m_1^* + m_2^* = m_1^a + m_2^a + m_1^f + m_2^f \quad (2)$$

$$m^* = \Omega + \rho^f V^*$$

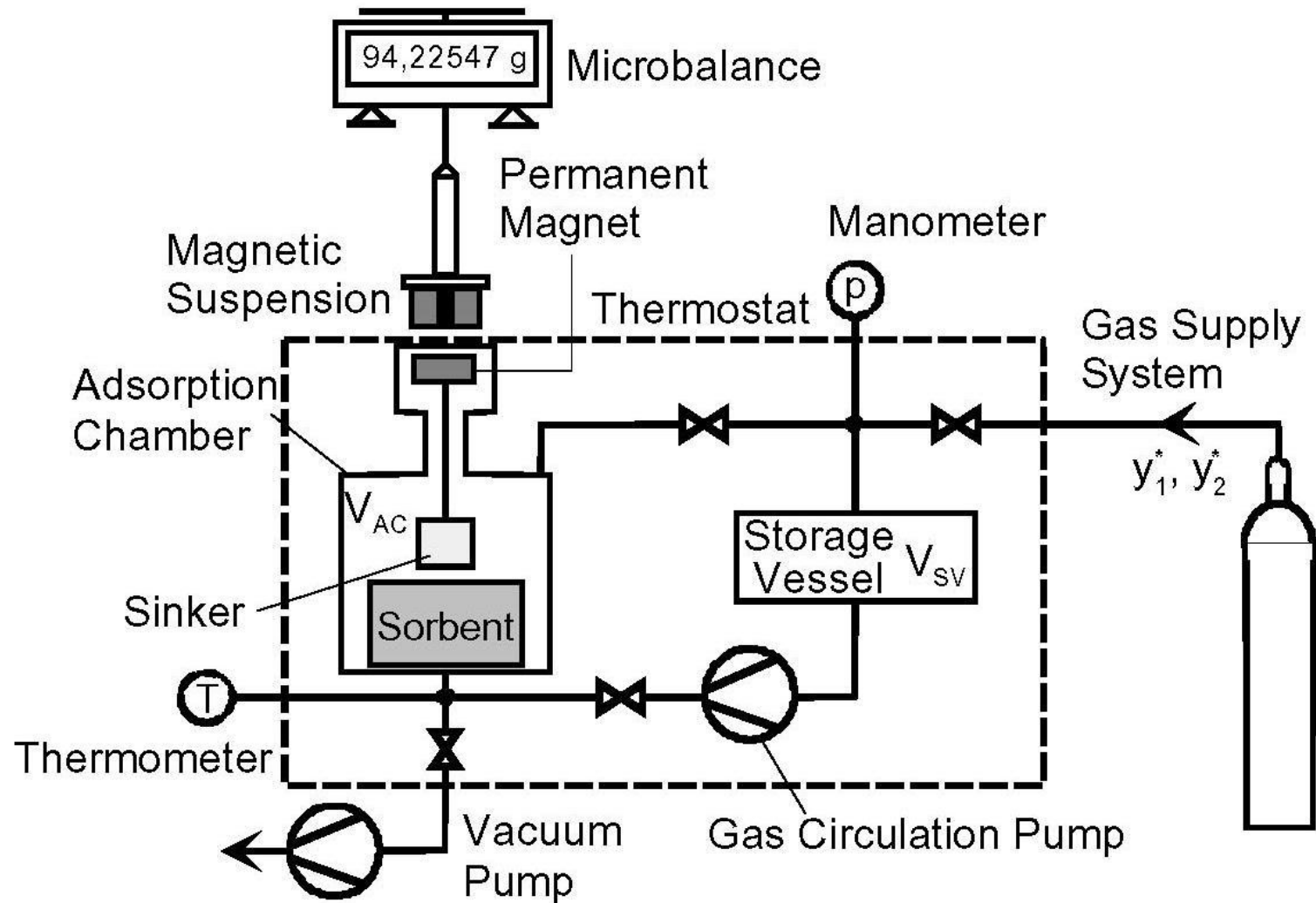
$$m_i^* = w_i^* m^* \quad (2A)$$

$$\text{Sorptive gas masses} \quad m_1^f + m_2^f = \rho^f V^* - V^{\text{as}} \quad (3)$$

$$\frac{m_1^f}{M_1} + \frac{m_2^f}{M_2} = \frac{p V^* - V^{\text{as}}}{RTZ p, T, w_i} \quad (4)$$

$$(1, 2A, 3, 4) \quad V^{\text{as}} = V_{\text{He}}^s \quad (5)$$

$$m_{i\text{GE}}^a = m_i^* - \frac{M_i}{M_i - M_{i+1}} \left(\rho^f - \frac{p M_{i+1}}{RTZ p, T, w_i} \right) V^* - V_{\text{He}}^s \quad (6)$$



Installation for DVMs of Binary Coadsorption Equilibria of Premixed Gases y_1^*, y_2^*

Mass balances $m_i^a = m_i^* - m_i^f \quad i = 1, 2 \quad (1)$

EOS $m_i^* = \frac{y_i^* p^* V_{SV}^*}{RTZ^*} M_i \quad Z = Z(p^*, T, y_i^*) \quad (2)$

Sorptive gas masses $m_1^f + m_2^f = \rho^f (V^* - V^{as}) \quad (3)$
 (m_1^f, m_2^f)

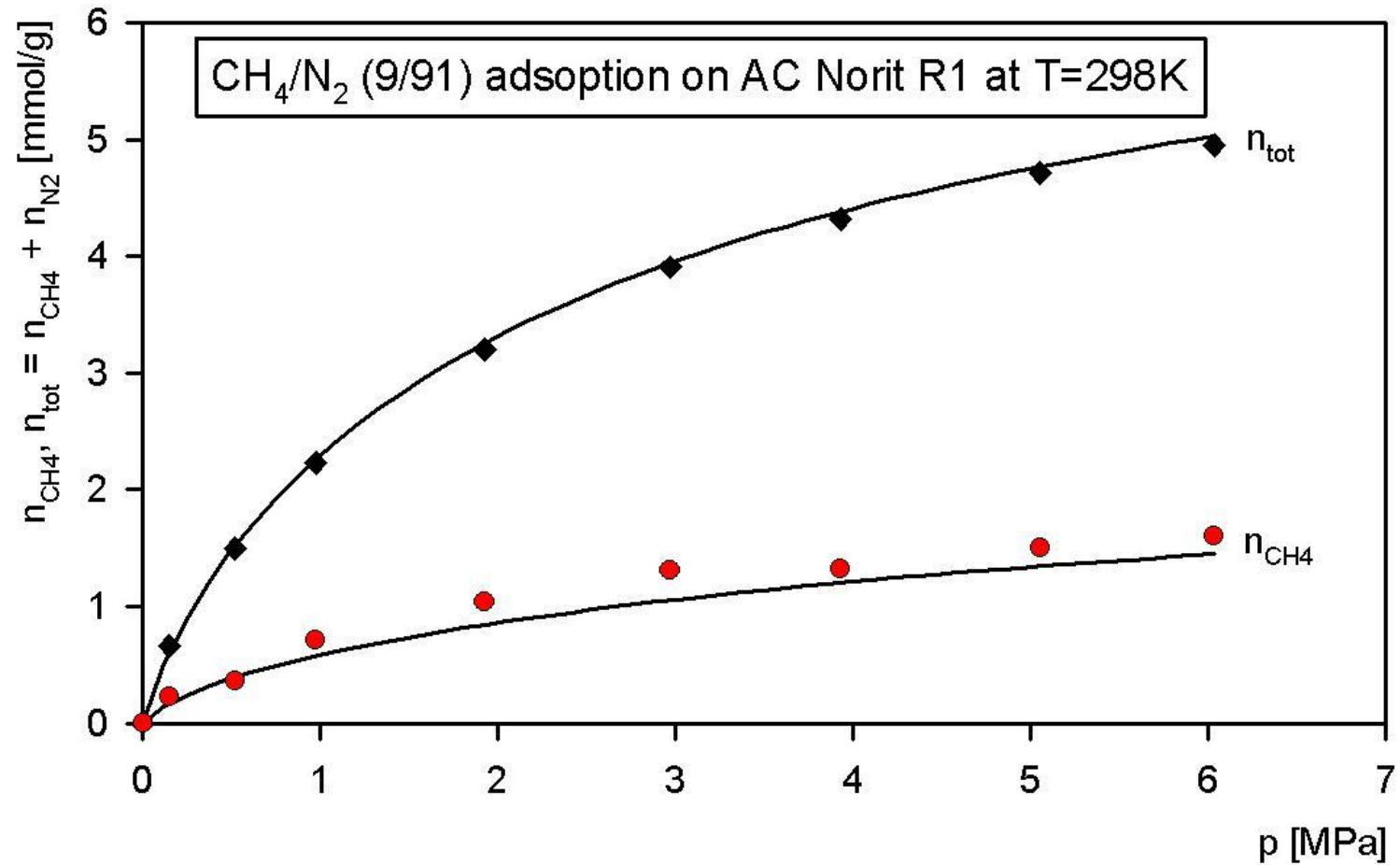
$$\frac{m_1^f}{M_1} + \frac{m_2^f}{M_2} = \frac{p (V^* - V^{as})}{RTZ(p, T, w_i)} \quad (4)$$

$$w_i = \frac{m_i^f}{m_1^f + m_2^f} \quad i = 1, 2$$

(1 - 4) $V^{as} = V_{He}^s \quad (5)$

$$m_{iGE}^a = m_i^* - \frac{M_i}{M_i - M_{i+1}} \left(\rho^f - \frac{p M_{i+1}}{RTZ(p, T, w_i)} \right) (V^* - V_{He}^s) \quad (6)$$

DVMs / Theory



Prediction of binary adsorption data with the 2-sites AI



**Automated MSB (2) (Rubotherm AG, Bochum)
for DVMs of binary coadsorption equilibria**

Gravimetrische Messung von Diffusionskoeffizienten (D)

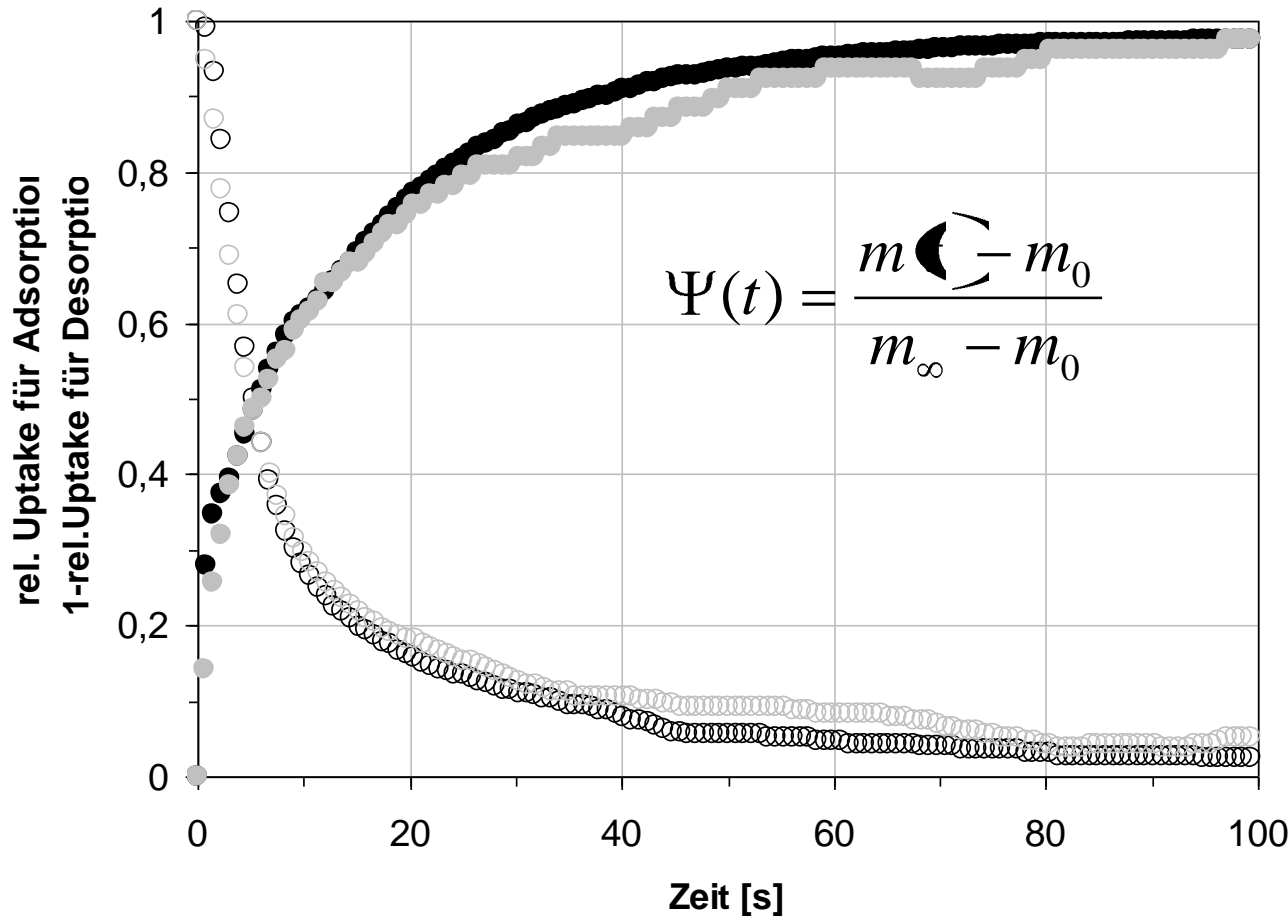


Abbildung 3.
 Vergleich von Adsorptions- und Desorptionsschritten für n-Butan an XY-155-NaCa76A bei 207,6°C,

- Adsorption von 0,3 auf 16,0 mbar, ○ Desorption von 10,3 mbar auf 3,5 mbar,

- Adsorption von 4,0 auf 10,0 mbar, ○ Desorption von 8,2 mbar auf 3,1 mbar.

$$\psi(t) = 1 - \frac{6}{\pi^2} \sum_{i=1}^{\infty} \frac{1}{i^2} \exp\left(-\frac{i^2 \cdot \pi^2 \cdot D \cdot t}{r^2}\right)$$

Gravimetrische Messung von Diffusionskoeffizienten

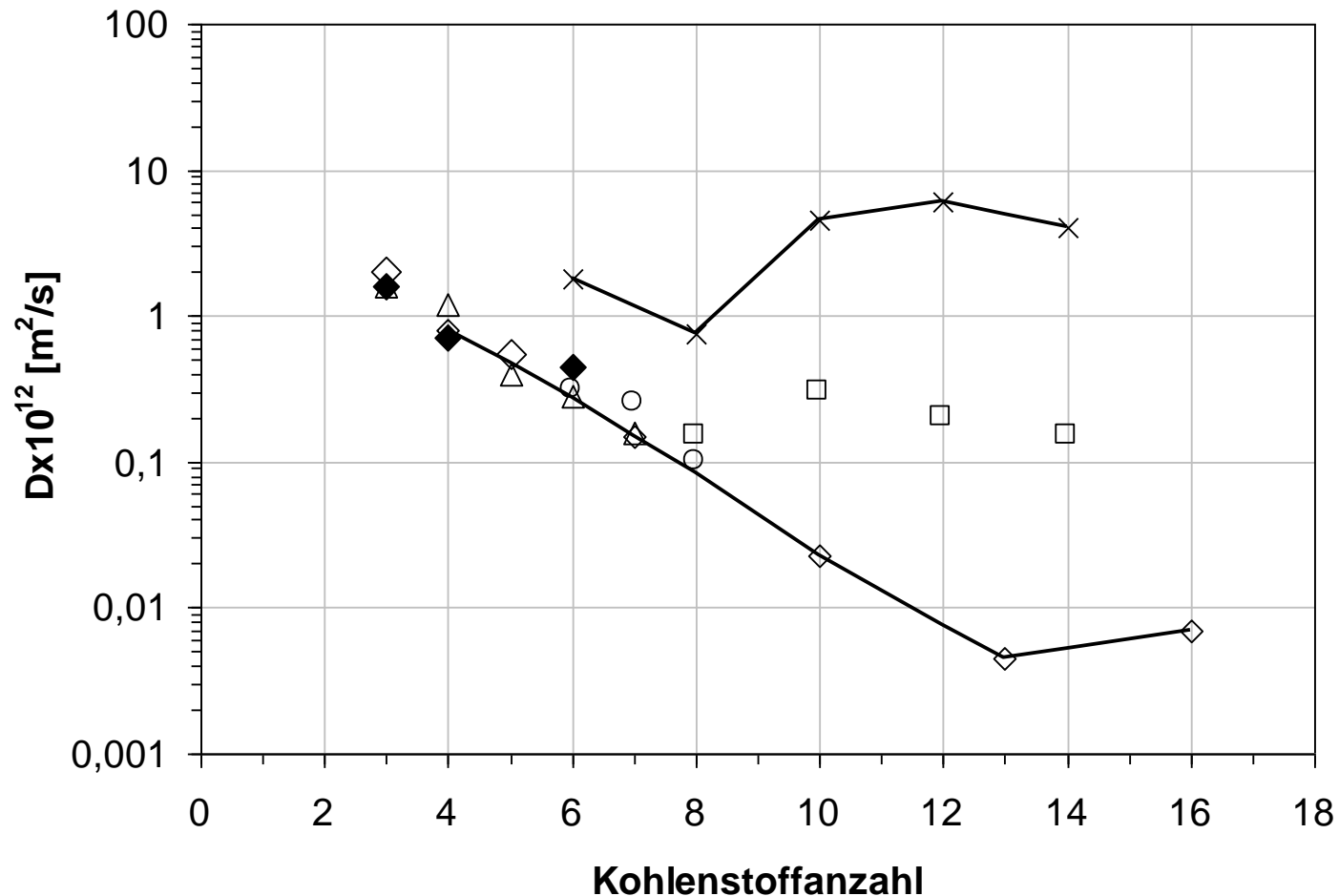
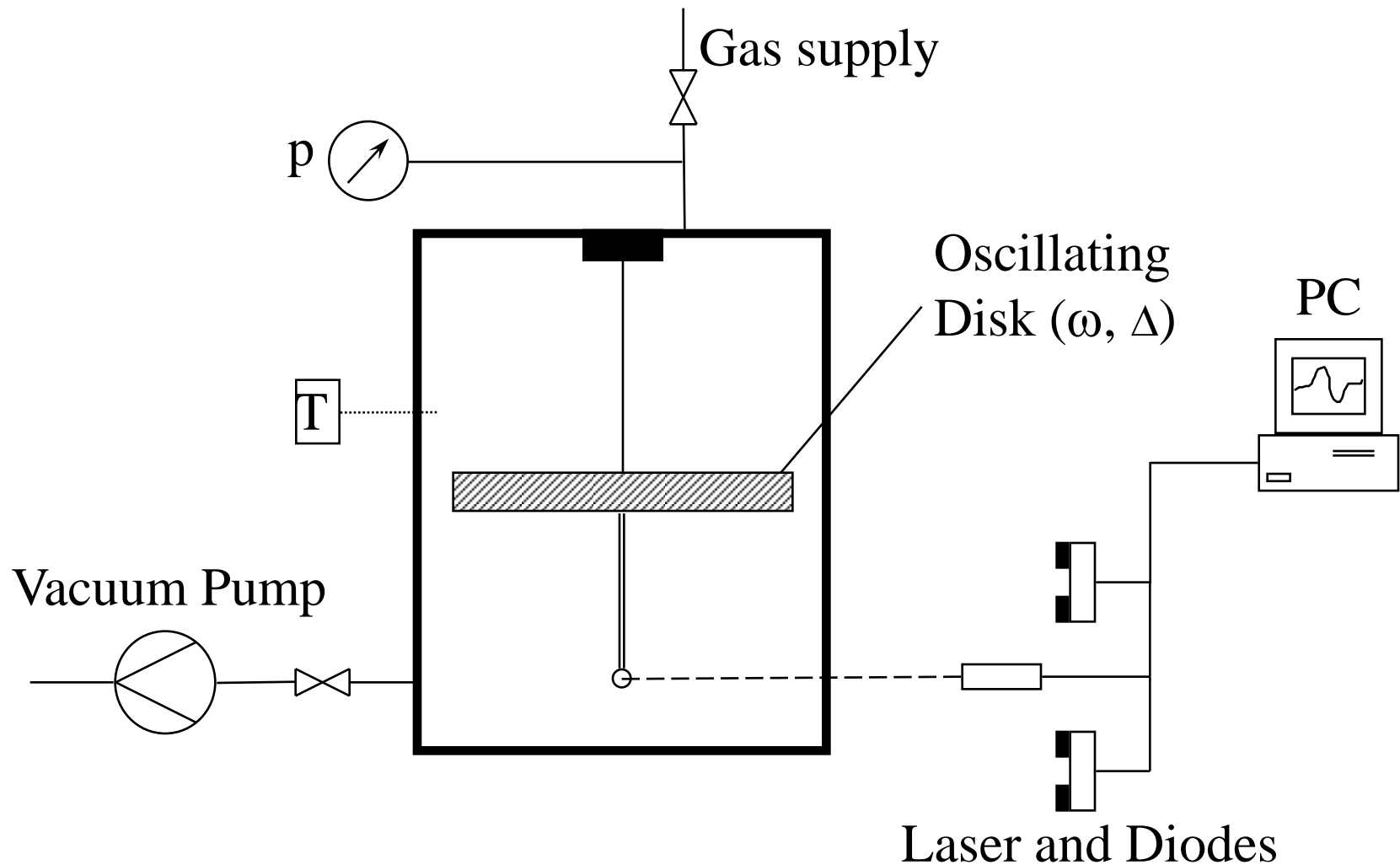


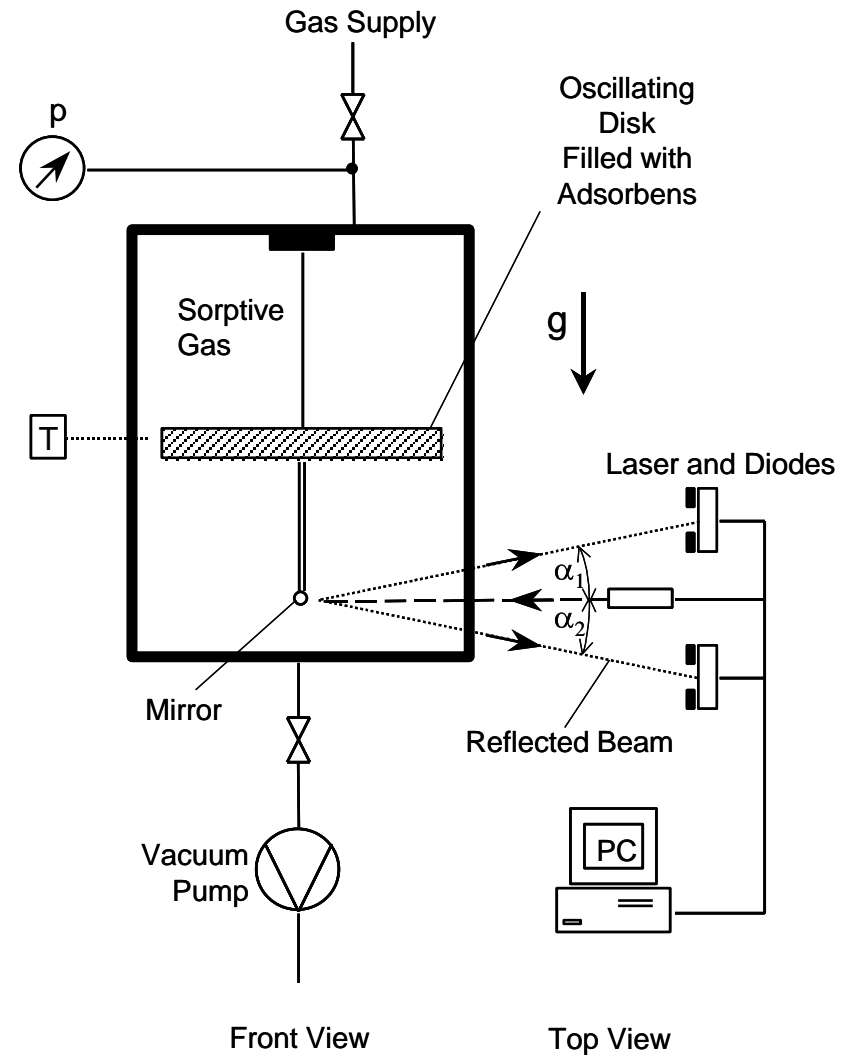
Abbildung 6. Vergleich der erhaltenen Diffusionskoeffizienten für die Probe XY-155-NaCa76A bei ca. 200°C mit den Ergebnissen anderer Methoden: ZLC [11], Δ \circ \square PFG-NMR [14], \times NSE [14]. Ref.: A. Möller, R. Staudt, CIT 6/2008



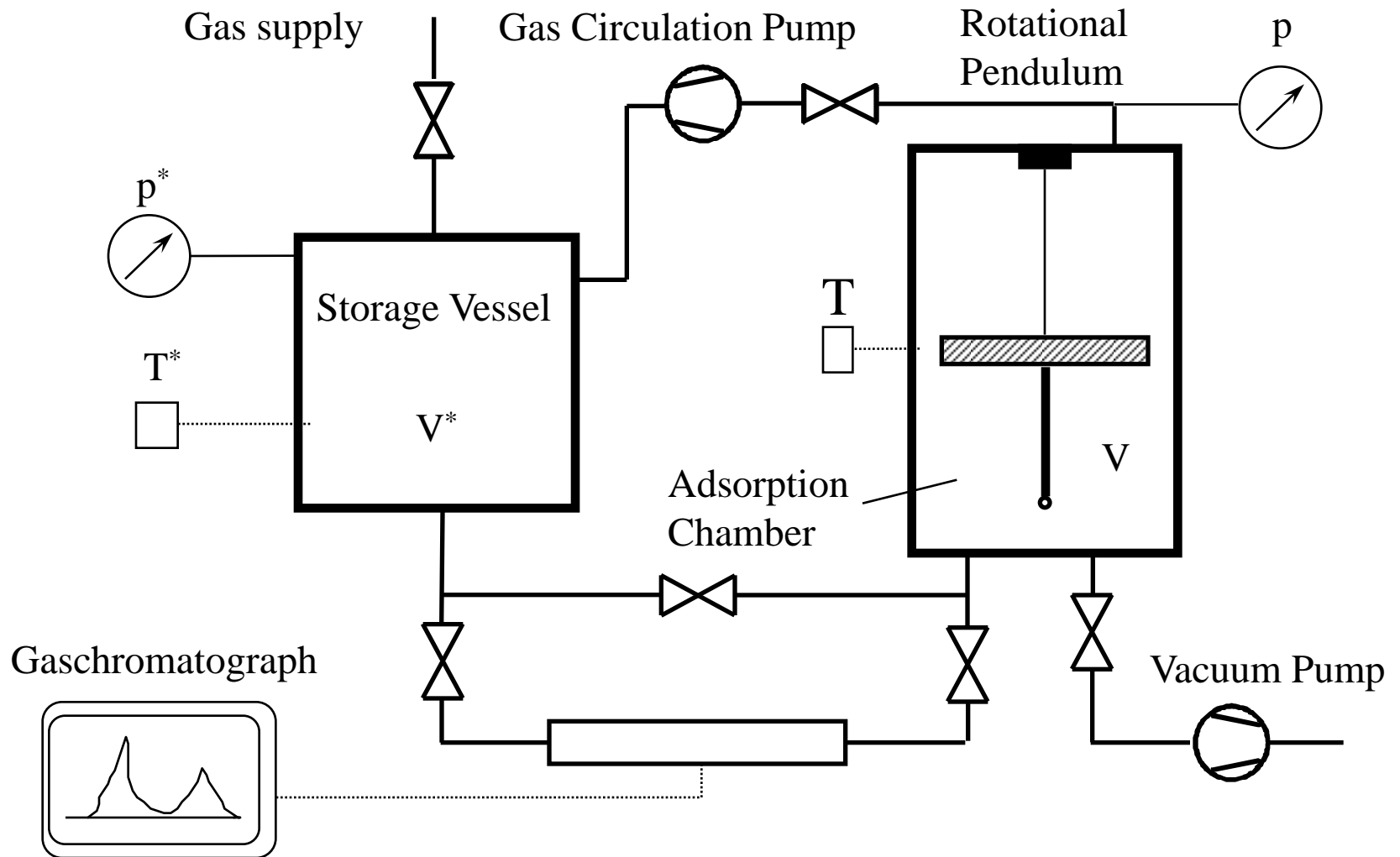
**Experimental Setup for Oscillometric Measurements
of Gas Adsorption Equilibria**



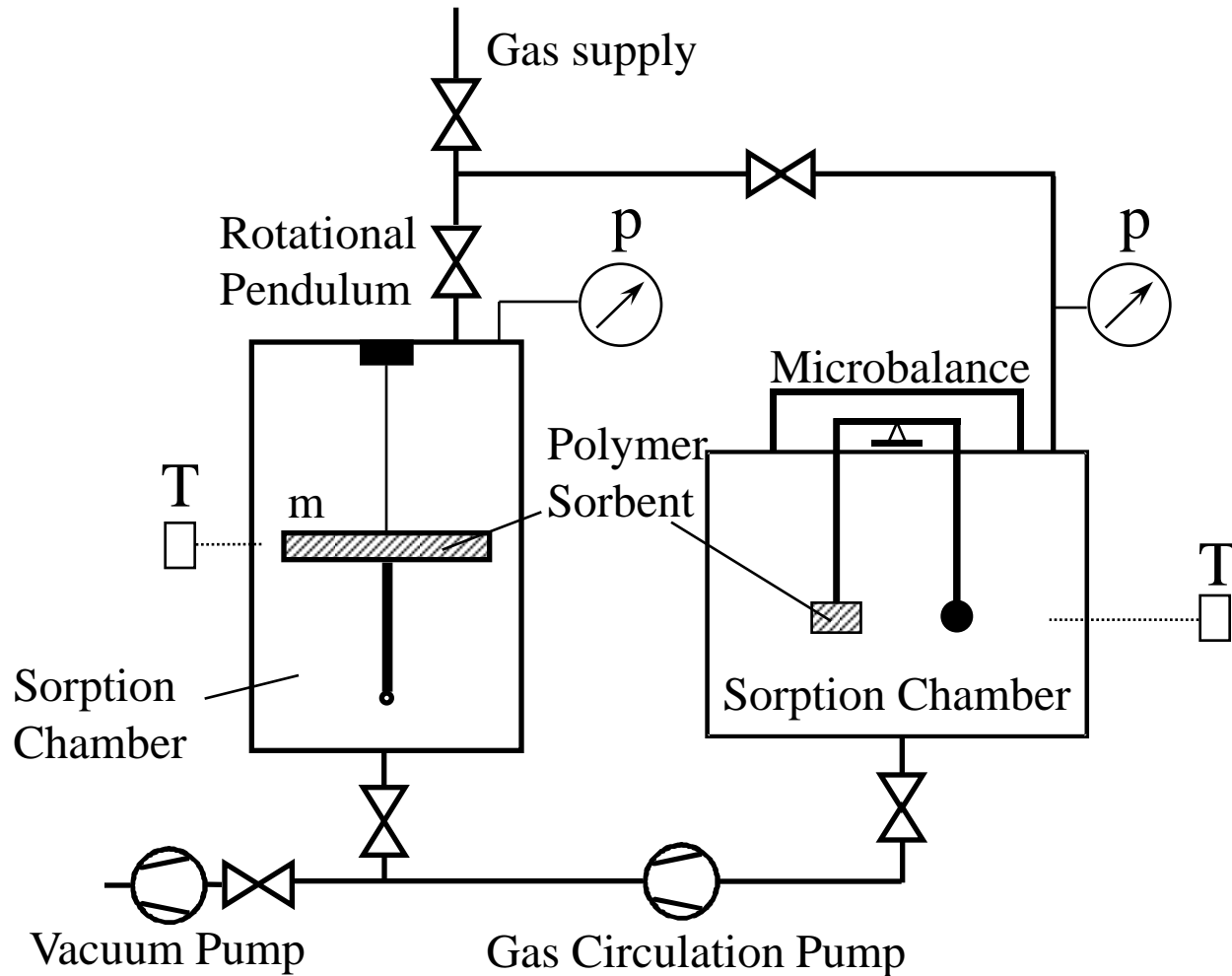
Rotational pendulum for measurements of gas adsorption equilibria by observing slow damped oscillations. Height of instrument: 1.5 m.



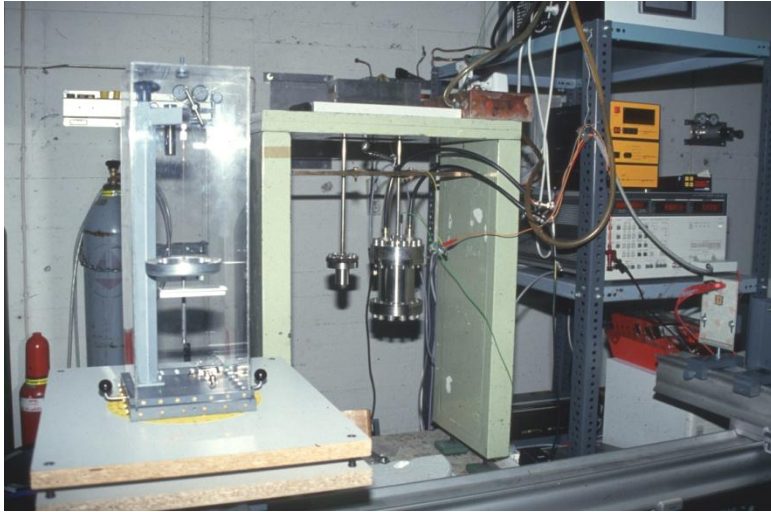
Experimental Setup for oscillometric measurements of gas adsorption equilibria using a rotational pendulum.



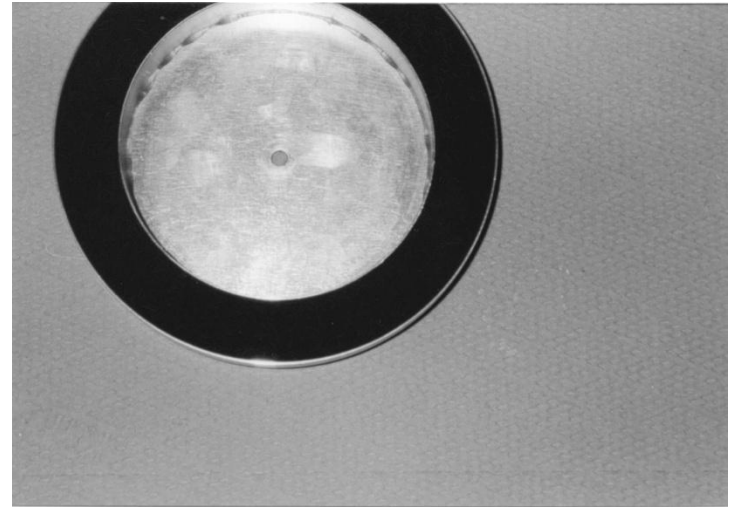
Experimental Setup for oscillometric-volumetric measurements



Experimental Setup for oscillometric-gravimetric measurements

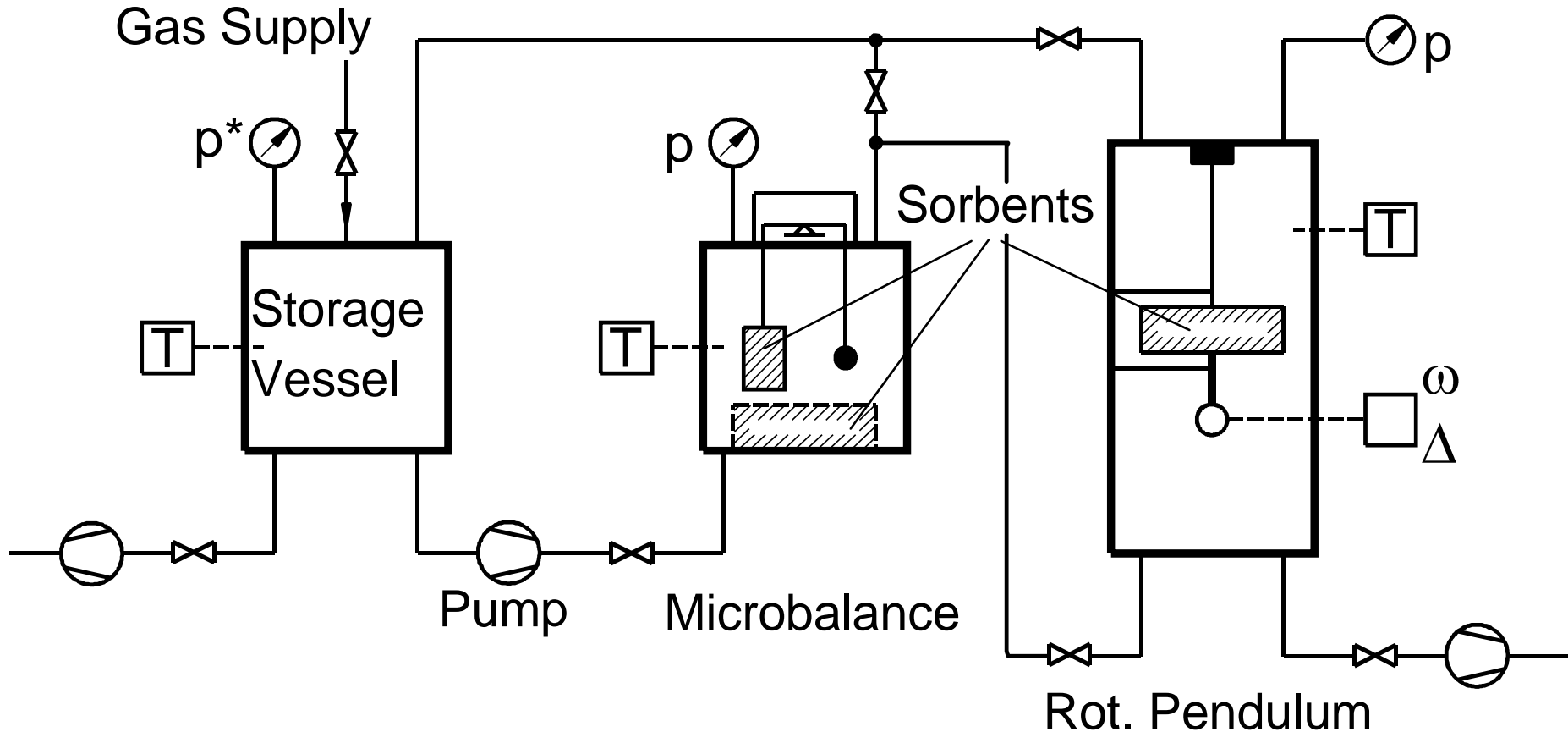


Training instrument for
oscillometric,
volumetric,
gravimetric and
dielectric
gas adsorption measurements .

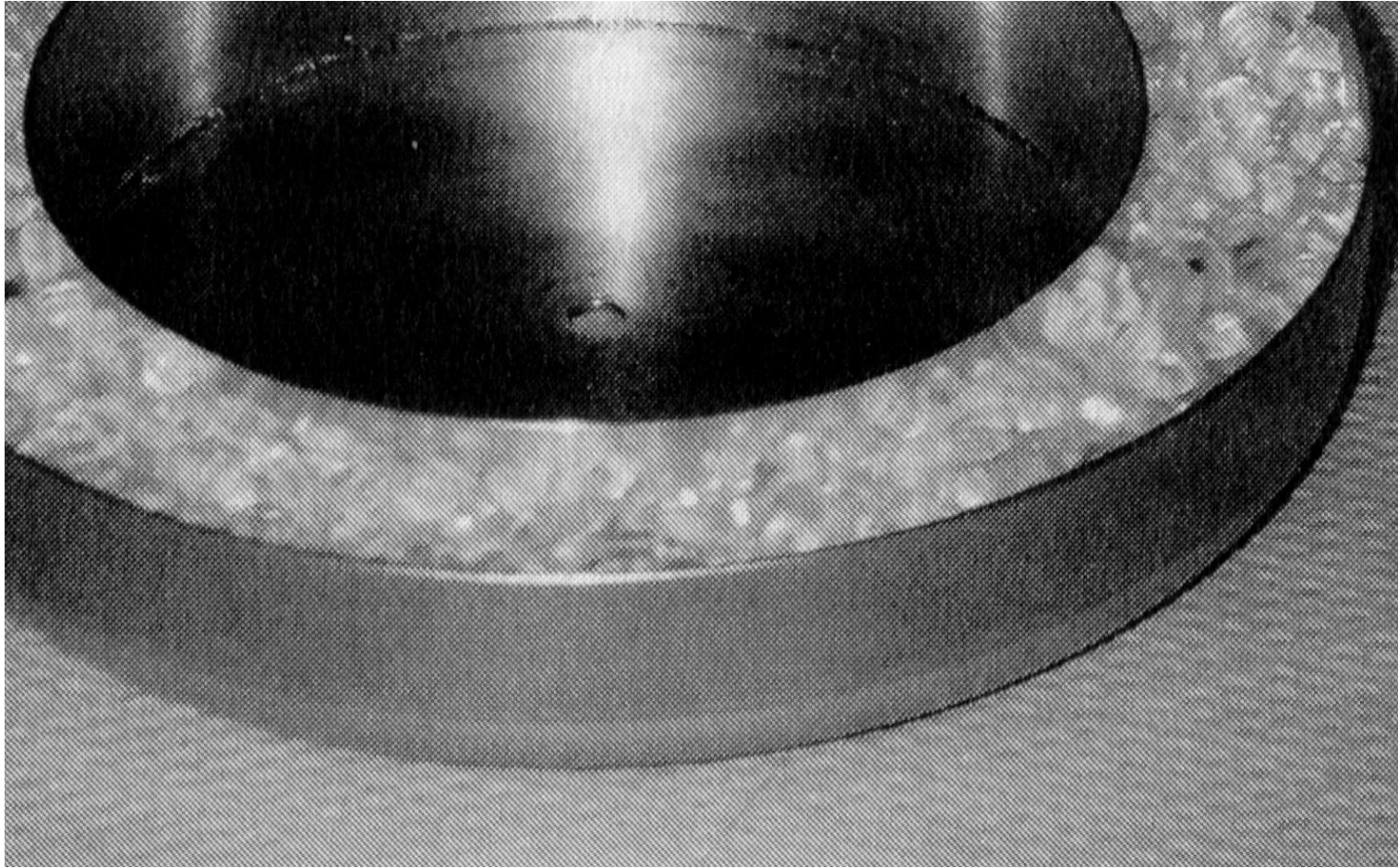


Ring-slit of pendulum
($R_i=3.75\text{cm}$, $R_a=5.5\text{cm}$)
filled with activated carbon
powder (Norit R1 Extra).

Oscillometric – Gravimetric - Volumetric Measurements

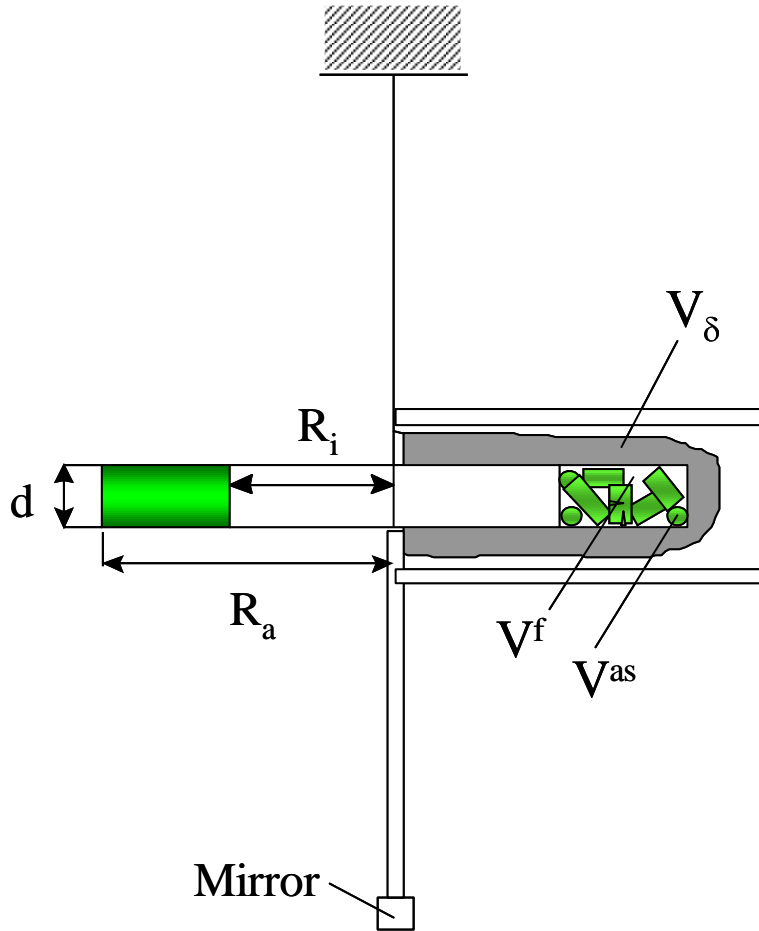


Scheme of an instrument for manometric-gravimetric-oscillometric measurements of binary coadsorption equilibria in swelling materials (polymers, resins etc.) without sorptive gas analysis by GC or MS.



Rotational pendulum and ring slit filled with polycarbonate pellets

Theory



$p: V^f, V^{as}$

$p = 0: V_0^f, V^s$

$$(1) V^f + V^{as} = \frac{1}{\rho^f} \Omega_{osc} + \Omega_{gra} - V_\delta$$

$$(2) \frac{V^s}{V^f} = \frac{V}{V_0^f} = \frac{1}{b(t)}$$

V_δ ...non - sorbing pellets

$$\Omega_{gra} = m - \rho^f V^s \rightarrow m$$

$$\frac{\Omega_{osc}}{m^s} = \frac{\frac{1}{J_0} - 1}{1 - \frac{J^*}{J_0}} = \frac{\frac{1 + \Delta_0^2 \left(\frac{\omega_0}{\omega_E}\right)^2}{1 + \Delta_E^2} - 1}{1 - \frac{\Delta_0 \omega_0}{\Delta^* \omega^*}}$$

Oscillometric Measurements of Gas Adsorption Equilibria. Theory*

Ideal Pendulum m^s, m

$$\frac{m}{m^s} = \frac{1 + \Delta_0^2 \left(\frac{\omega_0}{\omega_E} \right)^2}{1 + \Delta_E^2 \left(\frac{\omega_E}{\omega_E} \right)^2} - 1$$

Physical Pendulum m^*, m^s, m

$$\frac{m}{m^s} = \frac{\frac{1 + \Delta_0^2 \left(\frac{\omega_0}{\omega_E} \right)^2}{1 + \Delta_E^2 \left(\frac{\omega_E}{\omega_E} \right)^2} - 1}{1 - \frac{\Delta_0 \omega_0}{\Delta^* \omega^*}}$$

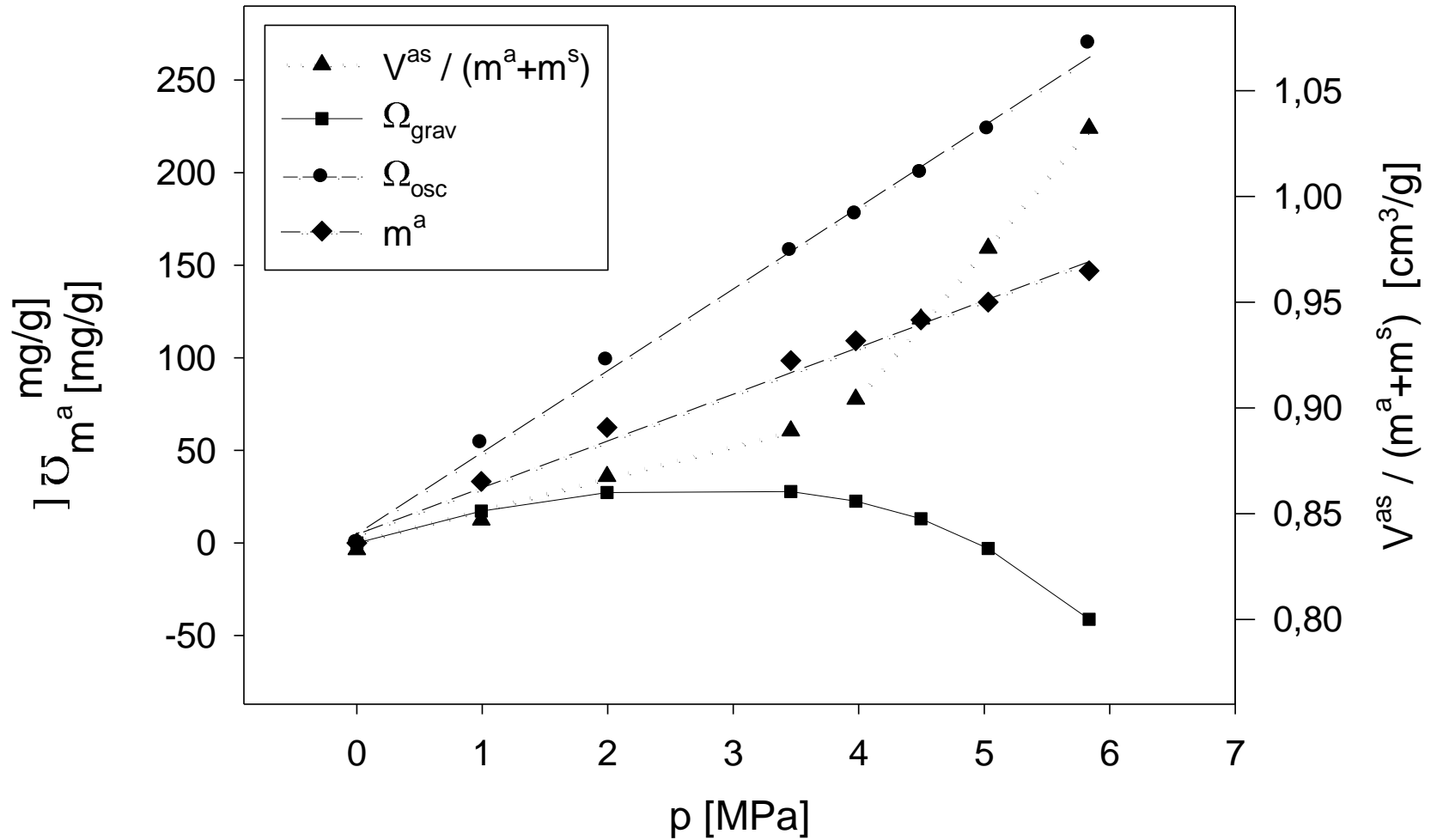
ω^*, Δ^* ... empty pendulum m^* , vacuum

ω_0, Δ_0 ... pendulum and adsorbent m^*, m^s , vacuum

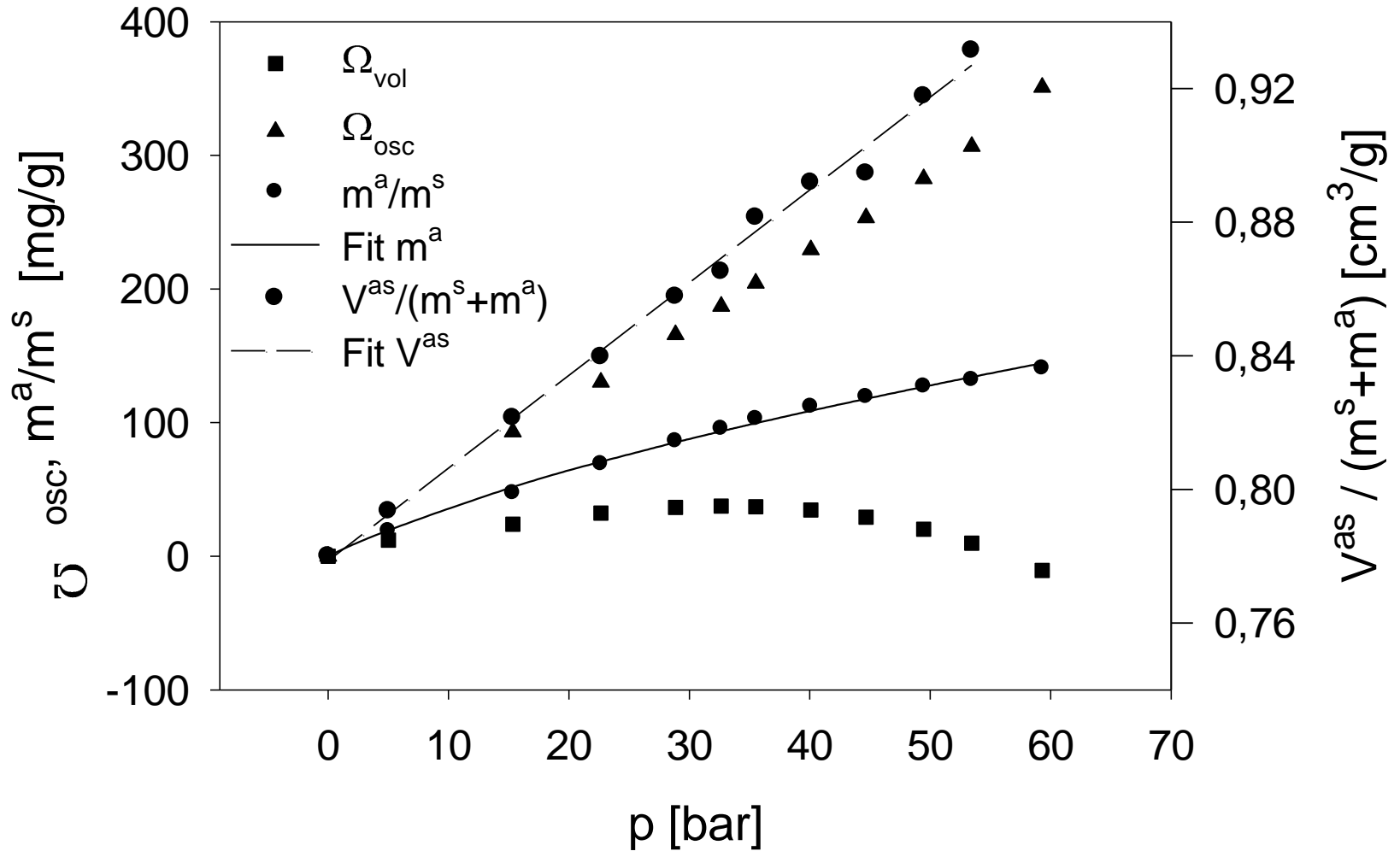
ω_E, Δ_E ... pendulum, adsorbent, adsorbate m^*, m^s, m , gas

* 1) Equation of motion of pendulum.

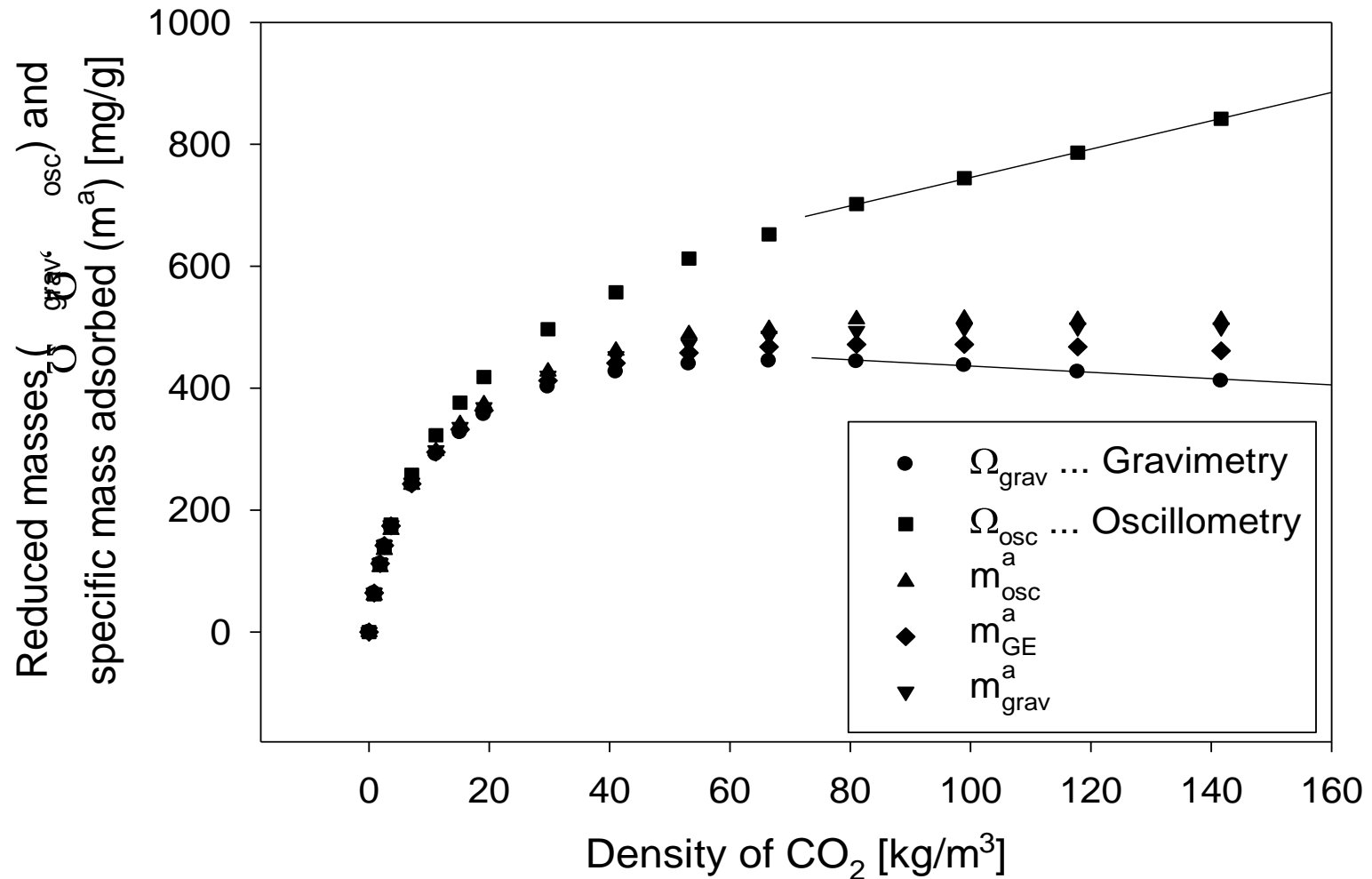
2) Navier – Stokes – equations for gas flow around the pendulum
Slow oscillations, Thick pendulum approximation.



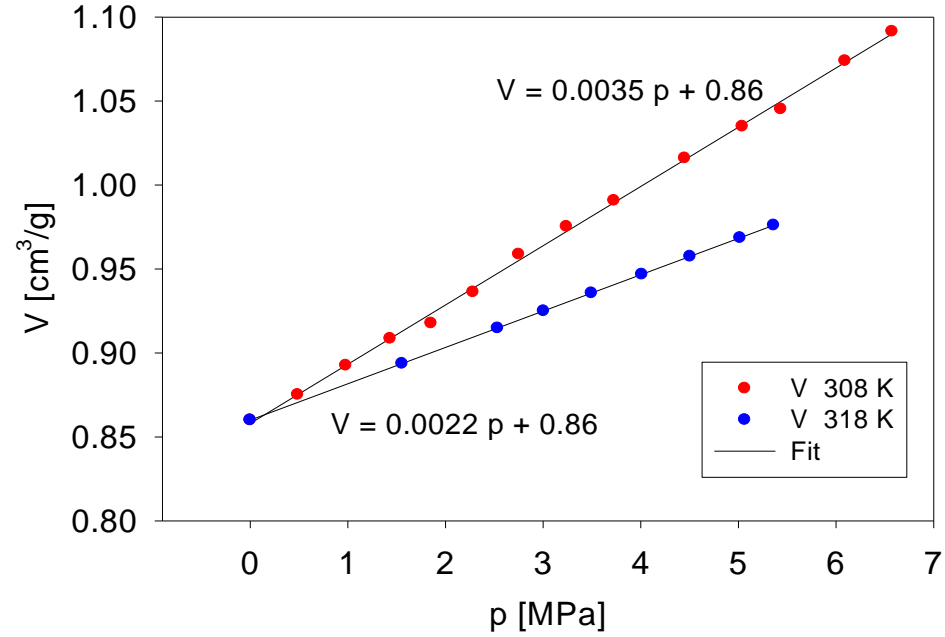
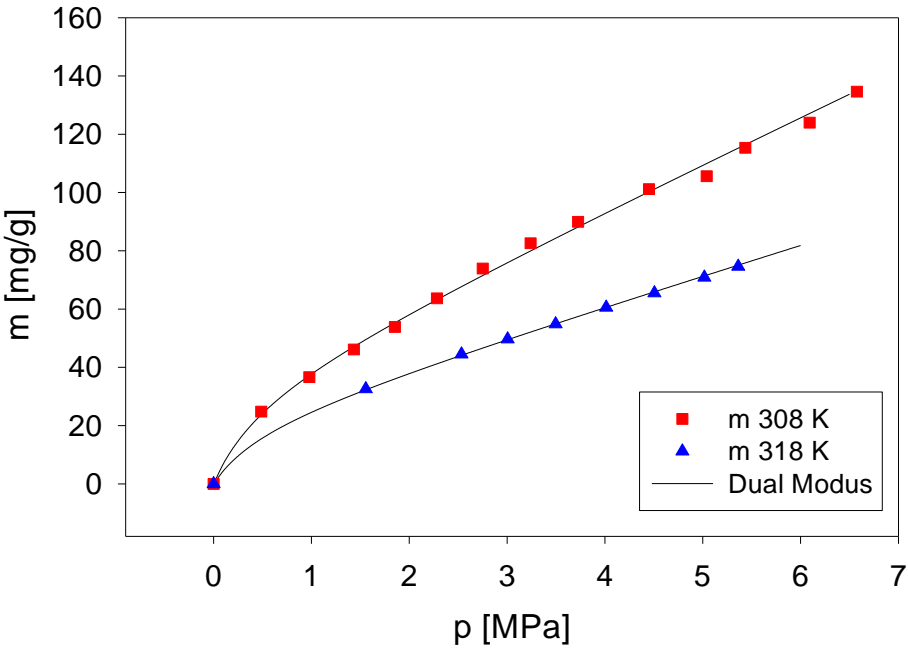
Swelling and sorption isotherm of polycarbonate/CO₂ at 293 K.



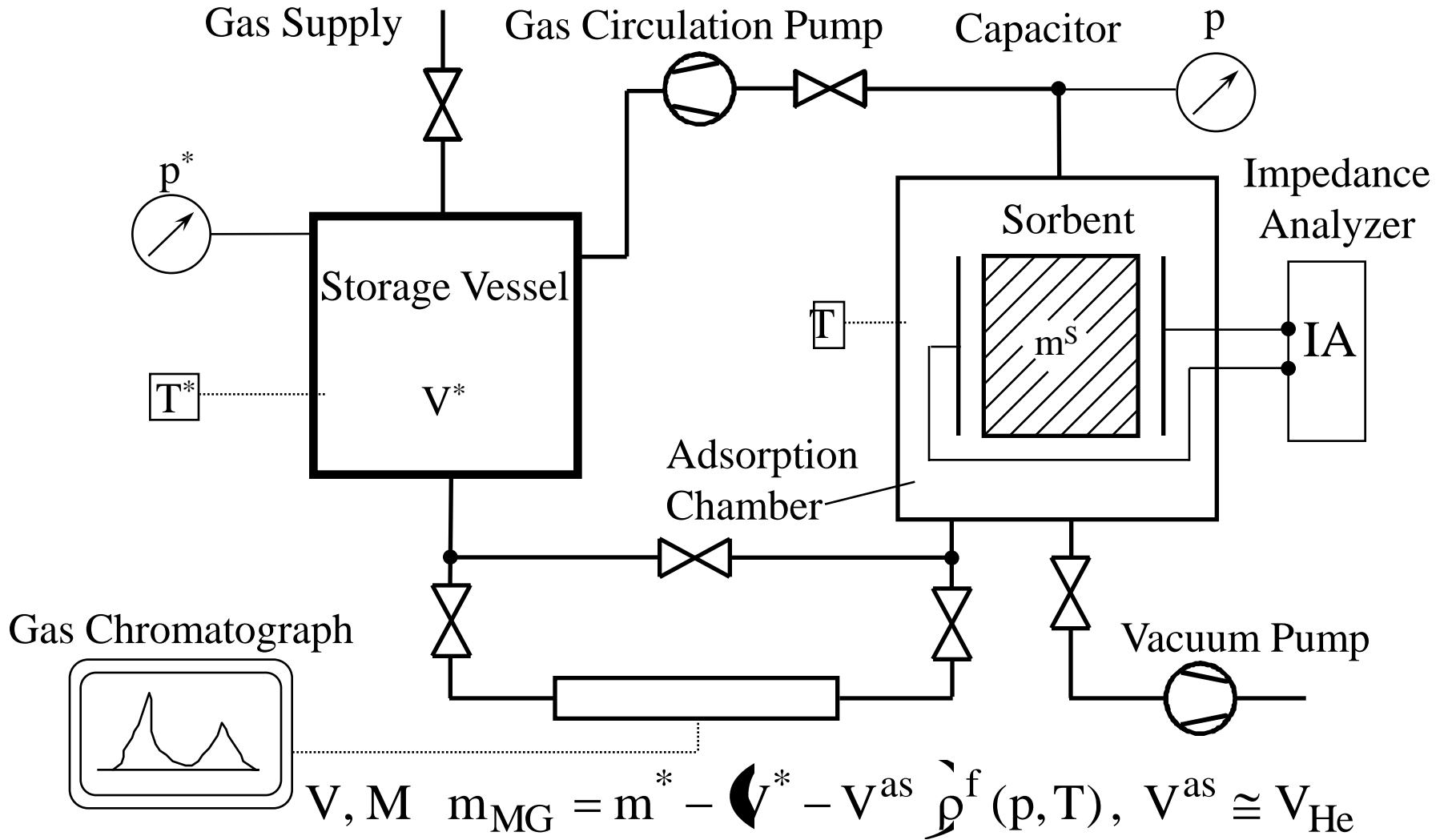
Swelling of volume (V^{as}) and sorption isotherm (m_a) of CO_2 on polymethylmethacrylate Makrolon 2400 (PMMA, Bayer) at 308 K.



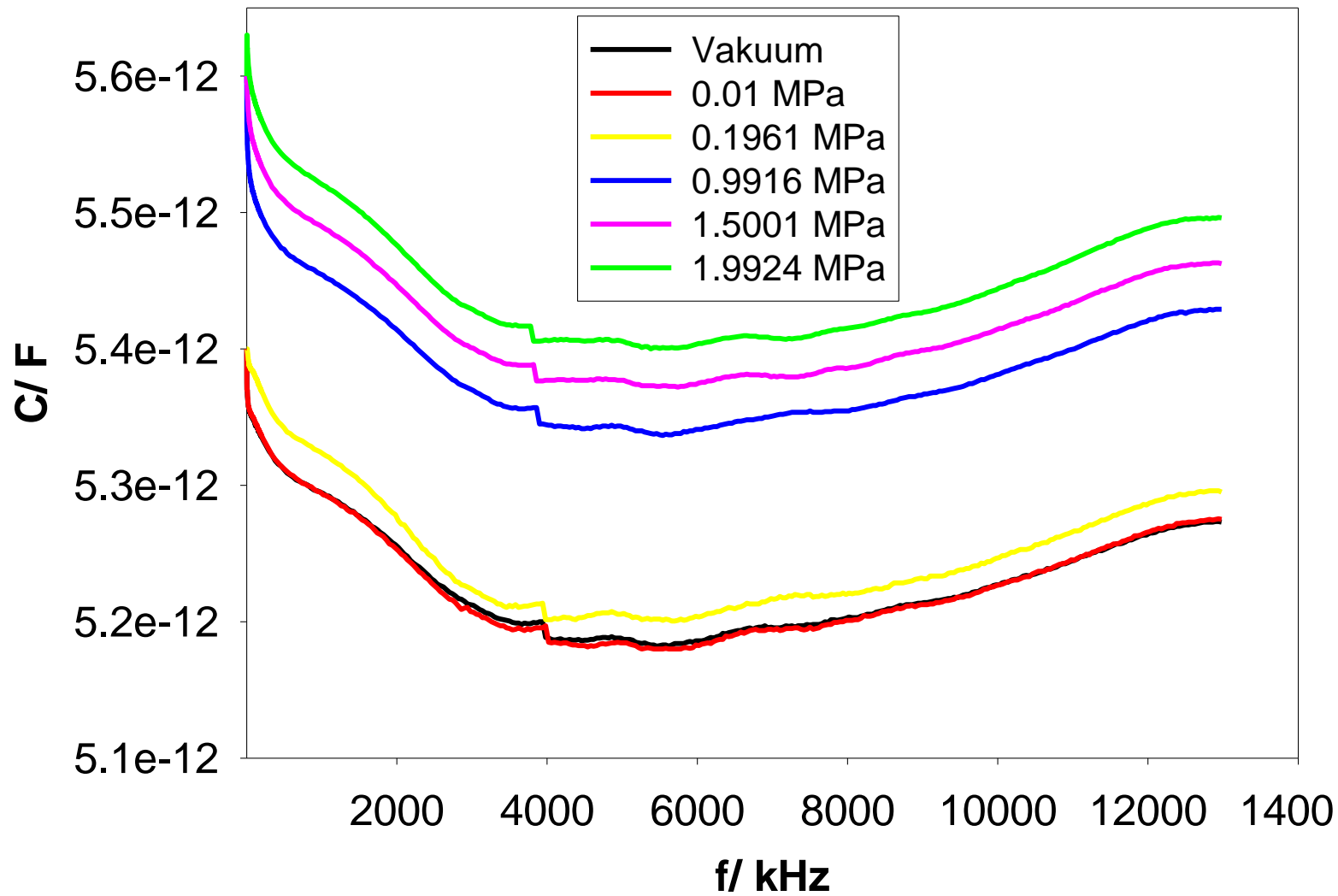
Reduced masses resulting from oscillometric and gravimetric adsorption measurements (Ω_{osc} , Ω_{grav}) of CO₂ on activated carbon (Norit R1 Extra) at 293 K. Gibbs excess masses (m_{GE}^a) and absolute masses adsorbed (m_{osc}^a , m_{grav}^a -data).



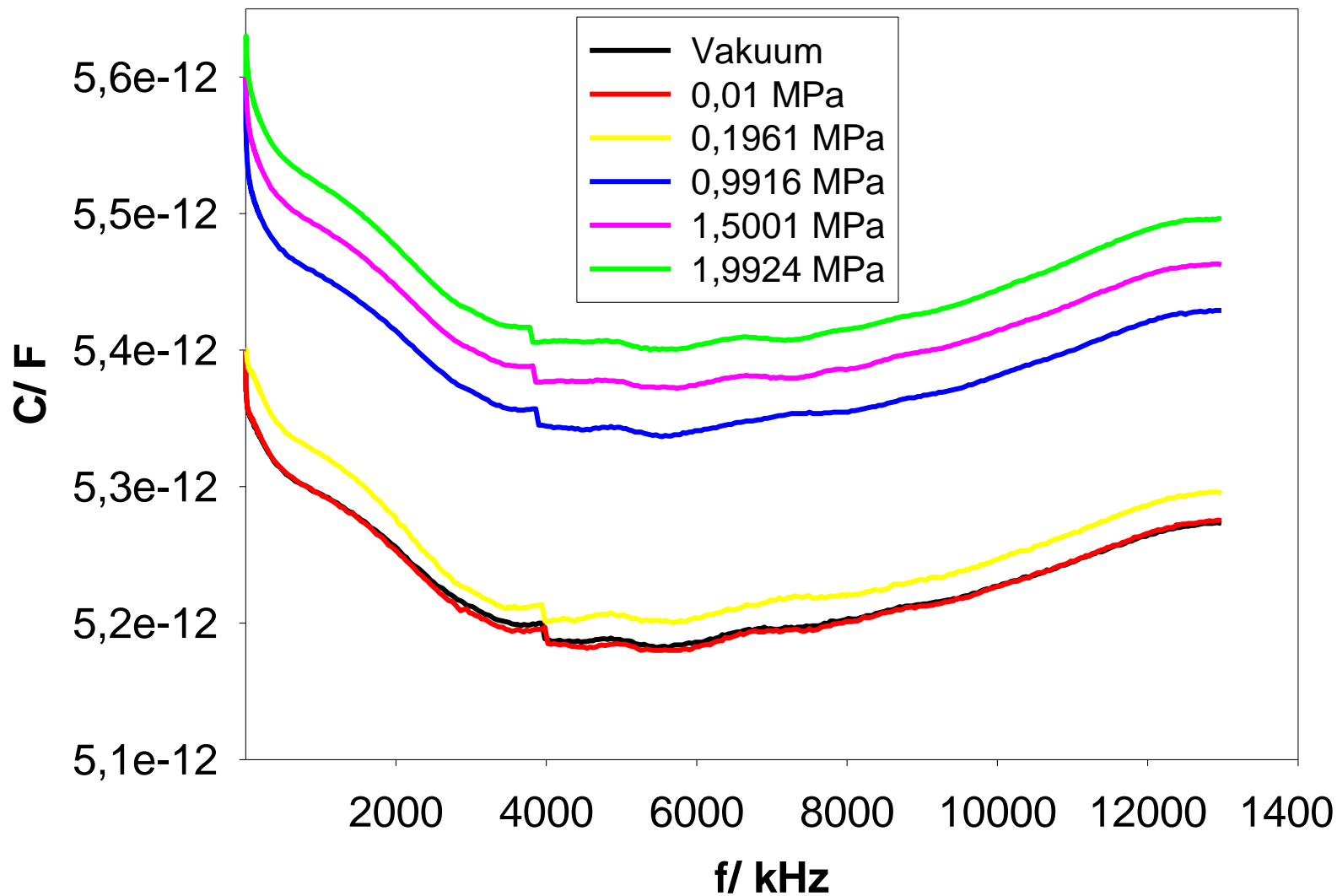
Swelling isotherms of polycarbonate/CO₂ at $T = 308$ K and $T = 318$ K.



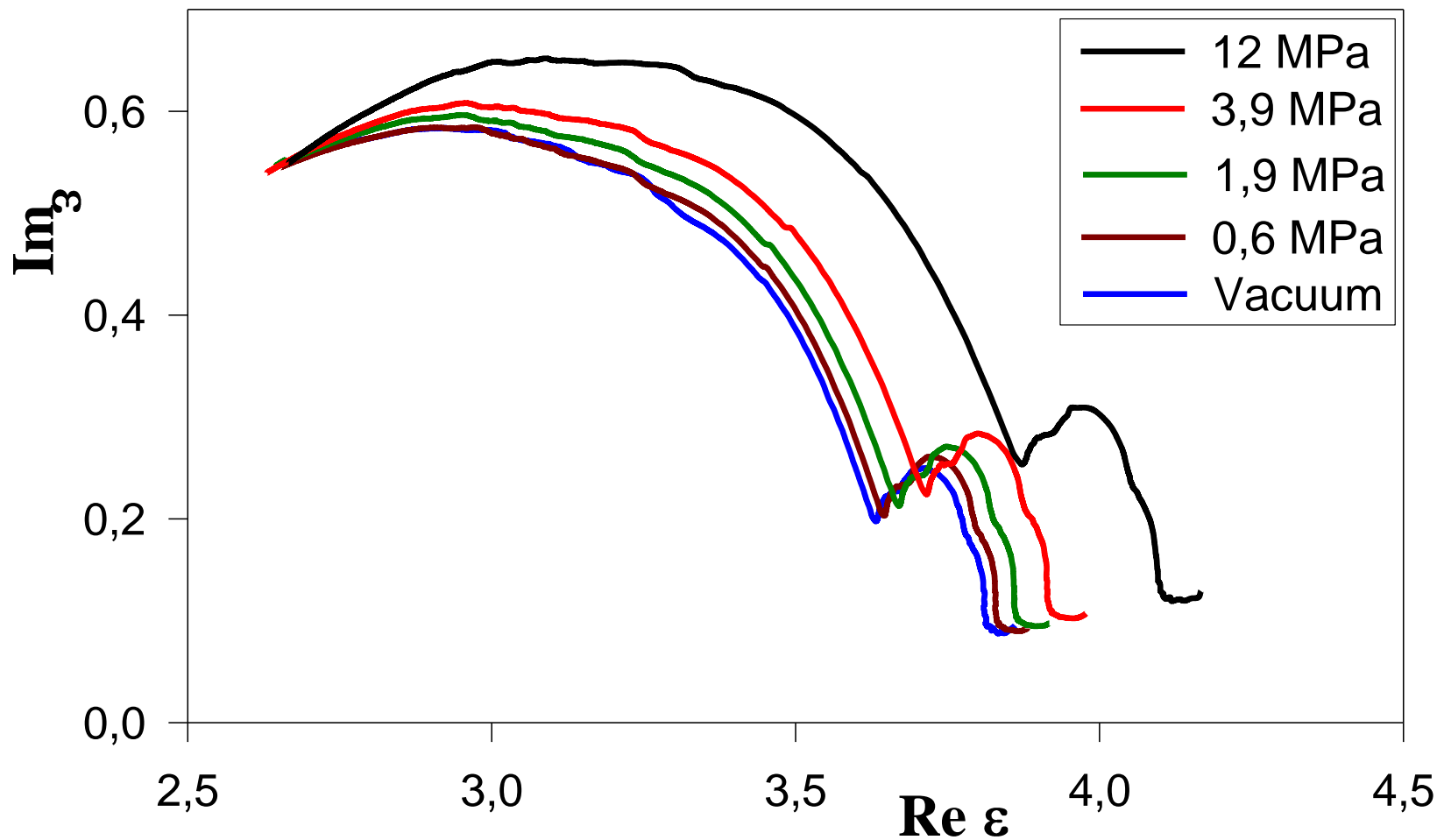
Experimental setup for volumetric-dielectric measurements



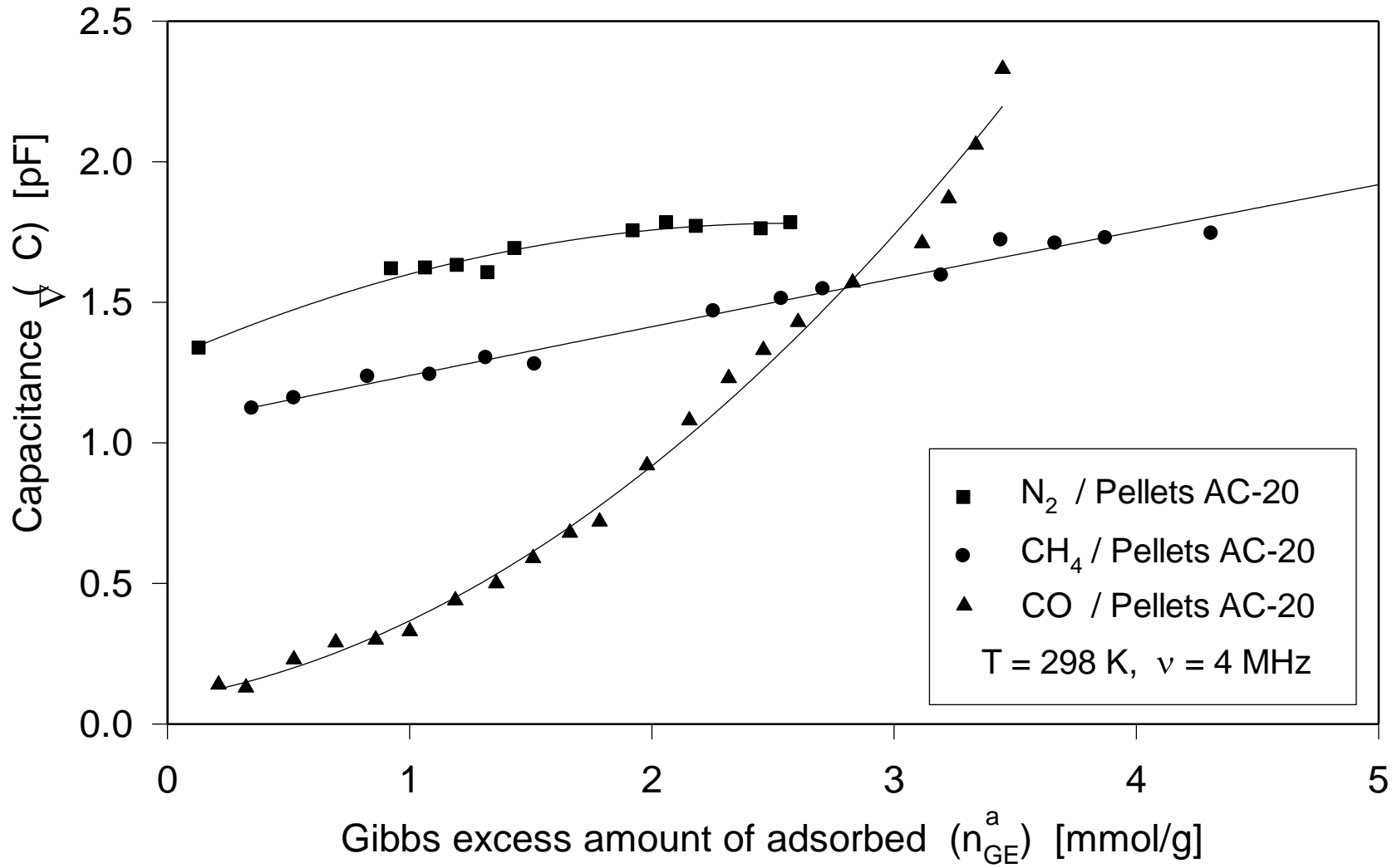
Impedance spectra of CO₂ on zeolite (DAY), T=298K



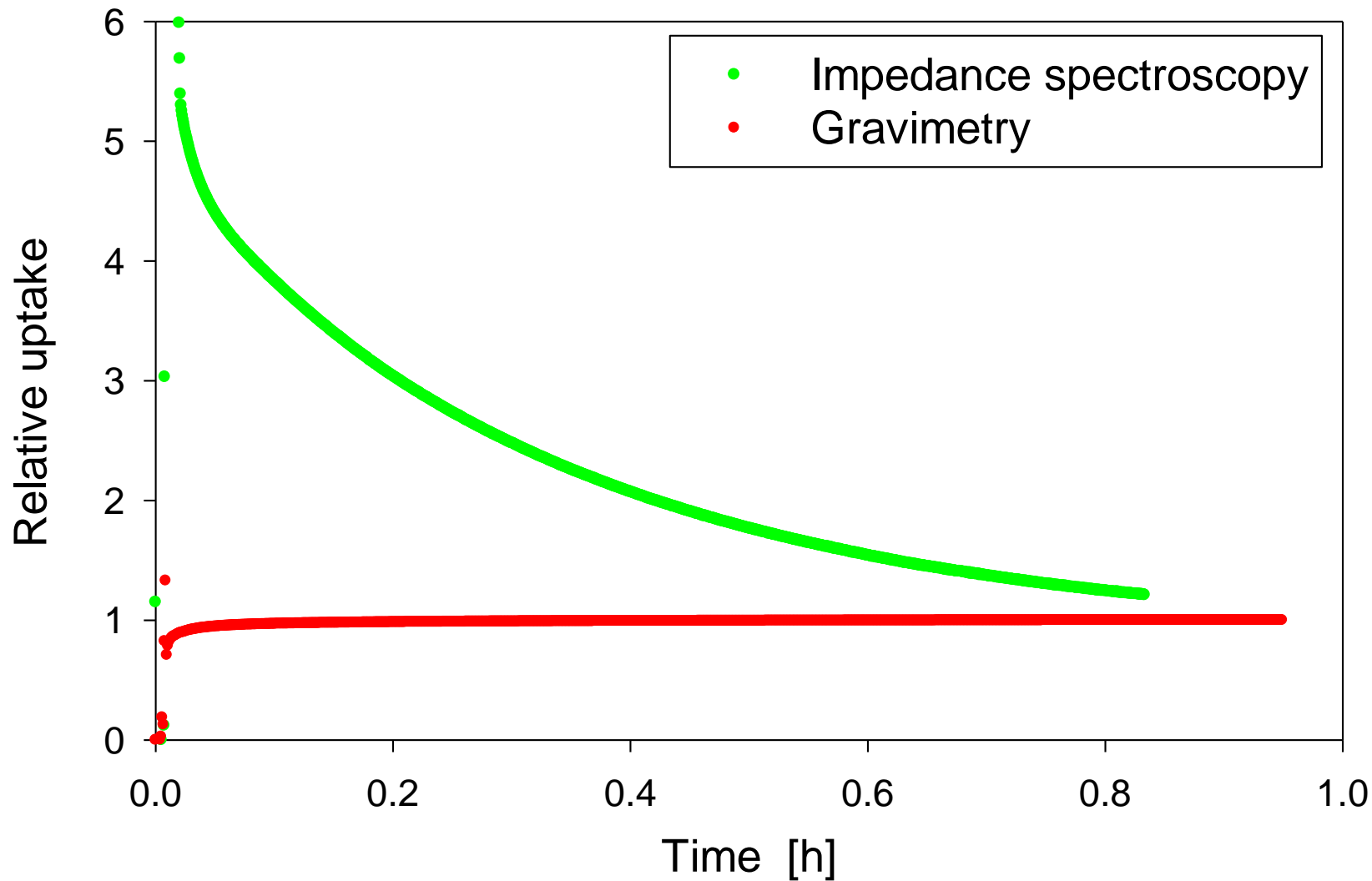
Impedance spectra of CO_2 on zeolite (DAY), $T=298\text{K}$



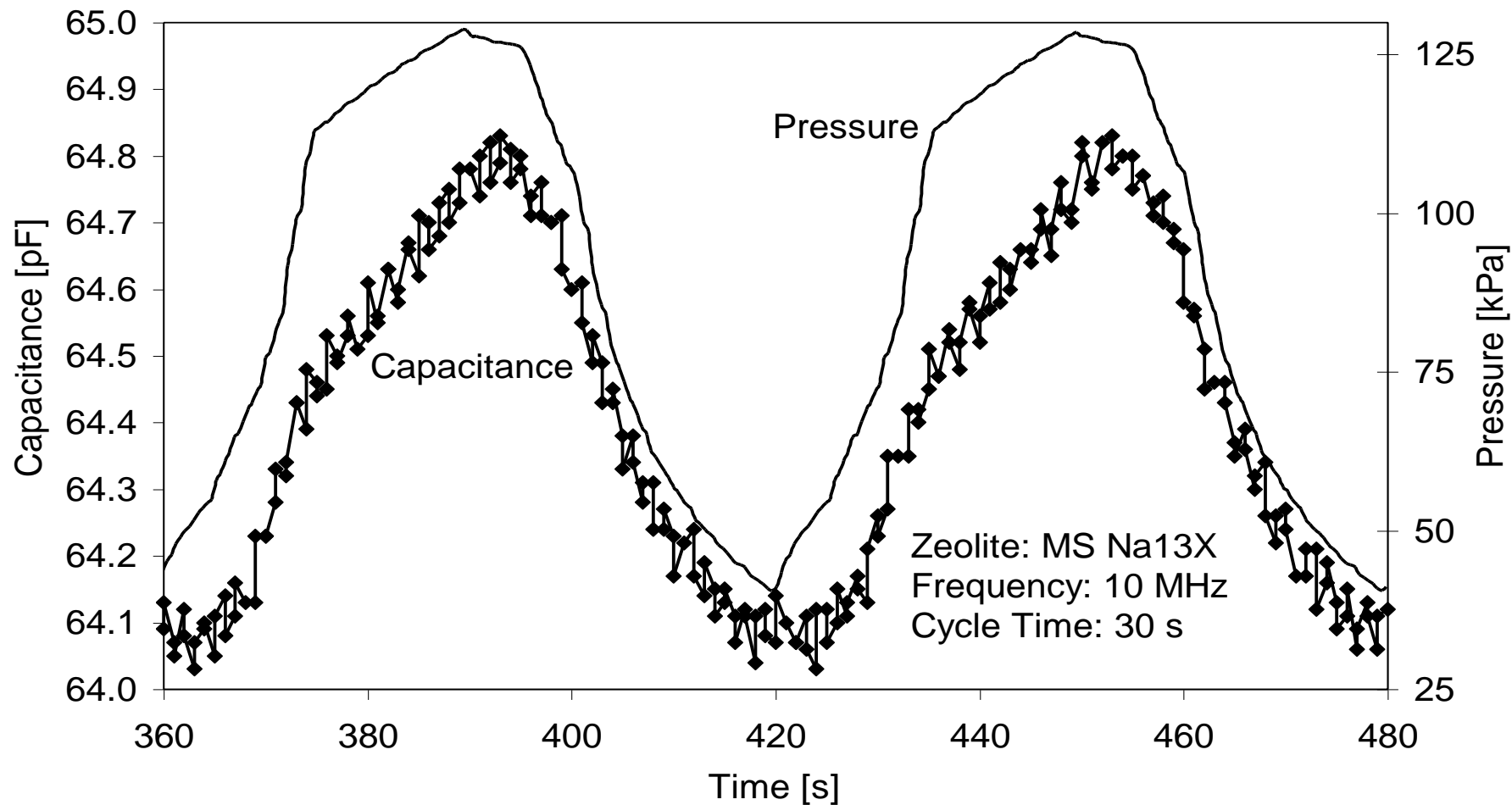
Cole-Cole-Plot for system CO / MS 13X, T=298K



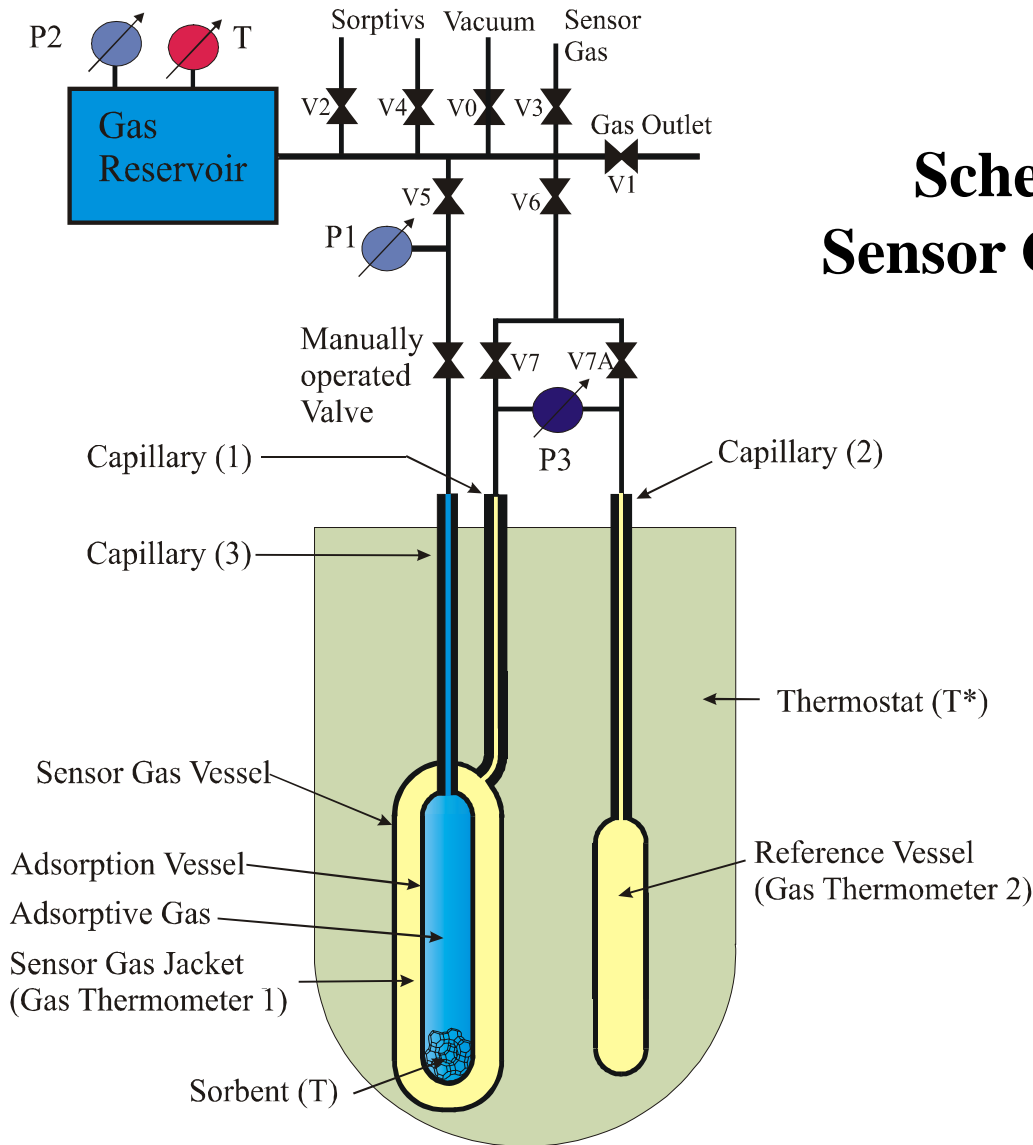
Change of the dielectric capacity (ΔC) of AC-20 pellets upon adsorption of gases (N_2 , CH_4 , CO) at 298 K, $\nu = 4$ MHz. Gas pressures ($p \leq 4$ MPa).



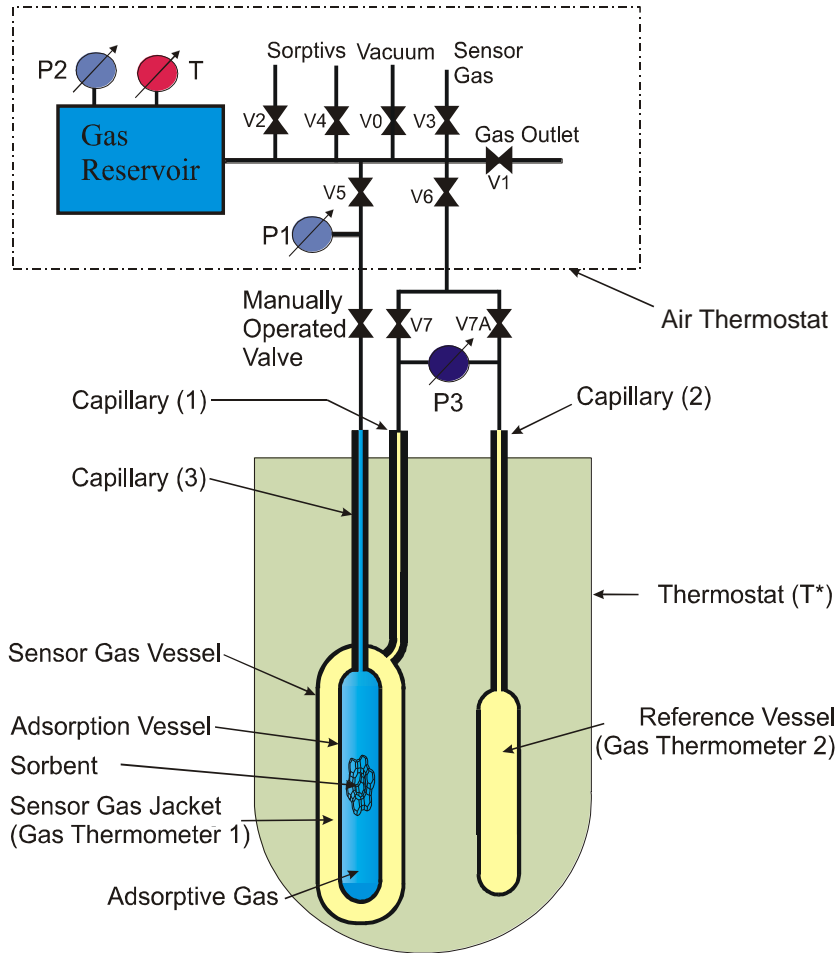
Uptake curves of H₂S on MS 13X, T=298K



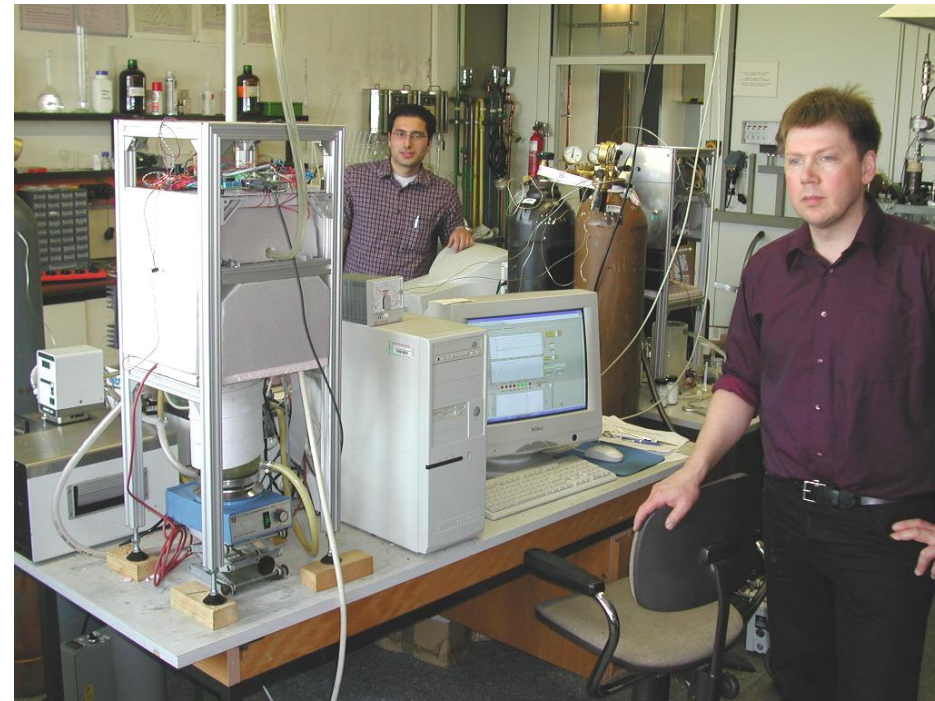
Combined manometric (p) and dielectric (ϵ_r) measurements of ad- and desorption of N_2 on MSNa13X (UOP) at 293K.



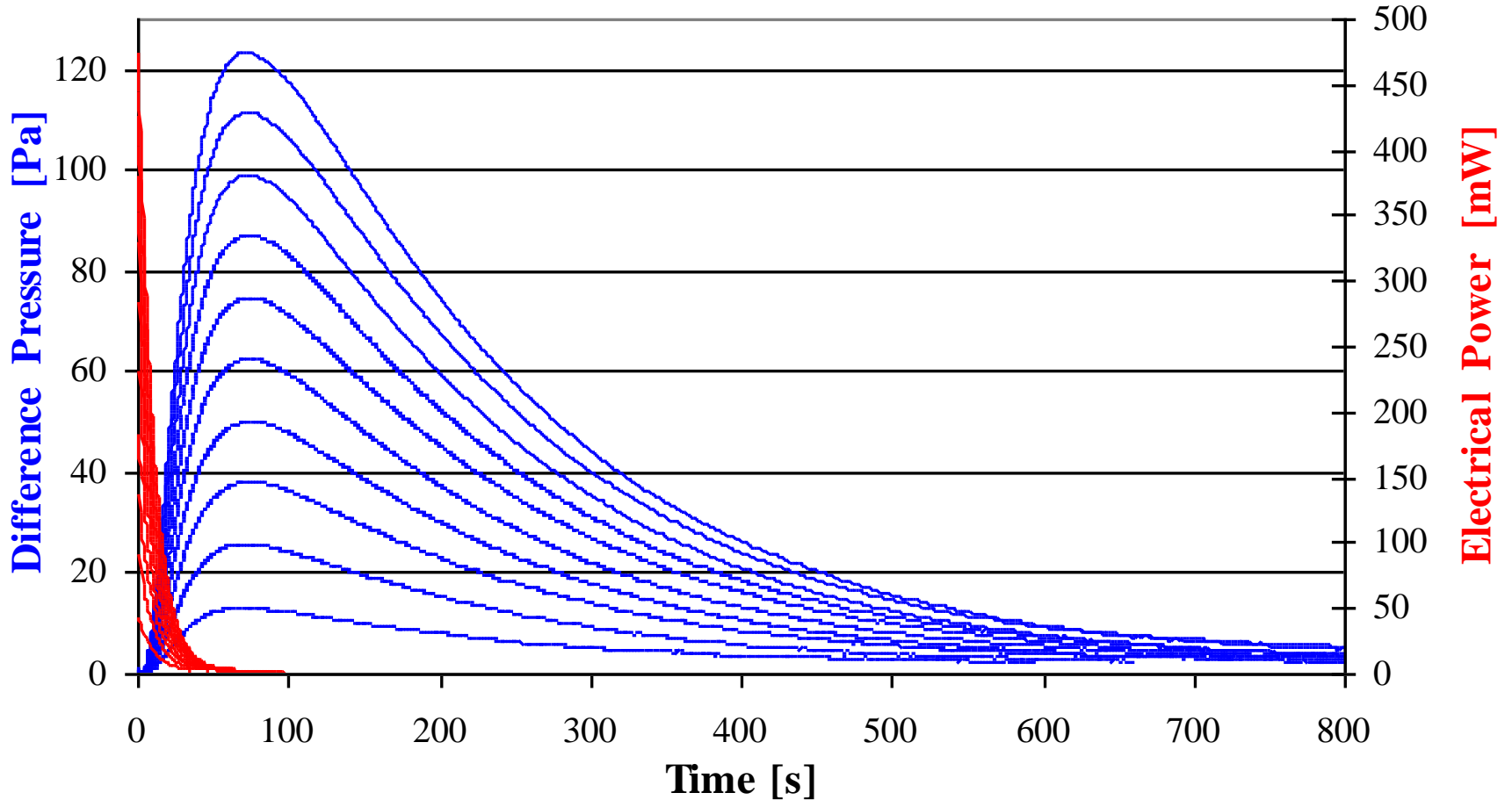
Schematic diagram of a Sensor Gas Calorimeter (SGC)



Schematic diagram of a sensor gas calorimeter (SGC)



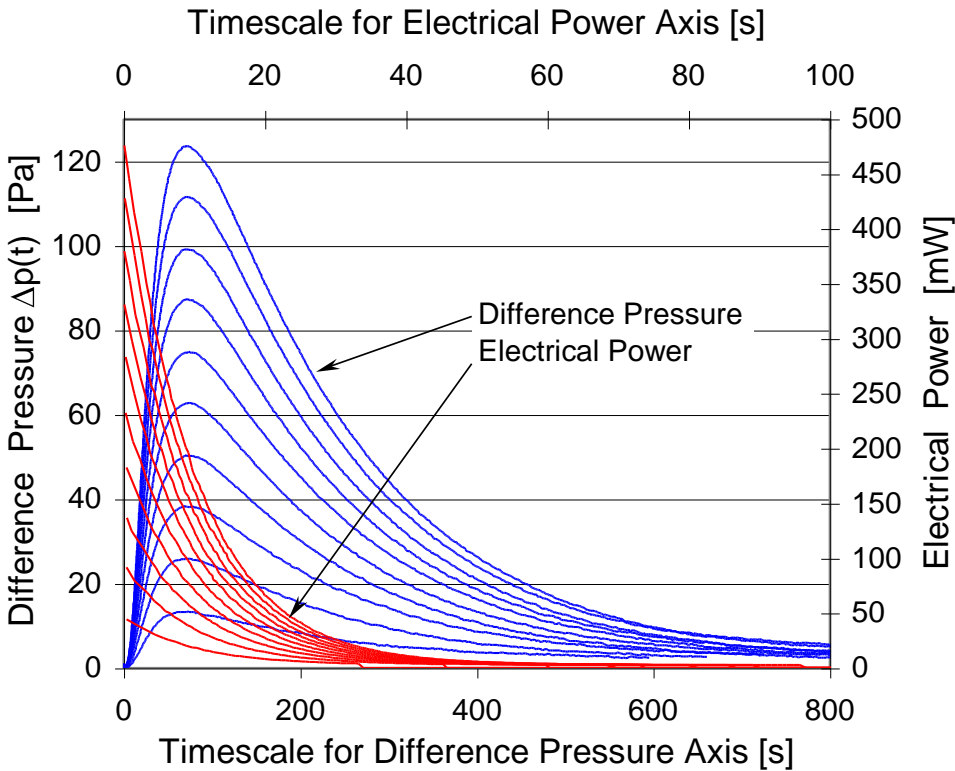
Sensor gas calorimeter (SGC) for simultaneous measurements of adsorption isotherms and enthalpies. © IFT, University of Siegen, 2003.



Calibration experiments in the SGC 0.5J to 5J

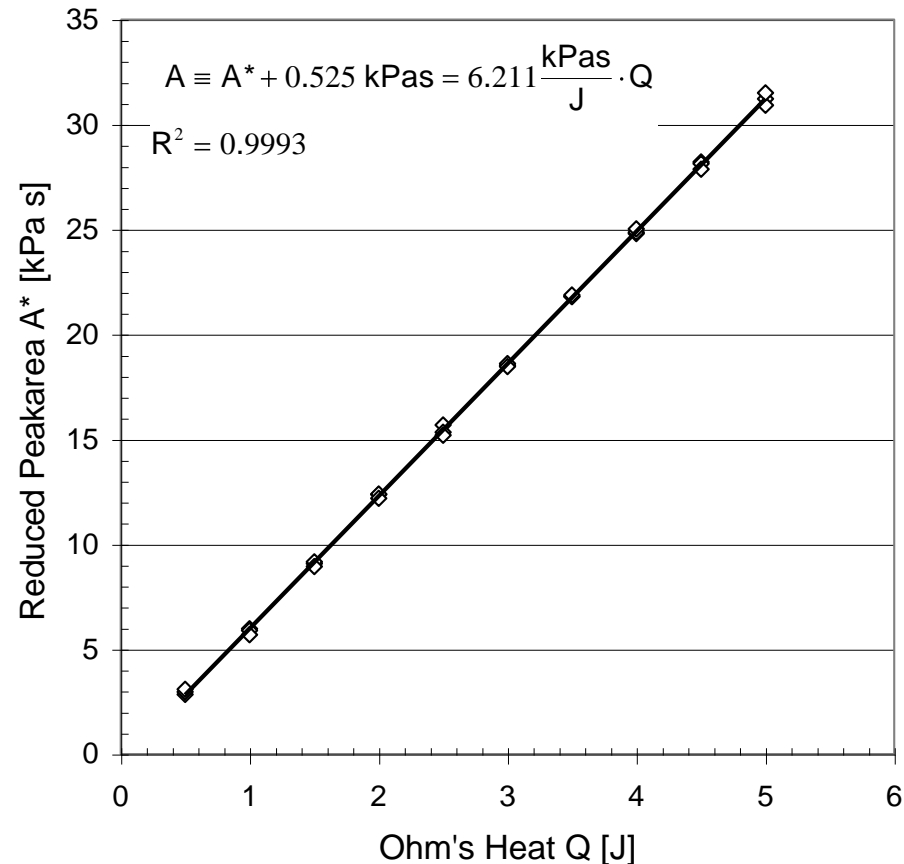
Sensor gas N₂ (1.6bar), T=298K, τ=10s

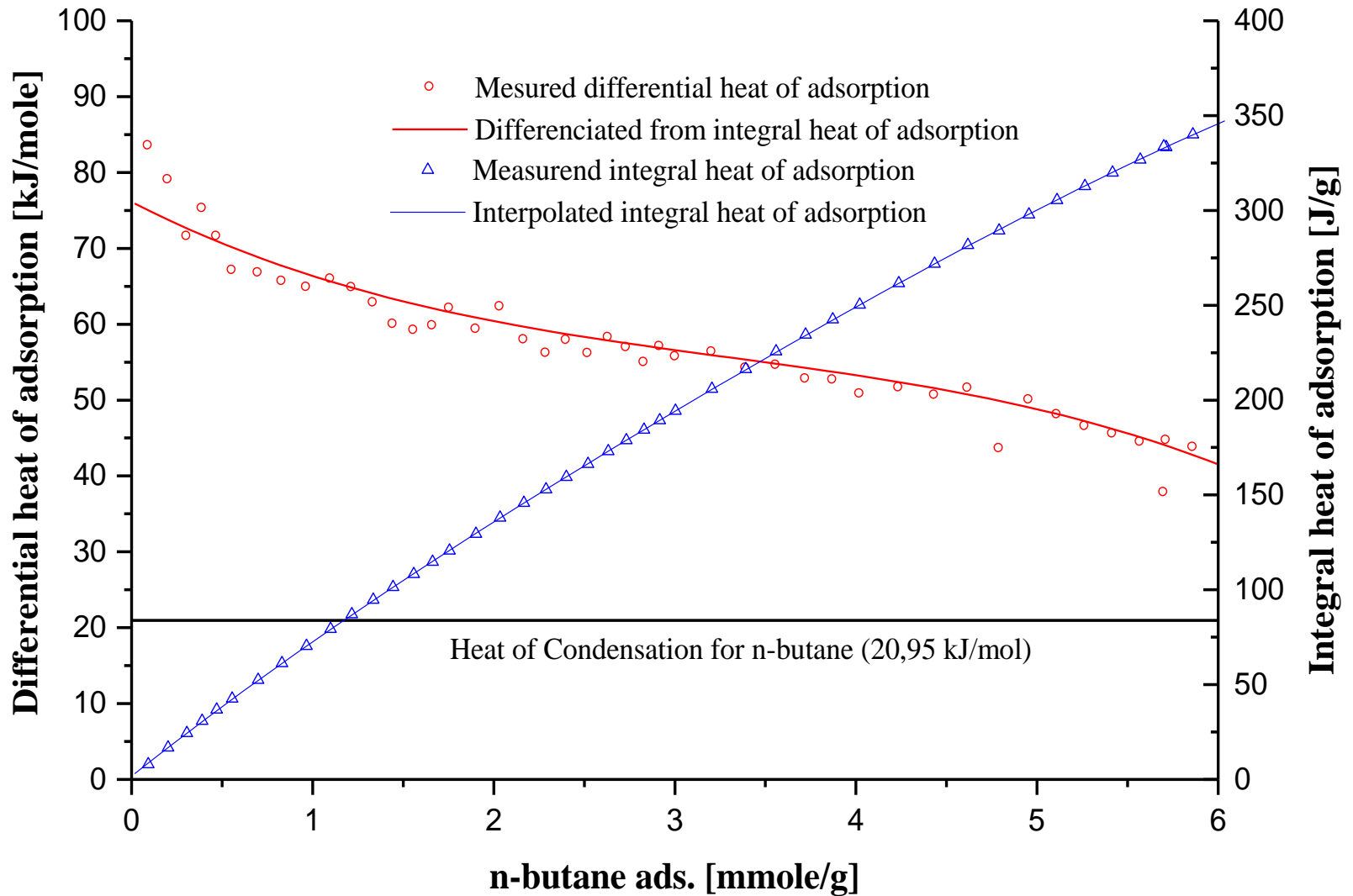
Ohm's heat release (red lines) → Pressure signal (blue lines)



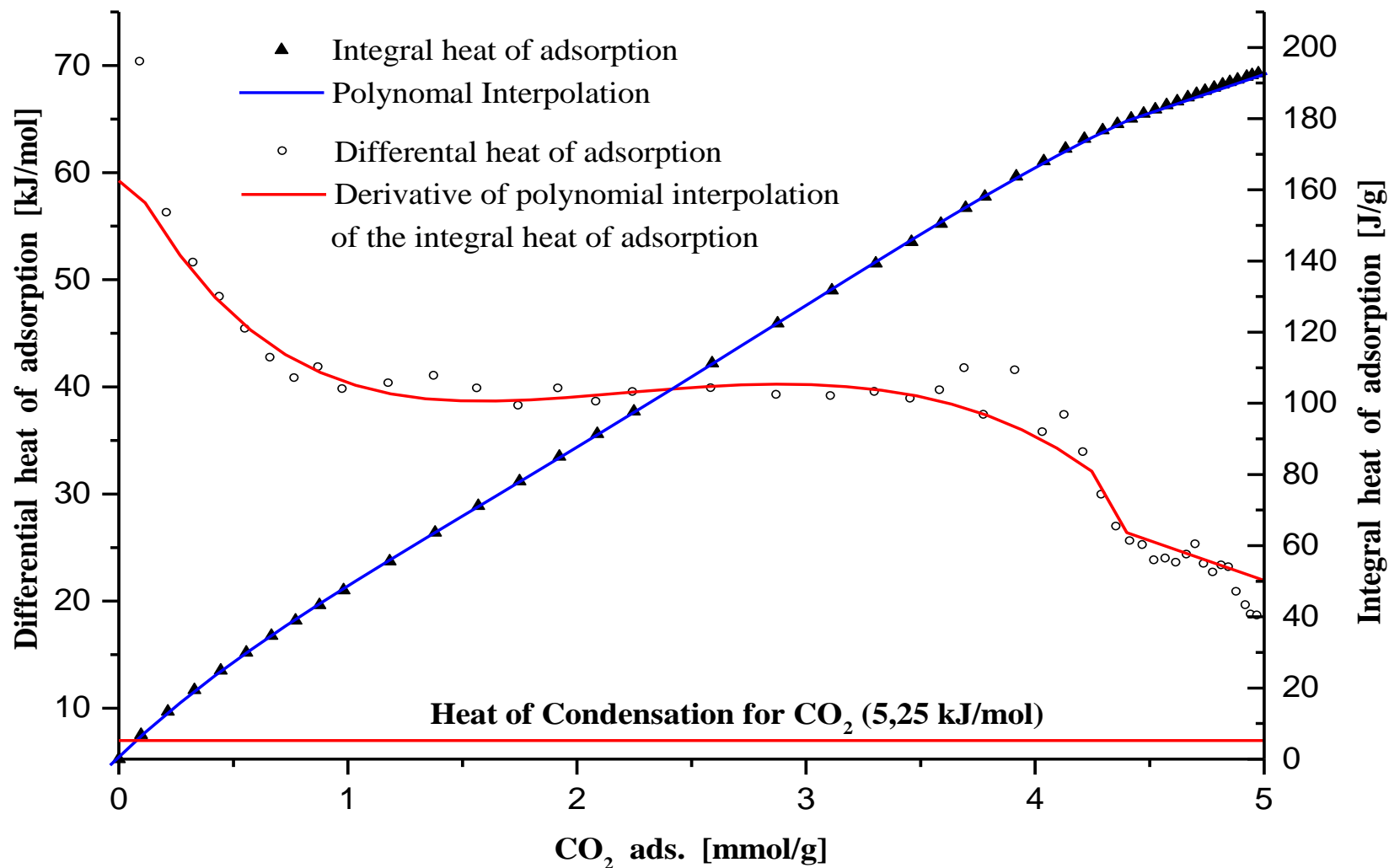
Calibration experiments of the SGC.
Ohm's heat : $Q = (0.5, 1.0 \dots 5.0) \text{ J}$
Sensor gas: N_2 , $p^* = 0.15 \text{ MPa}$,
 $T^* = 298 \text{ K}$

Correlation
Peak Area (A / Pas)
Ohm's heat (Q / J)





Differential and integral heat of adsorption for activated carbon AC BAX 1500 / n-butane (C₄H₁₀) at 298K



Heat of adsorption for CO₂ / Na13X, T=298K

Gas Mixture Sorption

Hybrid Measurement Methods

Method	Material Physics	V	G	O	SP	CH	D	C
Volumetry (V)	Extensivity		++	+	0	++	++	0
Gravimetry (G)	Gravity	2		+	0	+	+	0
Oscillometry (O)	Inertia	1, V	1, V		0	0	0	0
Spectroscopy (SP)	Electric Changes	1	1					
Chromatography (CH)	Molecules	N	N	(N)				
Densimetry (D)	Extensivity	2	2	1, V				
Calorimetry (C)	Thermal Inertia	1	1	1				

Measurement Methods for Gas – Adsorption Equilibria

Pure Gas Method

Volumetry/Manometry

Gravimetry

Oscillometry

Dielectric Permittivity

Purpose

Characterization of porous solids

Equilibria, Kinetics, Gas Density

Process Control

Swelling Material

Industrial Process Control

Gas Mixtures (N=2)

Volumetric-Densimetric M.
(2-sites Magnetic Balance)

Equilibria, Process Control

Gas Mixtures (N>2)

Volumetric/Gas Phase Analysis

Process Design

Ref: J.U. Keller, R. Staudt, *Gas Adsorption Equilibria*, Springer, New York, 2004.

4. Erzeugung hochreinen Wasserstoffs (4.5)

Wasserstoff: Weltjahresproduktion und Markt

Reinheitsanforderungen an H₂ – Gas

Druckwechseladsorptionsprozess
Grundprinzip (PSA)

PSA-Entwicklung, Patentsituation

PSA-LOFIN Prozess

Sorbentien für PSA – Prozesse

Weiterentwicklungen der PSA-Technik

Oberflächenaktive Membranen (SSM)

Wasserstoff: Weltproduktion und Markt

Weltjahresproduktion (WJP) (2007)

> 50 M t

> 500 G Nm³

> 17 T SCFT/YR
(1m³ = 35.315 CFT)

Welthandelsmenge: 5% WJP

SCFT: Standard Cubic Foot

Verwendung von Wasserstoff

95% Herstellung von

Ammoniak

Methanol

Raffinerieprodukte (CW)

5% Nahrungsmittelindustrie

Chemie

Elektronik

Metallurgie

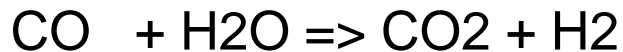
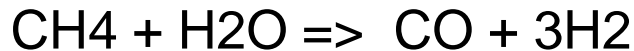
Verkehr !?

Erzeugung wasserstoffreicher Gase(1)

Methode	Jahresproduktion (2006) / G Nm ³	
	Welt	D
Reformierung Methan, Naphta	190	6
Oxidation Schweröl	120	3
Reformierung Benzin	90	2.5
Ethylen (Produktion, Umwandlung)	33	3.6
Elektrolyse (Chlor-Alkali)	10	1
Kohlevergasung (Wassergas)	50	2
<hr/>		
Summe	~ 500	~18

Erzeugung wasserstoffreicher Gase(2)

1.Reformierung Methan



Reformergas (SMROG)*

	% mol
H ₂	70 - 80
CO ₂	15 - 25
CO	1 - 3
N ₂	Spuren

Sättigungszustand Wasserdampf
 $p = (4-30) \text{ bar}$, $T = (20-40) \text{ C}$

*Steam-Methane-Reformer-Off-Gas

** Refinery – Off – Gas

2.Raffineriegas (ROG)**

Kopfprodukt bei
 Trennkolonnen für Erdöl

H₂, CH₄, C₂H₆, C₃H₈

	% mol
H ₂	65 - 90
CH ₄	3 - 20
C ₂ H ₆	4 - 8
C ₃ H ₈	1 - 3
N ₂	Spuren

Wasserdampf (Sättigung)

3.Reformergas aus Biomasse

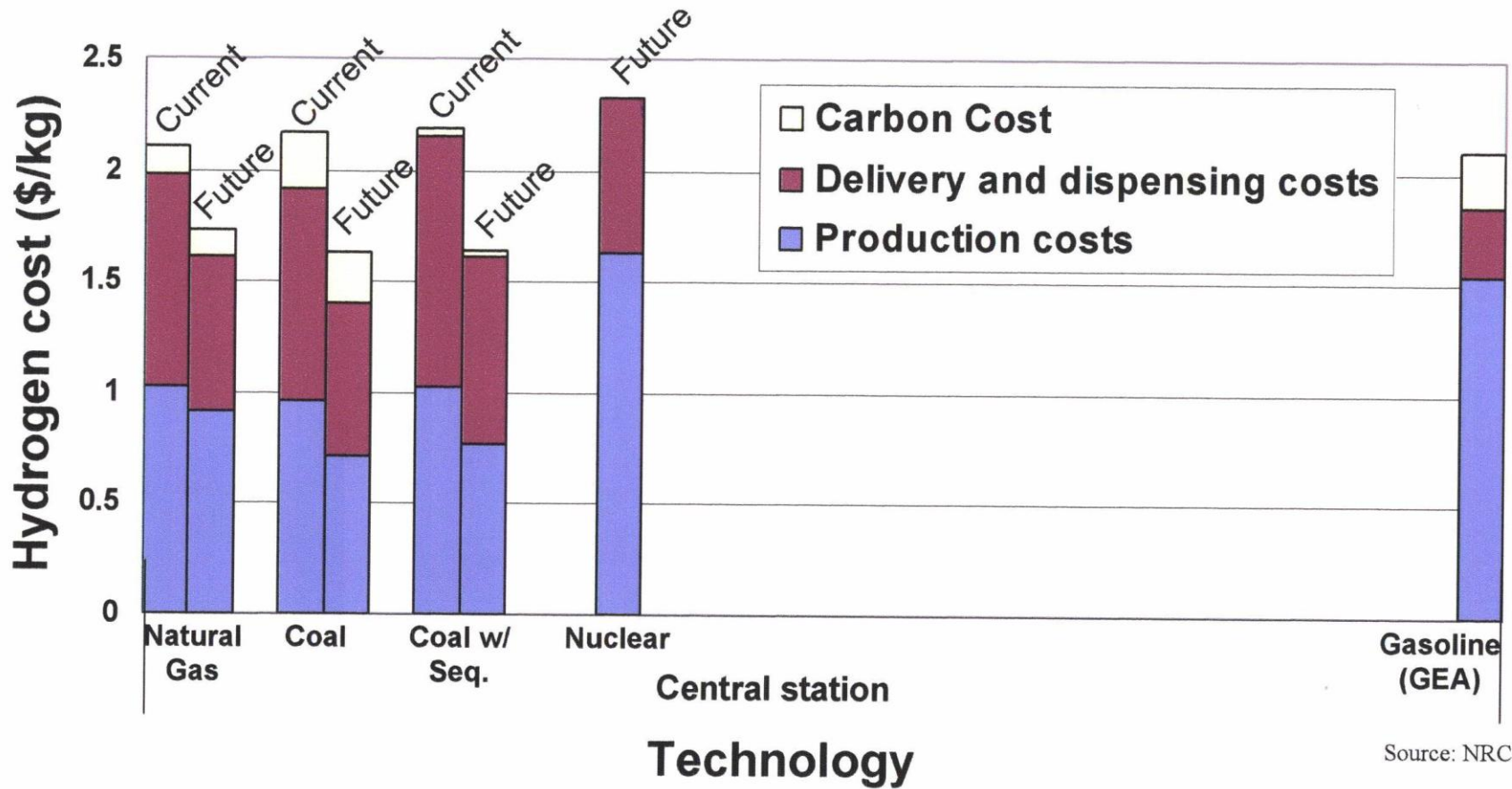
Pyrolyse von Biomasse

Reinheitsanforderungen für Wasserstoff(gas)

Anwendung	Reinheit
Ammoniak-Synthese	<10 ppm COX, X=1,2
Druckgas(leitung)	< 10 ppm COX, 100 ppm CH ₄ , < 200 ppm N ₂
Brennstoffzelle (PEM)	< 30 ppm CO
Elektronik	< 10 ppb N ₂ , O ₂ , CH ₄ , CO, HCs
Nahrungsmittelindustrie	3.1 – 5.5 (%Vol H ₂)

Ausbeute von Wasserstoff aus Rohgas ! (1 – 2)% Abweichungen können Wirtschaftlichkeit entscheidend verändern.

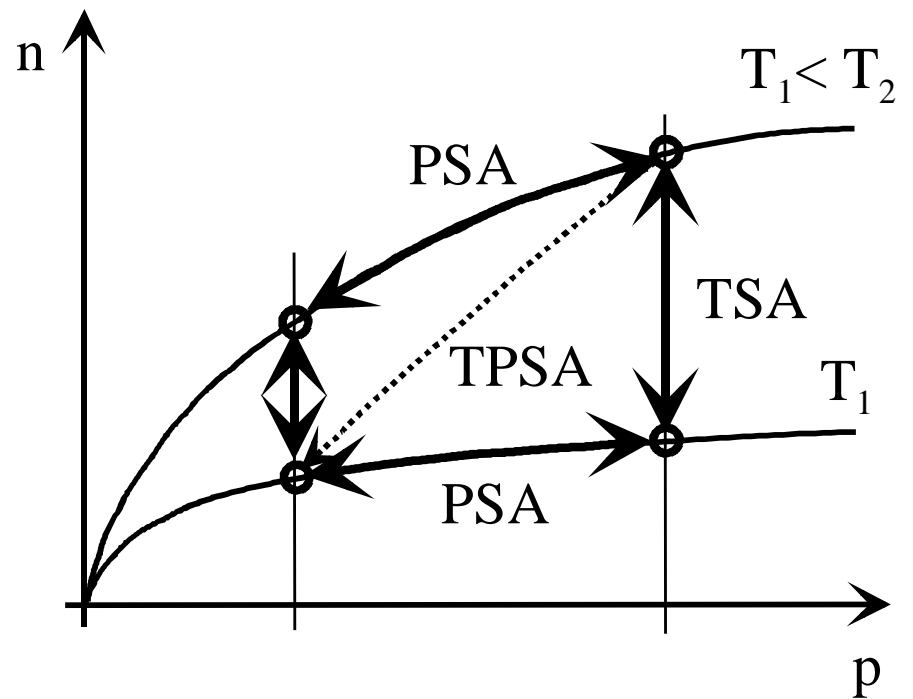
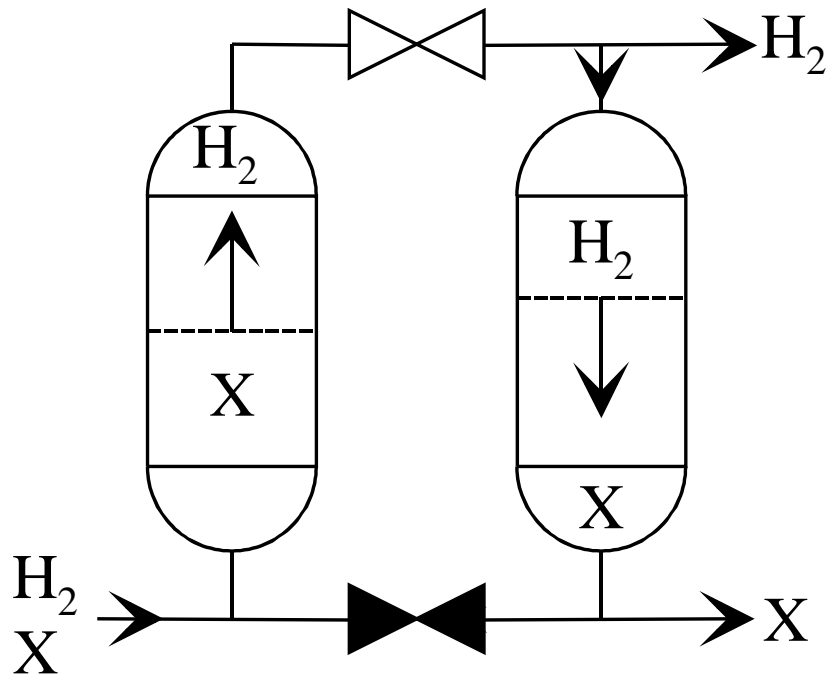
Production Cost Hydrogen (\$ / kg) (USA, 2006)



GEA = Gasoline Efficiency Adjusted – scaled to hybrid vehicle efficiency

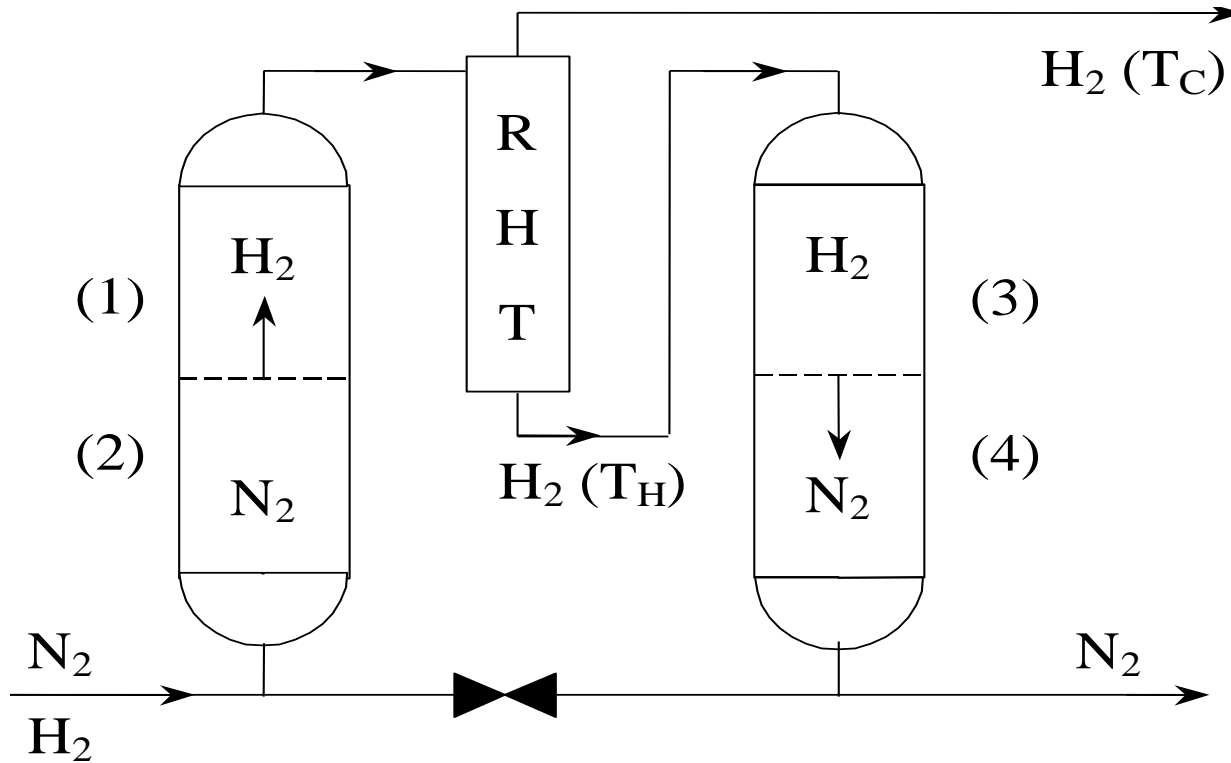
Erzeugung hochreinen Wasserstoffs (4.5)

Druckwechseladsorptionsprozesse (PSA)
 Basisprozess, 2 Festbettadsorber (geschichtet)



X:Adsorption, H2:Durchgangskomponente

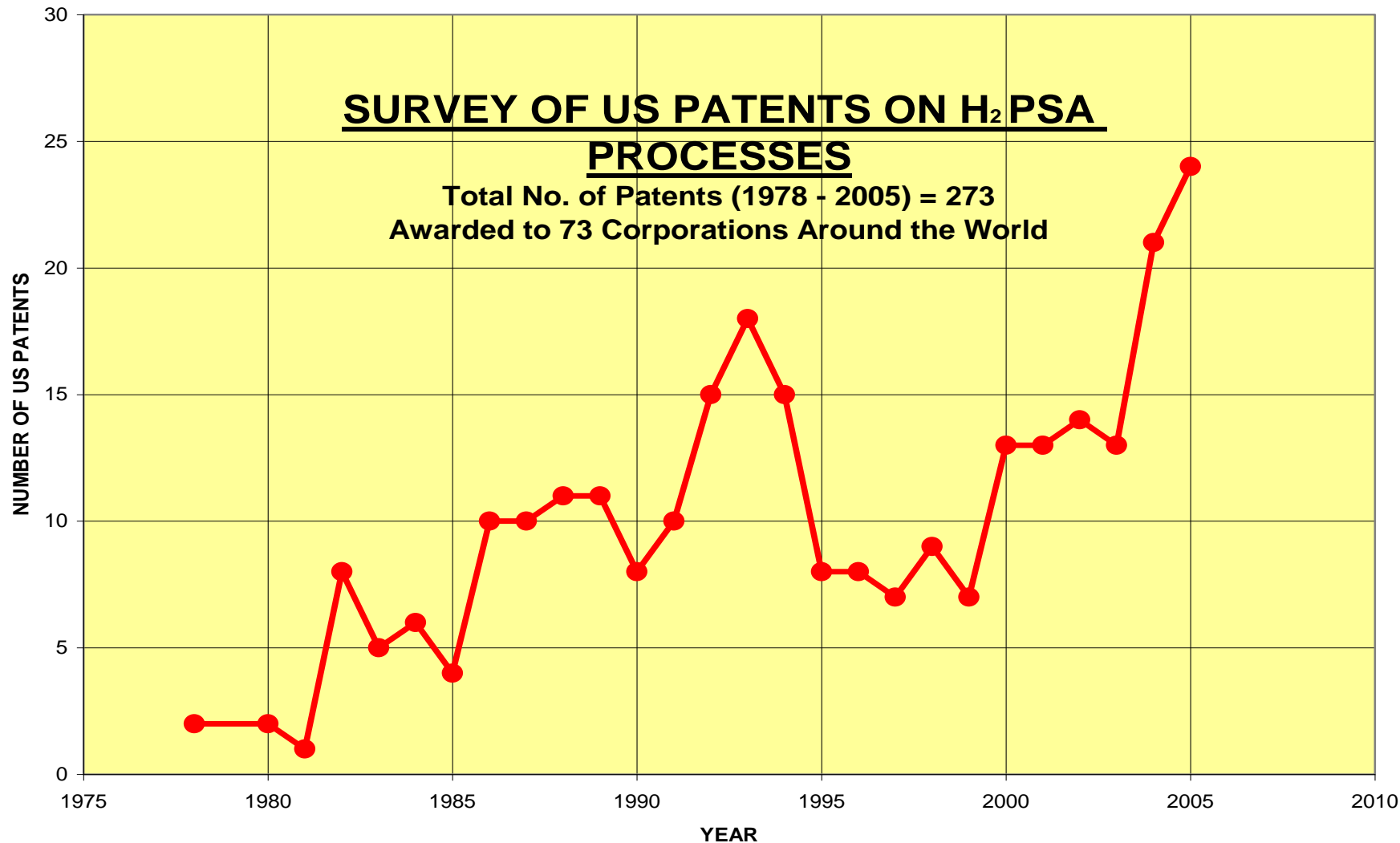
H₂ – Separation Process, Skarstrom - Cycle Vortex Tube Expansion PSA – VTE^{*}



1) Pressurization
2) Adsorption

3) Blowdown
4) Purge with hot product gas

^{*}Patent pending.



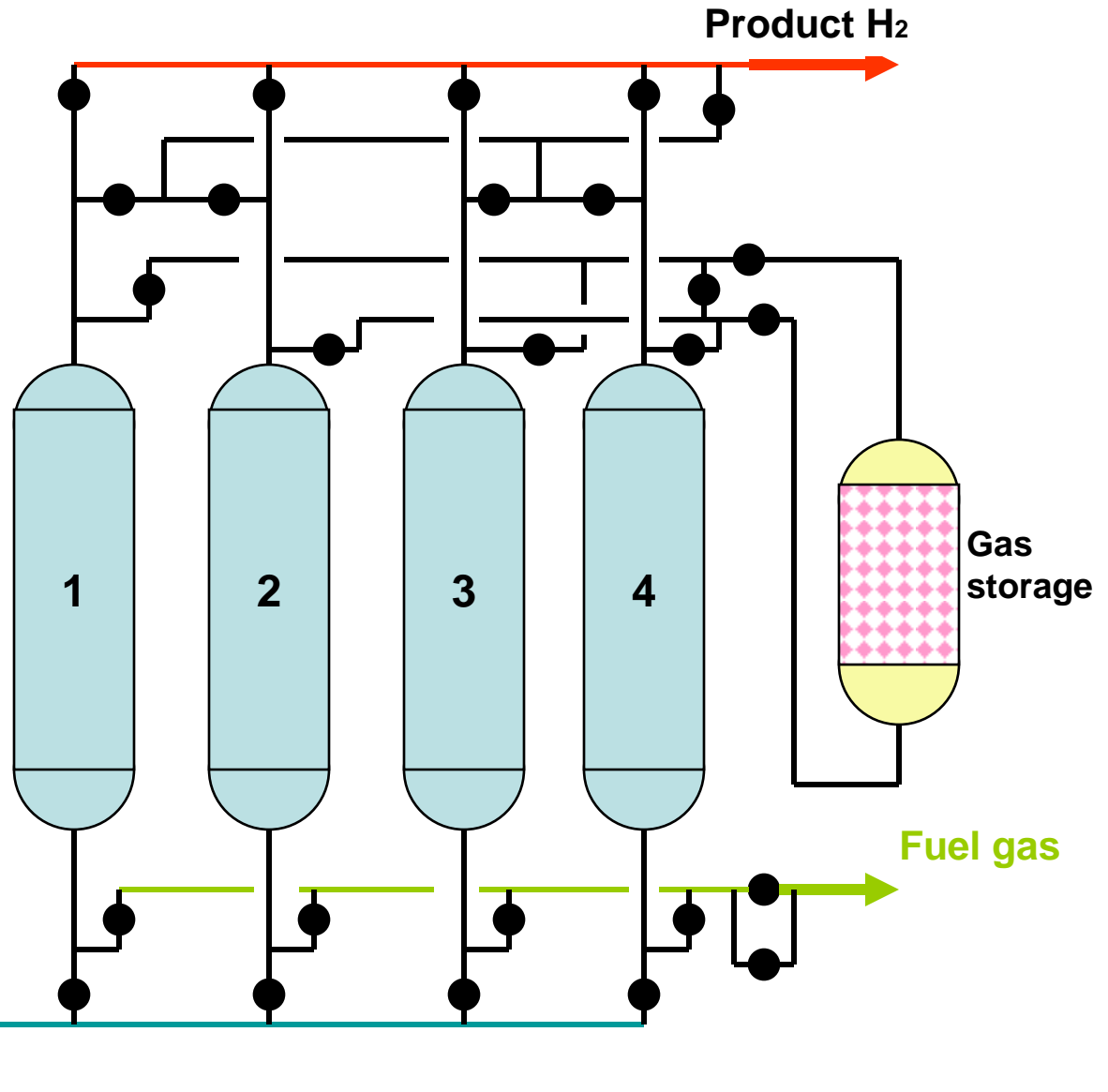
Druckwechseladsorption mit LOFIN-Schaltung

Toyo Engng. Corp.
Gewinnung H₂ aus
ROG

1, 3, 4,
Adsorption
Druckentlastung
Speicherung (H₂, X)
in Gastank (GS)

Gegenstromdesorption
Von (X) in 2 durch
(H₂,X) aus GS etc.

Erhöhung H₂ -
Ausbeute



Sorbentien für Druckwechsel-Adsorptionsprozesse

Geschichtete Festbettadsorber

Sorbens

Störkomponente

Reformergas (SMROG)

Aktivtonerden (Al₂O₃)

H₂O

Aktivkohlen

CO₂

A-Zeolithe

CO, CH₄, N₂

Raffineriegas (ROG)

Aktivtonerde

H₂O

Silikagele

C₃ H...

Aktivkohle

CH₄, C₂H₆...

Zukünftige Entwicklungstrends der PSA-Technologie

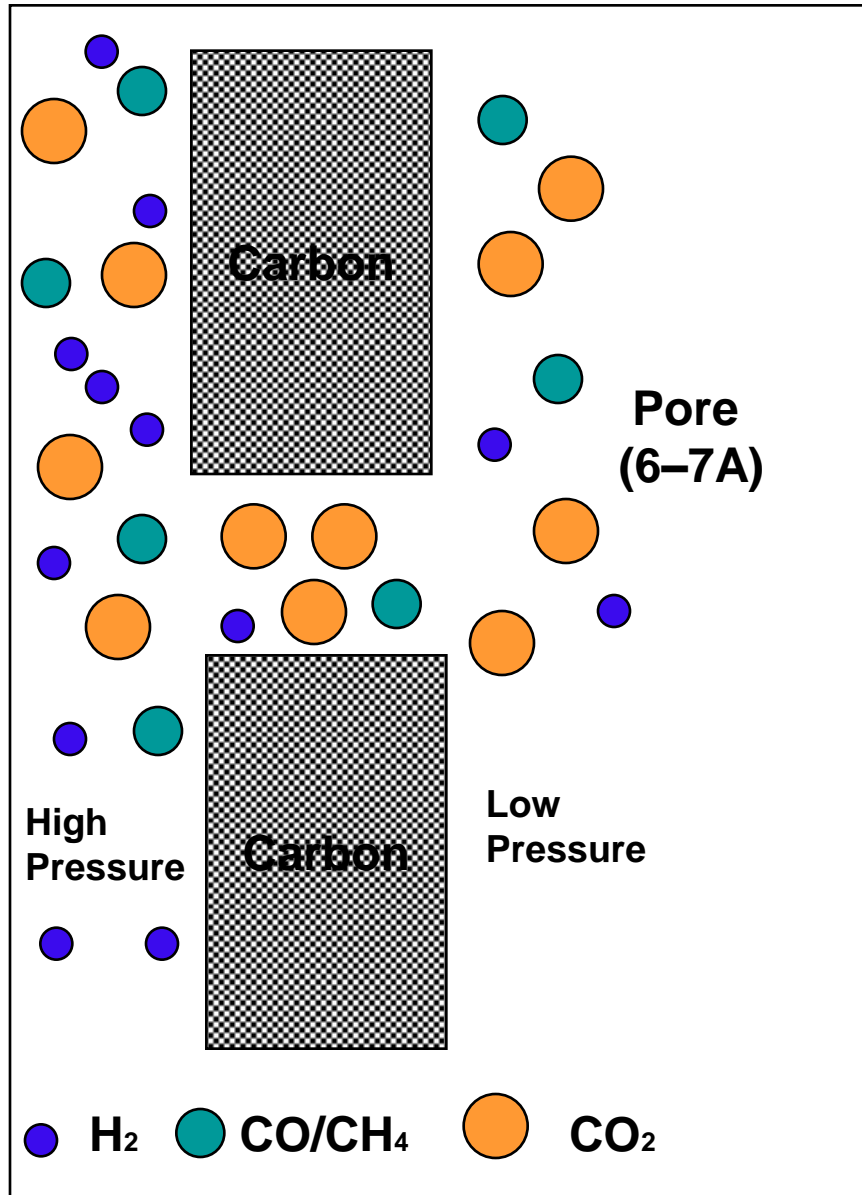
Rasche Druckwechselprozesse ($t < 1\text{min}$) (RPSA)
Verkleinerung der Reaktoren

Hybridsorbentien (LAT, AC, BASF) zur Speicherung der Sorptionswärme (PKW, Benzindämpfe, Polizeifilter)

Sorptionsunterstützte Reaktionen zur Erzeugung von H_2 (SERP)
Störkomponente bei H_2 -Erzeugung - z.B. CO_2 - wird sorbiert.

Hybridtechniken zur Erhöhung der Wasserstoffausbeute
Adsorptions – und Membrantechnik
Selective Surface Membranes (SSF Membranes)

Literatur: Sircar S., Golden T. C., Pressure Swing Adsorption Technology for H_2 Production, Chap. 12 in „Hydrogen Production Technologies“, Liu K., Song C., Eds., Wiley-Interscience, New York, 2006.



Oberflächenselektive Membranen

Schema des Transportmechanismus:

Nanoporen der Kohlenstoffmembran besitzen selektive Kinetik für Gaskomponenten H₂, CO, CO₂, CH₄ etc.

Zusammenfassung Wasserstofftechnologie

1. Wasserstoff: Saubere Sekundärenergie

2. Produktion:

85% Jahresweltproduktion aus SMROG, ROG

PSA-Verfahren

Verbesserungen (Reinheit, Ausbeute), SERP, SSM

Zukunft:

Elektrolyse, Thermochemie, Biochemie

Solarenergie, Kernenergie (?)

3. Probleme

Bedarfsdeckung (VR China, Verkehr)

Speicherung, Verteilung

4. H₂-Technologie ist Wachstumsmarkt

Brennstoffzellen, BHKW, Verkehr, Kommunikation

Literatur Wasserstoff (Auswahl)

1. Geitmann S., Wasserstoff & Brennstoffzellen – Die Technik von Morgen, Hydrogeit Verlag, Kremmen, 2004.
2. Rühle A.-S., Wasserstoff & Wirtschaft – Investieren in eine saubere Zukunft, Hydrogeit Verlag, Kremmen, 2005.
3. Heinloth K., Die Energiefrage, Bedarf und Potentiale, Nutzung, Risiken und kosten, 2.Aufl., Vieweg, Braunschweig, 2003.
4. Nitsch J., Luther J., Energieversorgung der Zukunft, Springer, Berlin etc., 1990.
5. Schnurnberger W., Hydrogen Technology, Subvolume C in Heinloth K., Energy Technologies, Springer, Berlin, 2003.
6. National Academy of Sciences (USA), The Hydrogen Economy, National Academy Press, Washington, D.C., 2004