Gas - Adsorption
# Measurement Methods and Separation Processes

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1. Basic Concepts
2. Sorbens Materials
3. Measurement Methods
   Equilibria, Heats of Adsorption,
   Kinetics, Diffusion

4. Hydrogen: Production and Purification
5. Engineering Adsorption Cycles

6. Literature
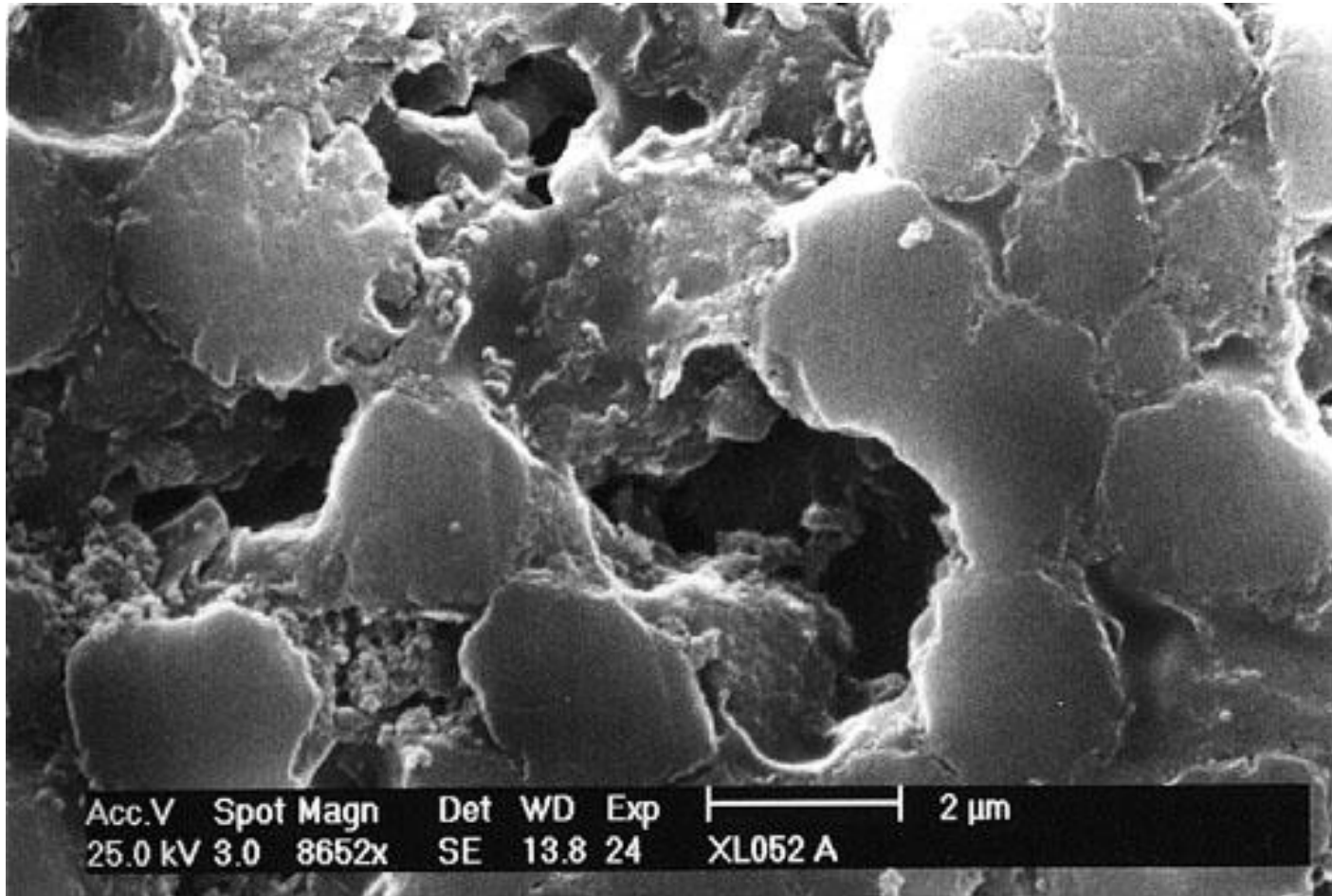7. Conclusions

Basic Concepts of Gas - Adsorption
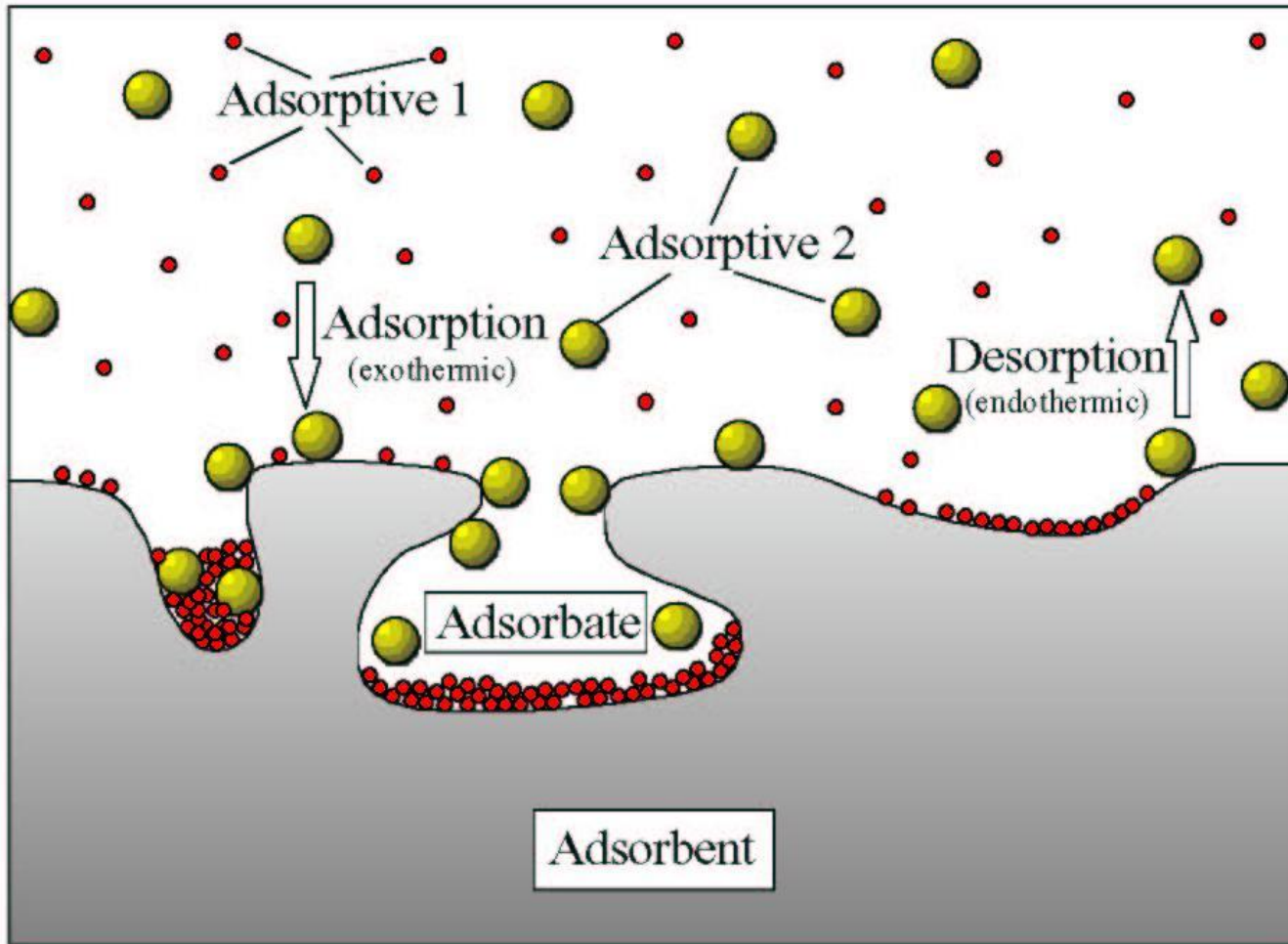
Gas / Vapor Phase

Adsorbed Phase Adsorbate (~L)

Inert Solid Phase Sorbent

Surface Structure of Zeolite Molecular Sieve UOP/Linde 13X

Acc.V   Spot Magn   Det WD Exp |——————| 2 µm
25.0 kV 3.0   8652x   SE   13.8 24   XL052 A

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

Sorbens Materials (Selection 2006)

Material's Name   Main Technical Use
BET Area (m2 / g)   Desorption Enthalpy (kJ / mol)

Alumina, activated   Air separation
 Al (OH)x   x<3   Dehydration agent
300 - 400   20 - 60

Biopolymers from starch etc.   Water, organic vapors, odorants
300 – 800   30 -60

Carbon, activated   Removal of organic substances
C(Hx)(Oy)   x>0, y>0   (VOCs) from air,technical gases etc.
600 – 3500   Hydrogen purification
                                               10 – 60

Polymeric sorbents, resins   Waste water treatment (ion exchange)
300 – 1100   10 - 50

| **Material's Name** | **Main Technical Use** |
| **BET Area (m2 / g)** | **Desorption Enthalpy (kJ / mol)** |

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

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

Mesoporous silica (MCM41)
600

Silica aerogels

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

Air separation, Drying of natural gas
Removal of CO_2 from exhaust gases
Separation of paraffinesTolefines etc.
40 -80

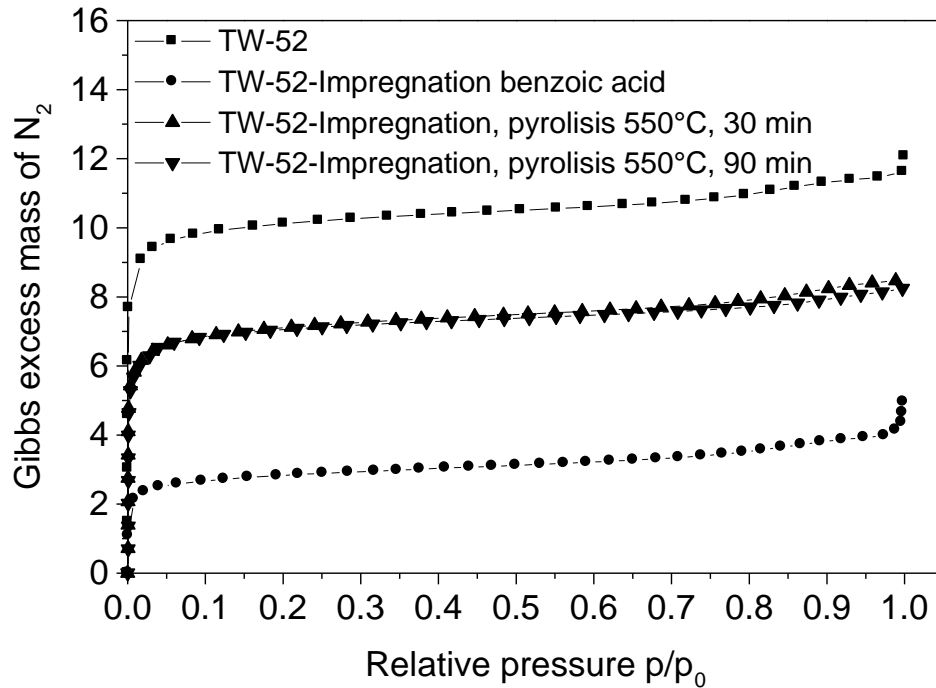# Gas Flow Porosimeter (He, N$_2$, BET, 77 K)
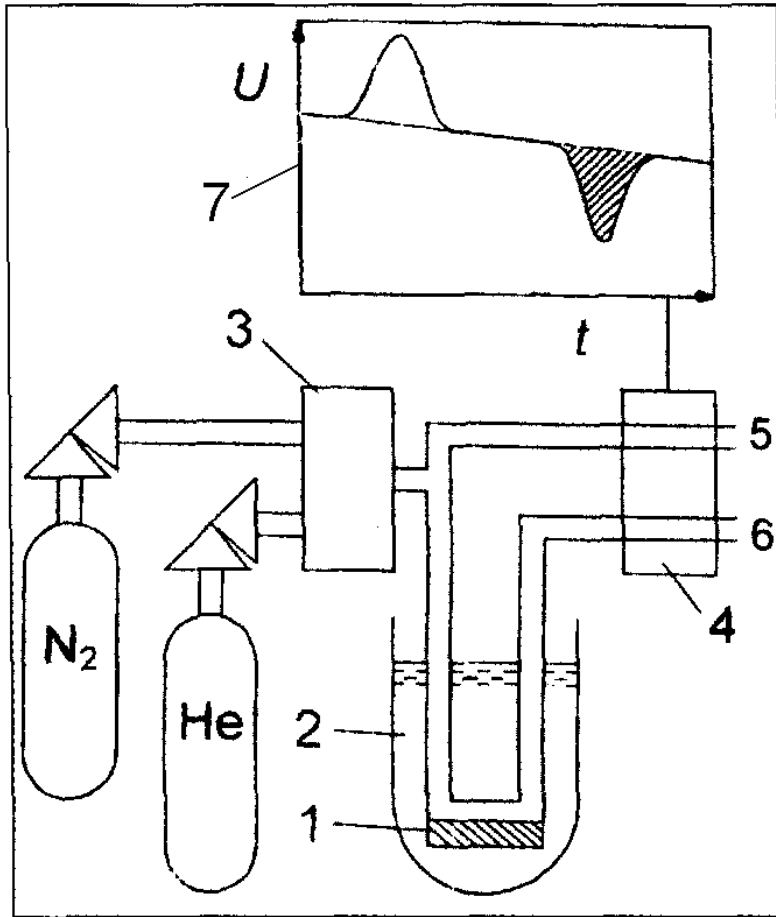
1 Sample / Sorbent

2 Dewar vessel (N$_2$, 77 K)

3 Mixing chamber

4 Thermal diffusivity detector(Δa)

5 Sorptive gas flow (original)

6 Reduced gas flow (changed)

7 Data display system (ΔU$\cong\Delta$a)

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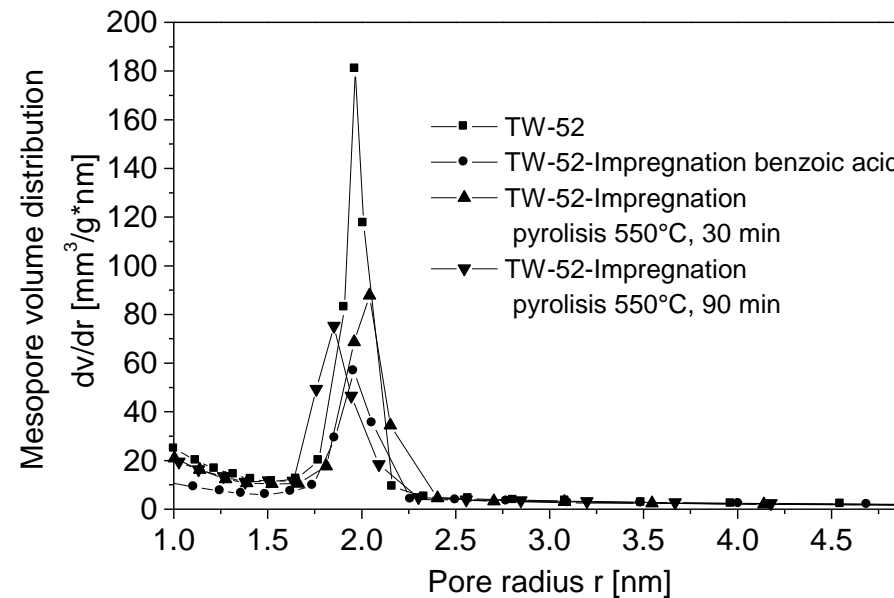
Sing K.S.W., Adsorption…

Academic Press, San Diego, 99

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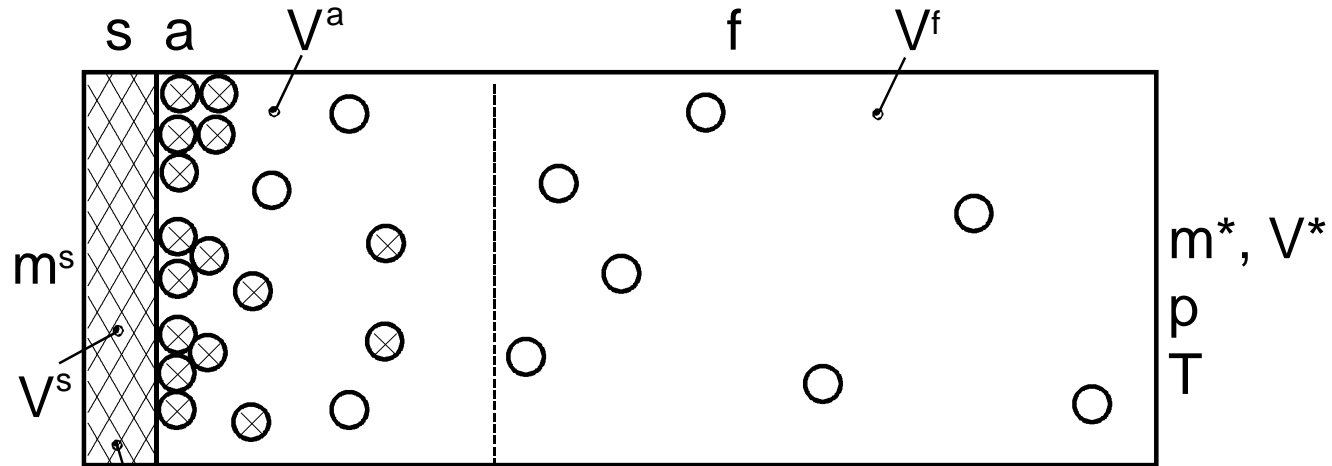< impregnation with bencoic acid (30 min.,90min.), 77K.

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

IUPAC Classification, K.S.W.Sing
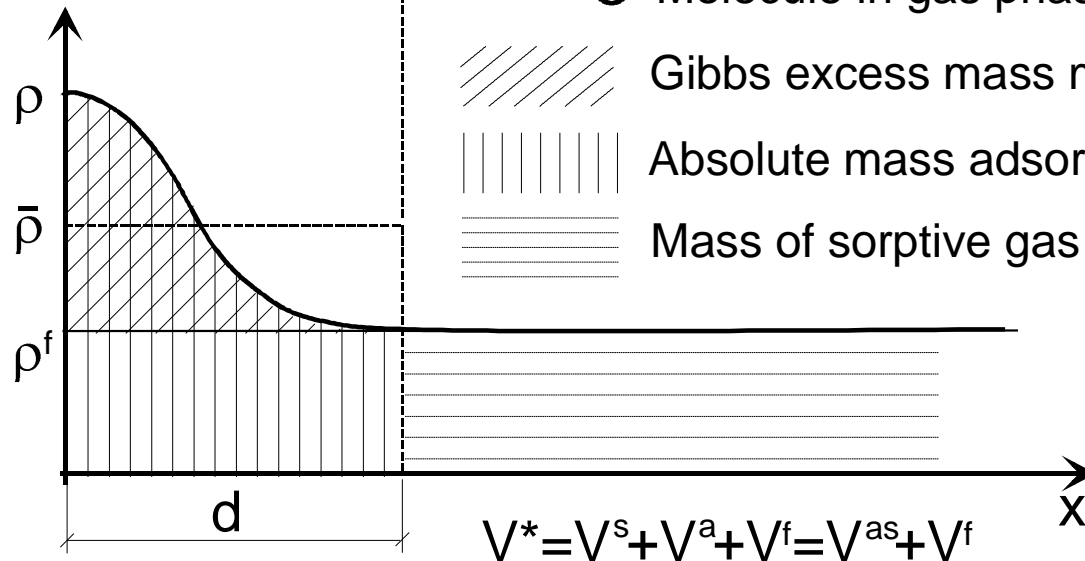0   < 2nm   <   50nm < 00
Micro-   Meso-   Macropores

Plane Surface Sorption System: Absolute/Excess Mass

s a V^a f V^f
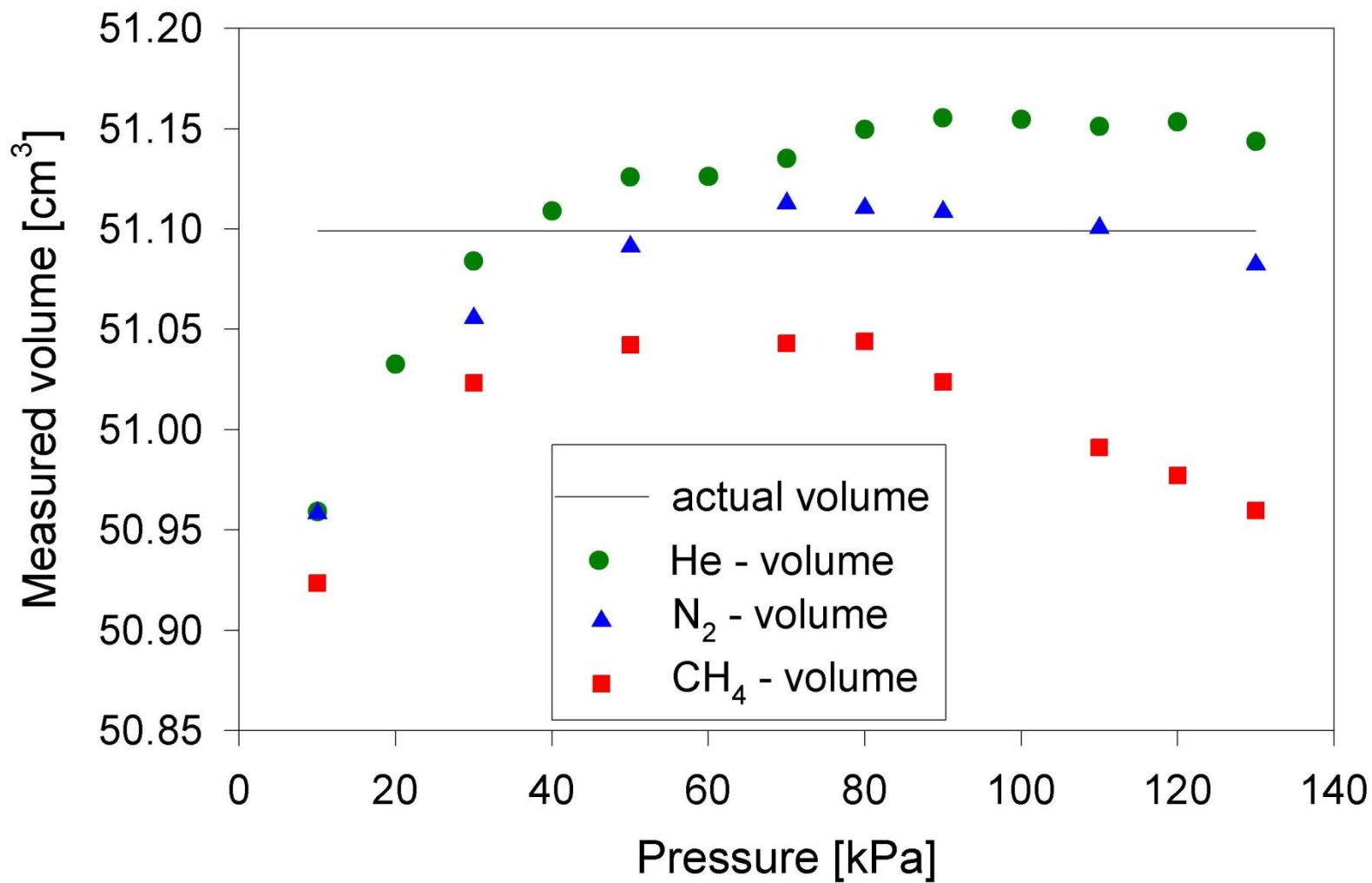
m^s

V^s

m^*, V^*
p
T

Sorbent material(s)

$\otimes$ Molecule adsorbed
$\bigcirc$ Molecule in gas phase

Gibbs excess mass m^a_{GE}

Absolute mass adsorbed m^a

Mass of sorptive gas m^f

ρ

$\bar{\rho}$

ρ^f

d

x

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

Determination of the (known) volume (51.10 cm^3) of a calibration cylinder by gas expansion experiments using gases He (5.0), N$_2$ (5.0) and CH$_4$ (5.5) at 298 K in a commercial gas pycnometer [1].
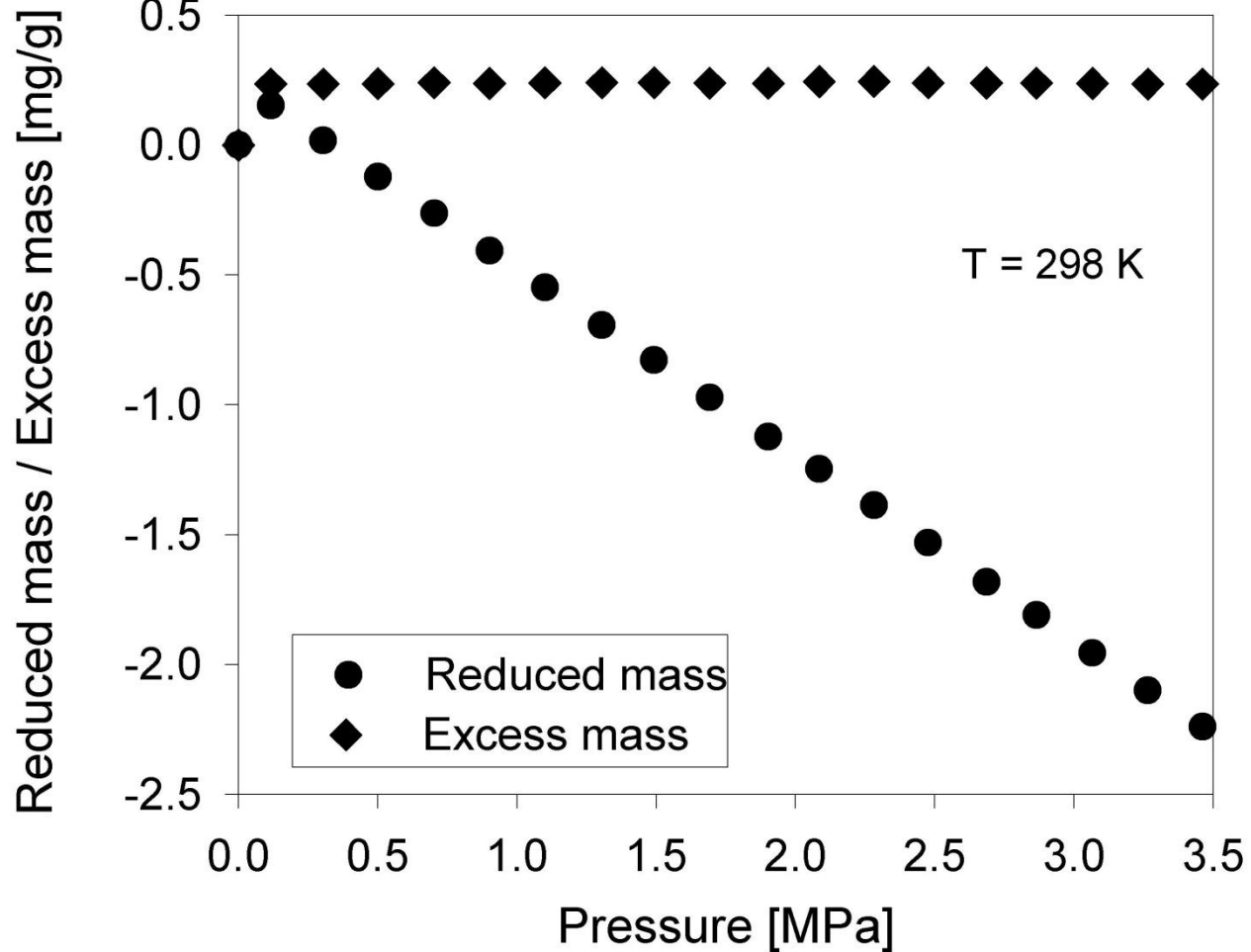
Adsorption isotherm of helium on activated carbon (AC) Norit R1 Extra at 293 K. Full circles present data of the reduced mass (Ω) defined by Eq. (1.5). As these can be correlated linearly as function of the helium gas density $\rho^f = p/R_{He}T$, the volume of the AC impenetrable to the helium molecules 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 $m^a = 0.25$ mg/g = const.

Adsorption of Helium on Porous Solids
Theory

Reduced mass to be measured by a helium pycnometer
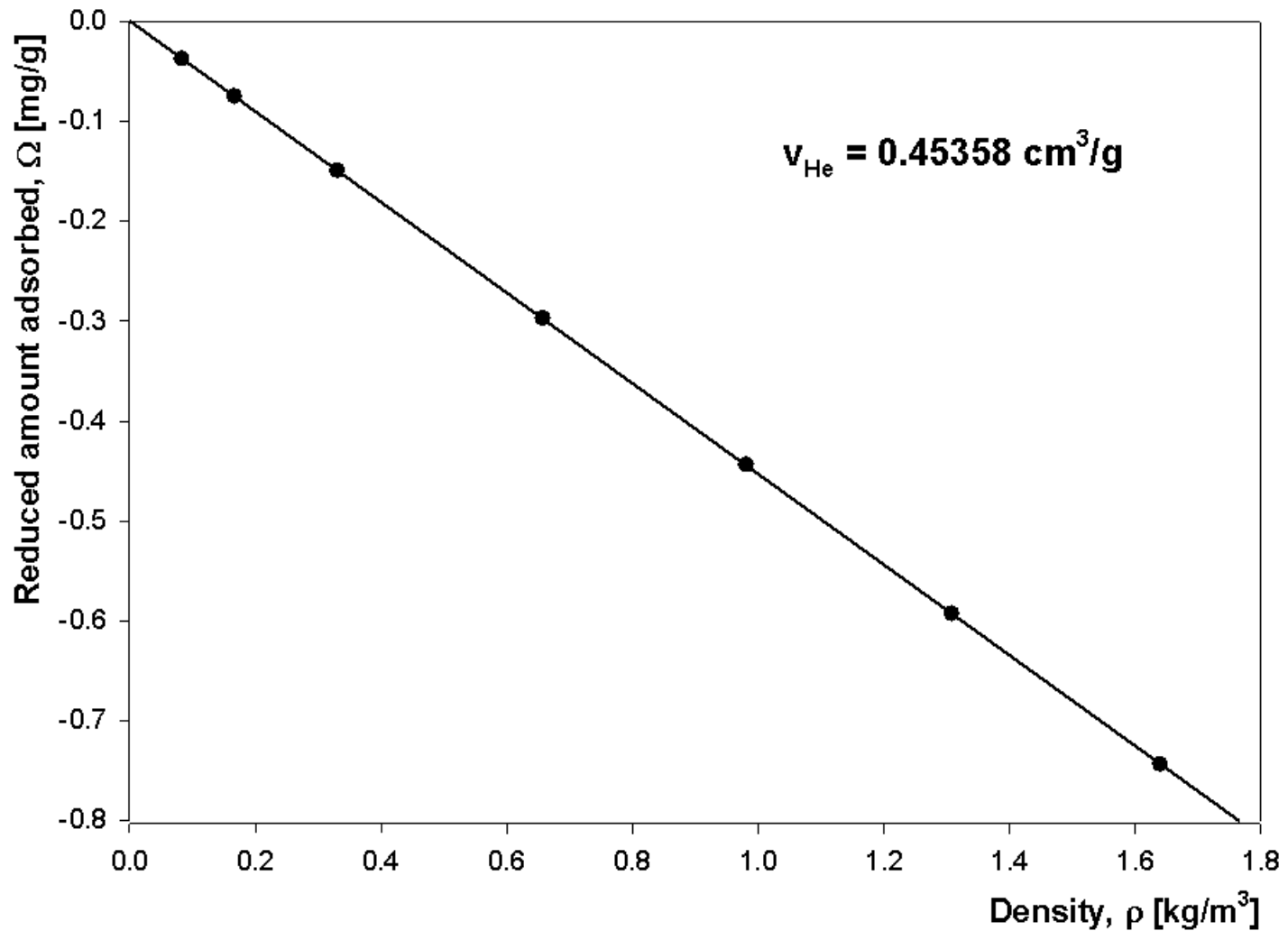
$$\Omega = m^a - \rho^f V^{as} \tag{1.5}$$

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

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

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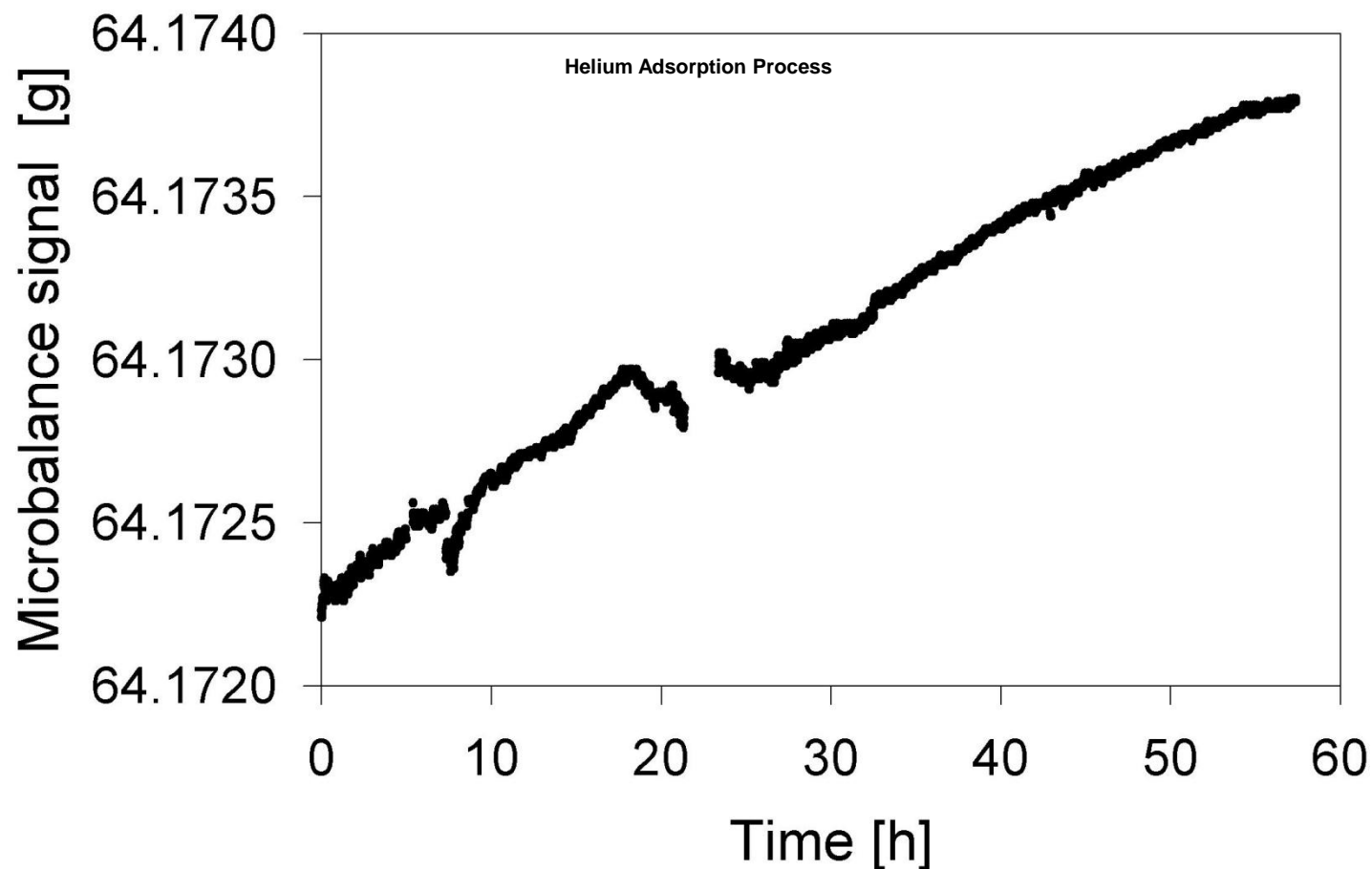
(1.5), (1.6):
$$m^a = \Omega - \rho^f \left(\frac{\partial \Omega}{\partial \rho^f}\right)_{T,\infty} \tag{1.7}$$

ρf …   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=298.17K 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.
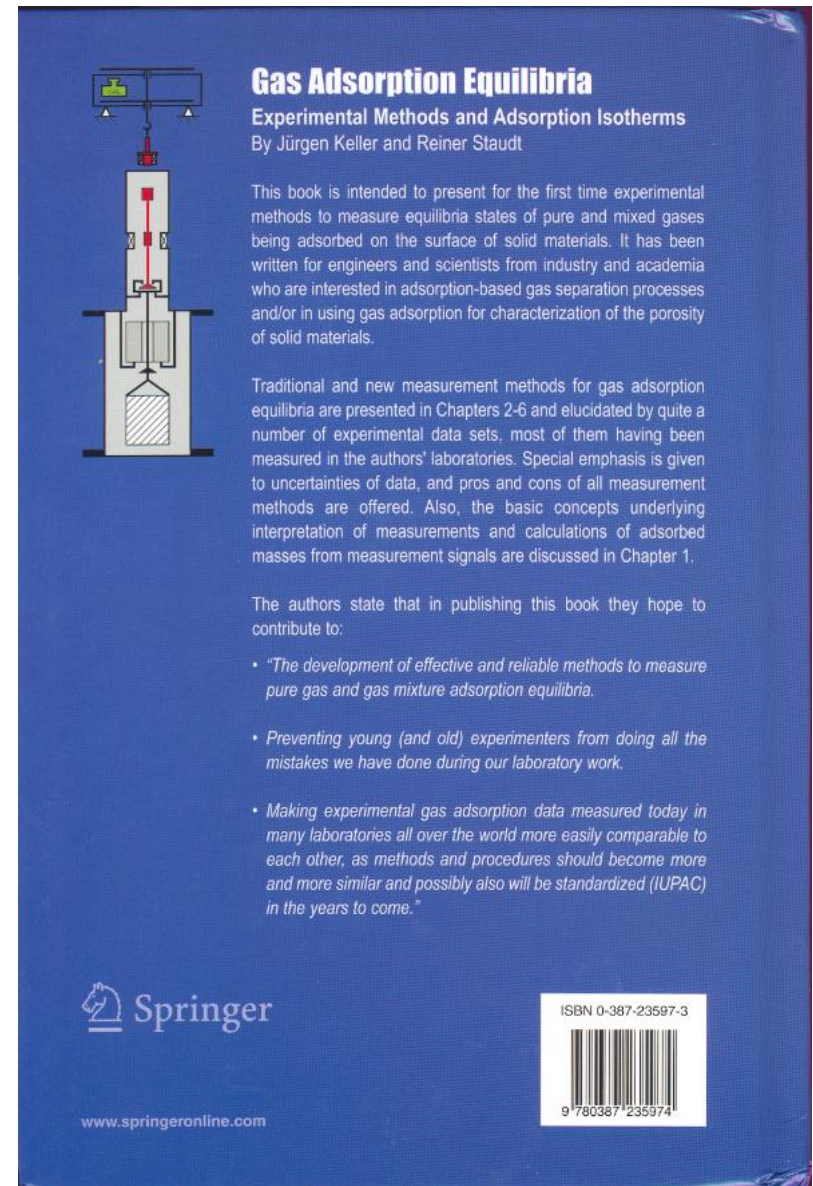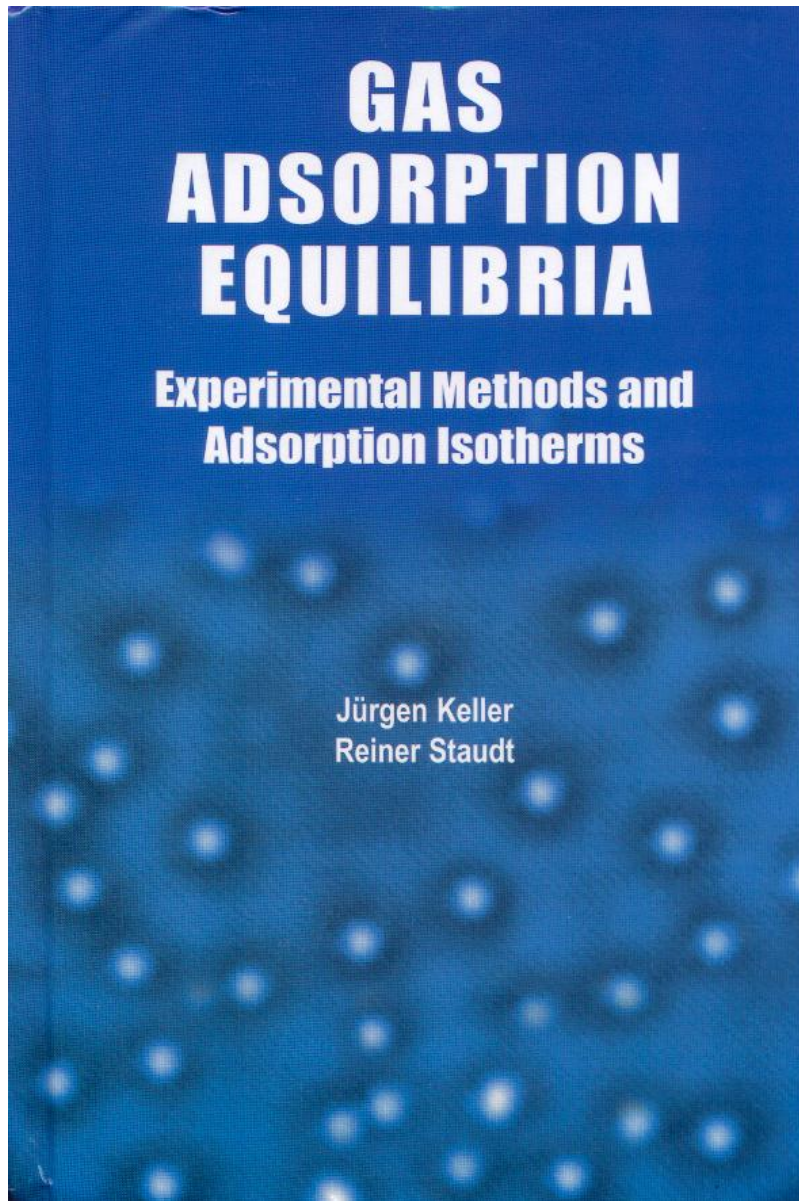
Gas Separation by Physical Adsorption

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	Purpose
Volumetry/Manometry	Characterization of porous solids
Gravimetry	Equilibria, Kinetics, Gas Density, Process Cont.
Oscillometry	Swelling Material
Dielectric Permittivity	Industrial Process Control

Gas Mixtures (N=2)

Volumetric-Densimetric M.	Equilibria, Process Control
(2-sites Magnetic Balance)	

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

$$V^{as} \cong V_{He}^s, \quad V^a = 0$$
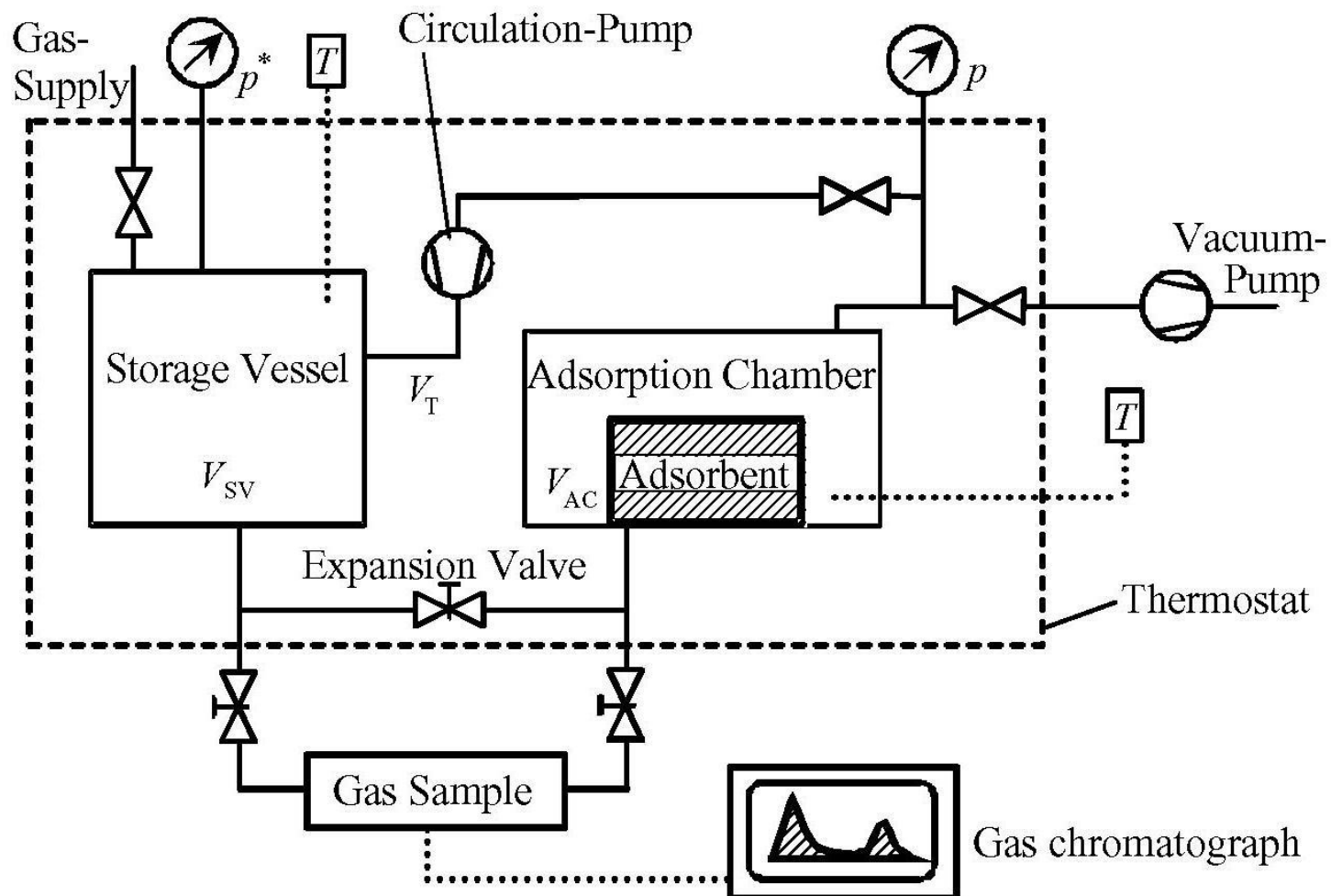
$$m_{GE}^a = \Omega + \rho^f V_{He}^s$$

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 $\qquad m_i^* = m_i^f + m_i \qquad i = 1...N$ $\qquad$ (1)

Total mass (i) $\qquad m_i^* = w_i^* \rho^f \left(T, p^*, w_1^* ... w_N^* \right) V_{SV}$ $\qquad$ (2)

Adsorptive's mass (i) $\quad m_i^f = \rho_i^f \left(V_{SV} + V_{AC} - V^S \right)$ $\qquad$ (3)
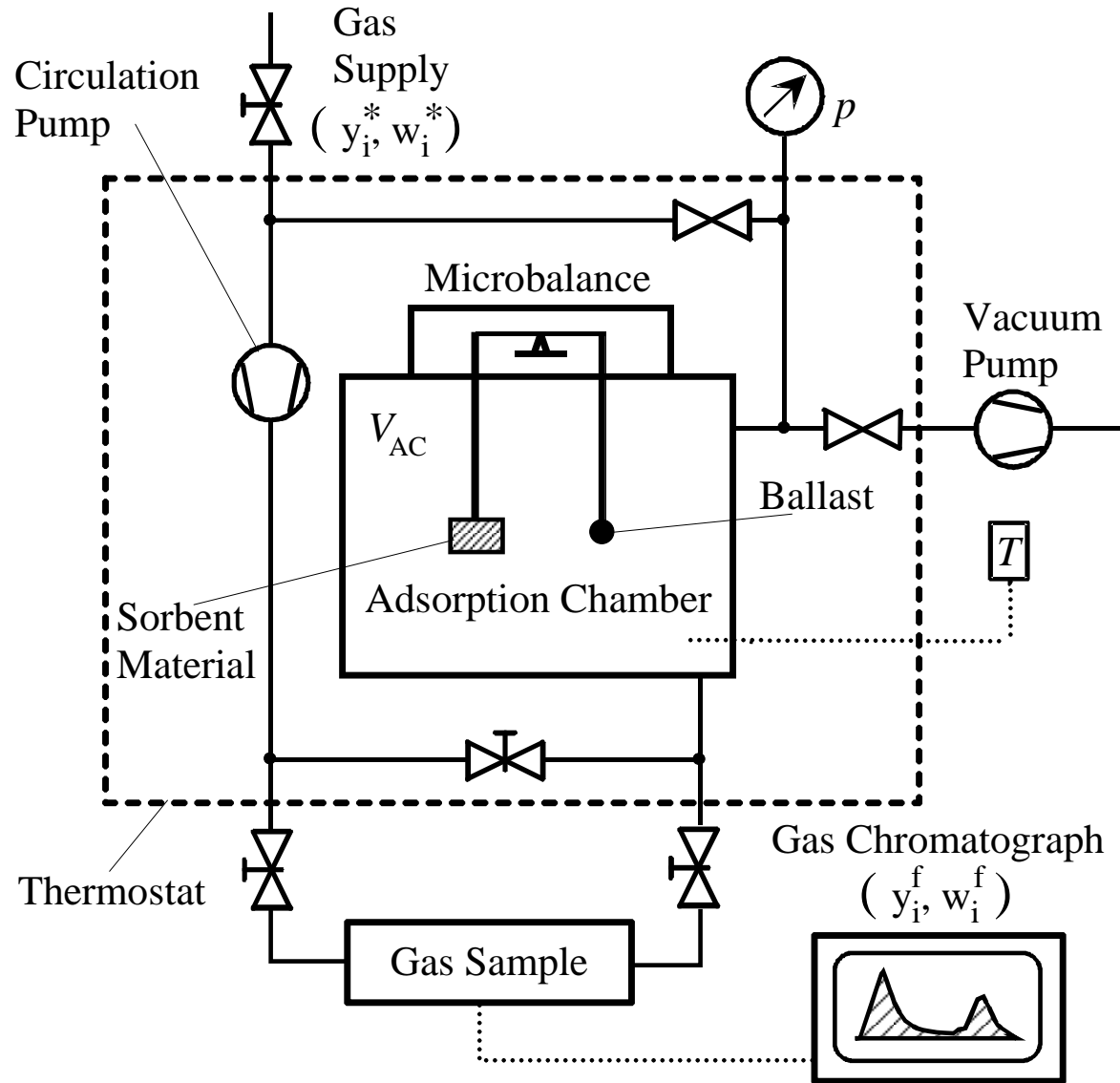
$$(1-3): \underline{\Omega_i = m_i - \rho_i^f V^S}$$ $\qquad$ (4)

$$\Omega_i = \left(\rho_i^* - \rho_i \right) V_{SV} - \rho_i V_{AC}$$

$$\rho_i^f = w_i \rho^f \left(T, p, w, ... w_N \right), \qquad w_i : GC$$

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

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

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

Total mass of gas supplied to system: Microbalance:

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

$$\Omega = m^a - \rho^f V^s_{He} \qquad\qquad 4$$

Sorptive mass / mole number:

$$m^f = M^f n^f = \left(\sum_i^N y^f_i M_i \right) n^f \qquad 2$$

$$m^a = \Omega + \frac{m^f}{V_{AC} - V^s_{He}} V^s_{He} \qquad 4A$$

$$n^f = \frac{p\ V_{AC} - V^s_{He}}{R\,T\,Z\ p,T,y^f_1 \dots y^f_N} \qquad\qquad 3$$

Mass of component   i=1...N adsorbed:

$$m^a_i = w^*_i m^* - w^f_i m^f$$

$$1-4\ :\ m^a_i = w^*_i \left[\frac{p\ V_{AC} - V^s_{He}}{R\,T\,Z} M^f + \Omega \right] - w^f_i \frac{p\ \left(V_{AC} - V^s_{He} \right)}{R\,T\,Z} M^f$$

Gravimetry / Chromatography (N $\geq$ 1)

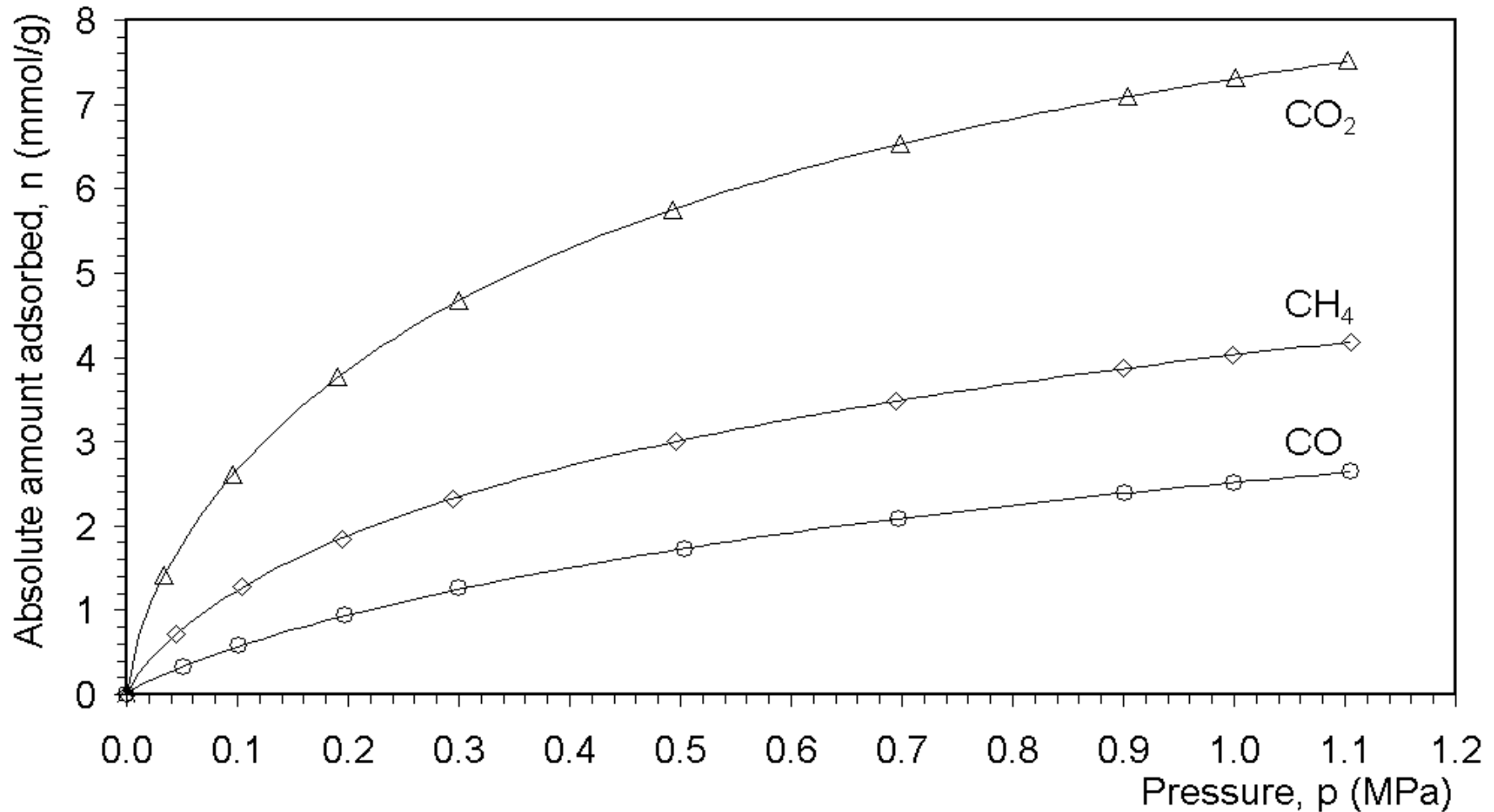# Data Correlation and Prediction of Mixture Adsorption: Generalized two-site (Dual-Place) AI (2LAI)

For pure gases:

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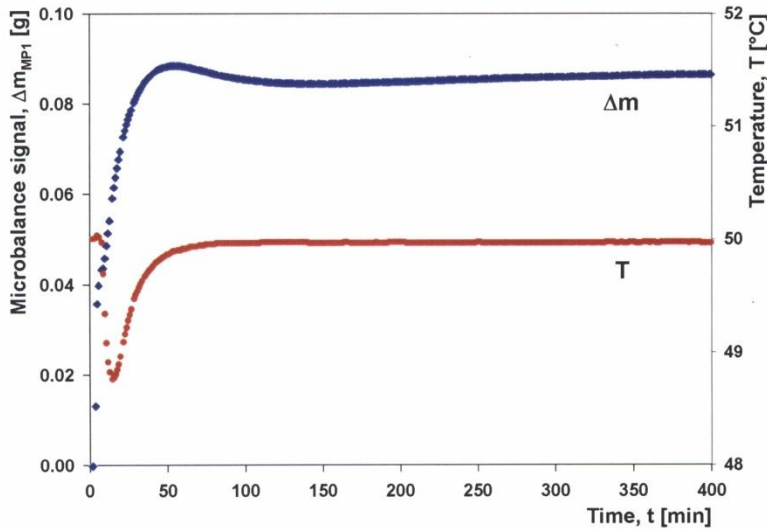
For mixtures:

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

$$n_{\infty,i}^S(T) \cdot \alpha_i^S \cdot \frac{(b_i^S(T) \cdot p_i)^{\alpha_i^S}}{1 + \sum_i (b_i^S(T) \cdot p_i)^{\alpha_i^S}} \ , \ i = 1, 2, 3 \ .$$
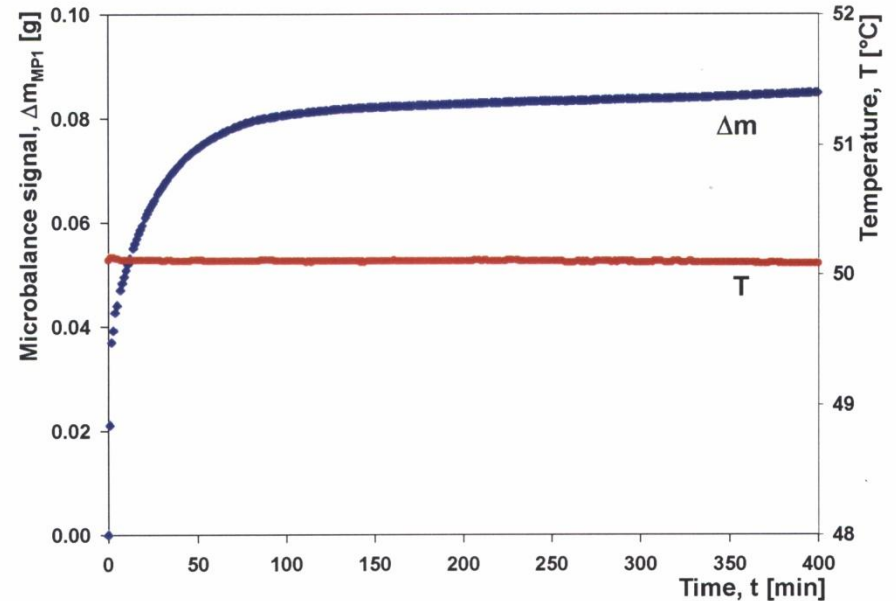
Adsorption equilibria of pure gases CO ($\circ$), CH$_4$ ($\diamond$) and CO$_2$($\triangle$) at 293K on industrial activated carbon (ACAL). Datafit: 2LAI ($\bar{}$).
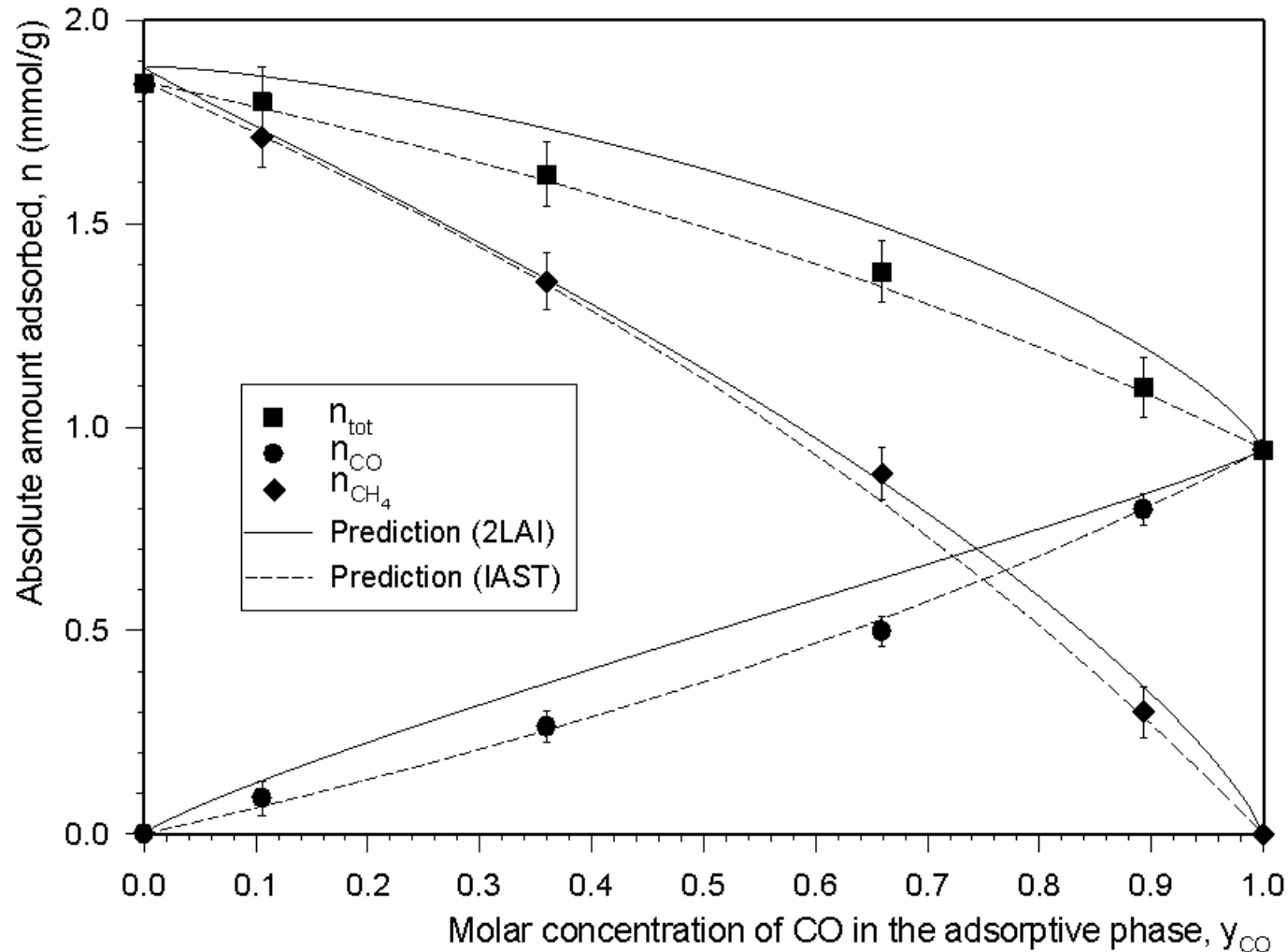
Kinetics of Adsorption of CO2 on MS Na 13X

< 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/CH$_4$ (n$_{tot}$ (■), partial amount of CO (●), partial amount of CH$_4$ (◆)) 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)

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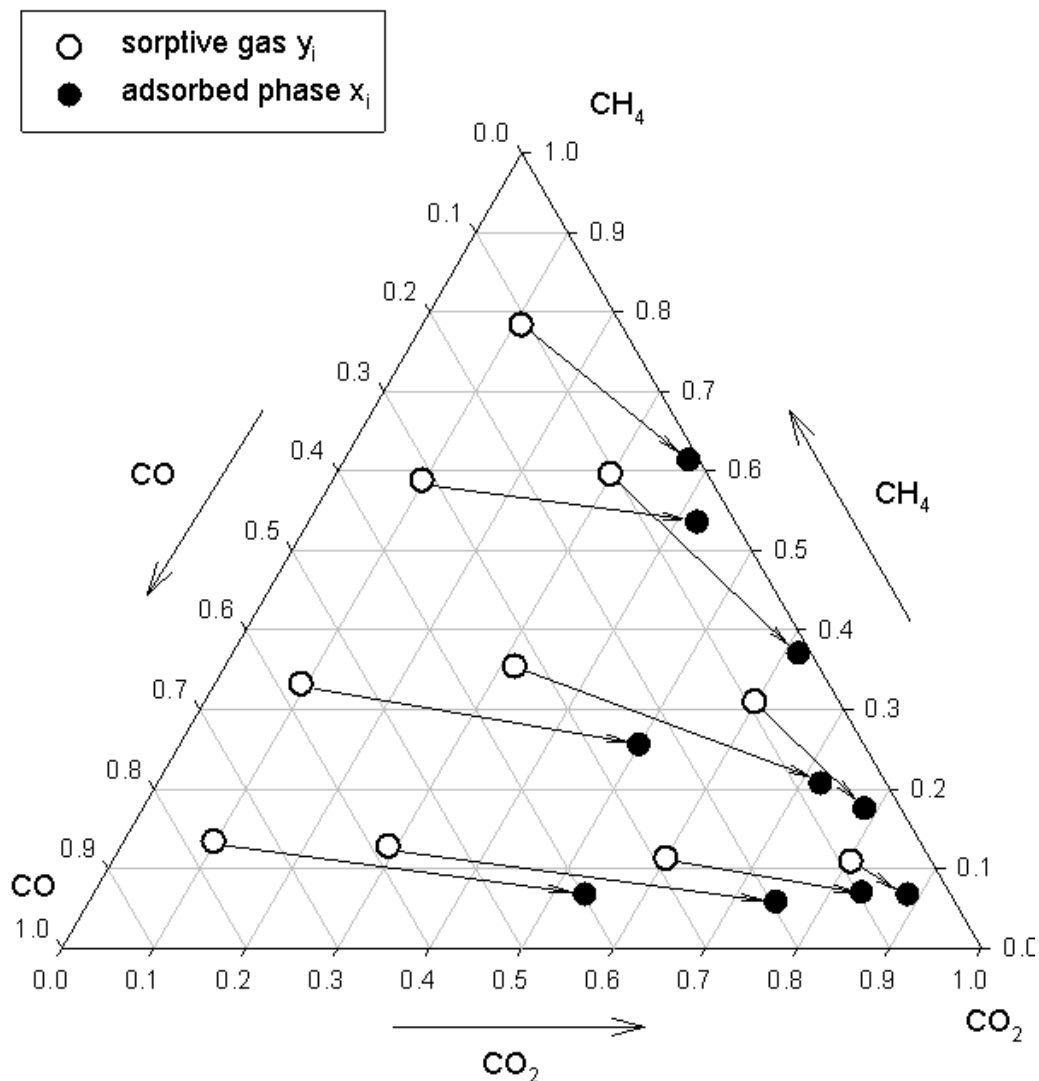
- Relative dispersion (σ)

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

$$N = 1...4$$

Statistical uncertainties (f_m, σ) of coadsorption data CO/CH$_4$ on ACAL at 293K and 0.2MPa, 1.0MPa predicted from pure adsorption data by two isotherms.
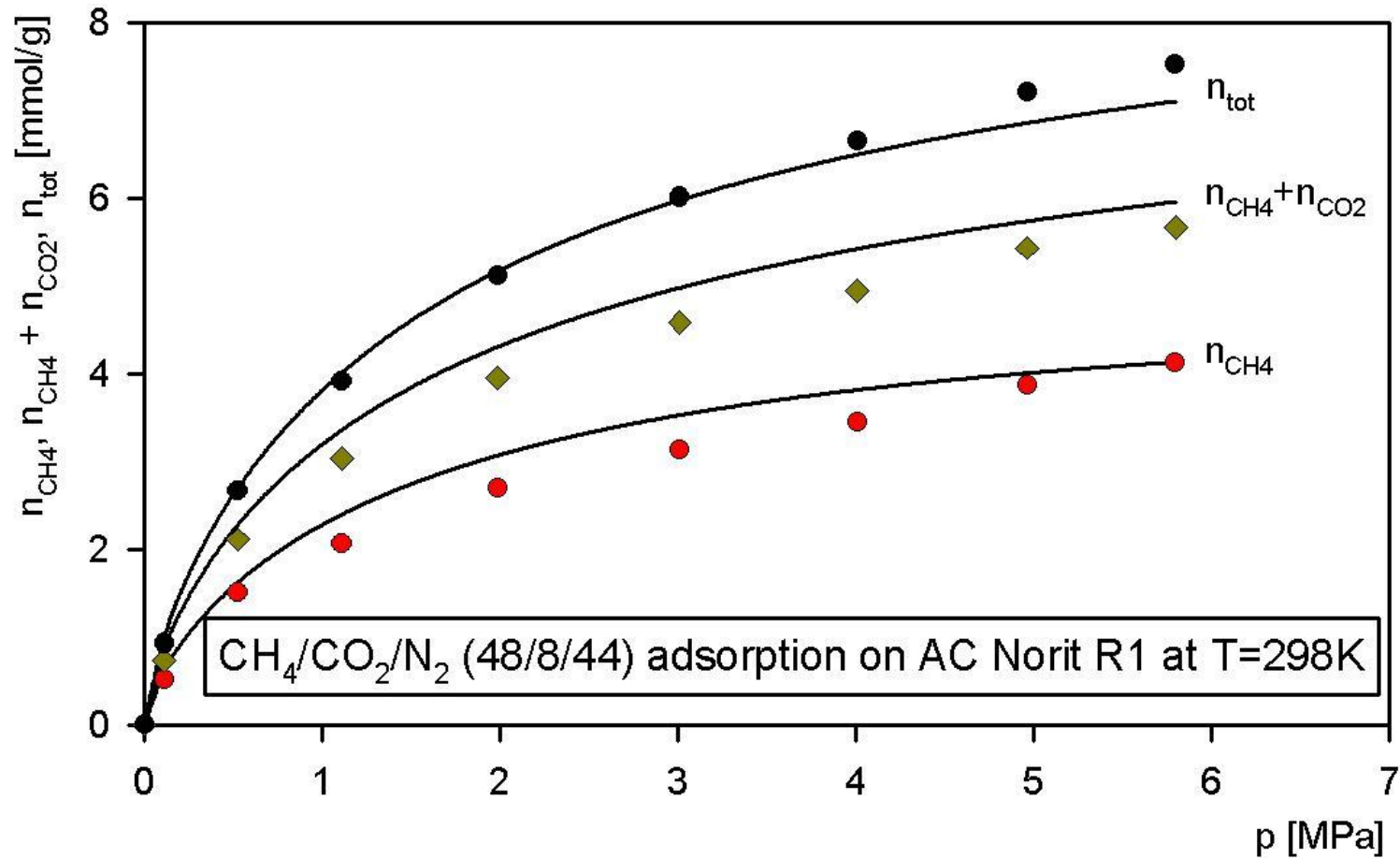
Prediction of tenary adsorption data with the 2-sites Al

Adsorption equilibria of ternary gas mixture CO_2/CH_4/CO (molar concentrations of the sorptive gases y (○), molar concentrations of the adsorbed phases x (●)) at 293K and 0.2MPa on ACAL.
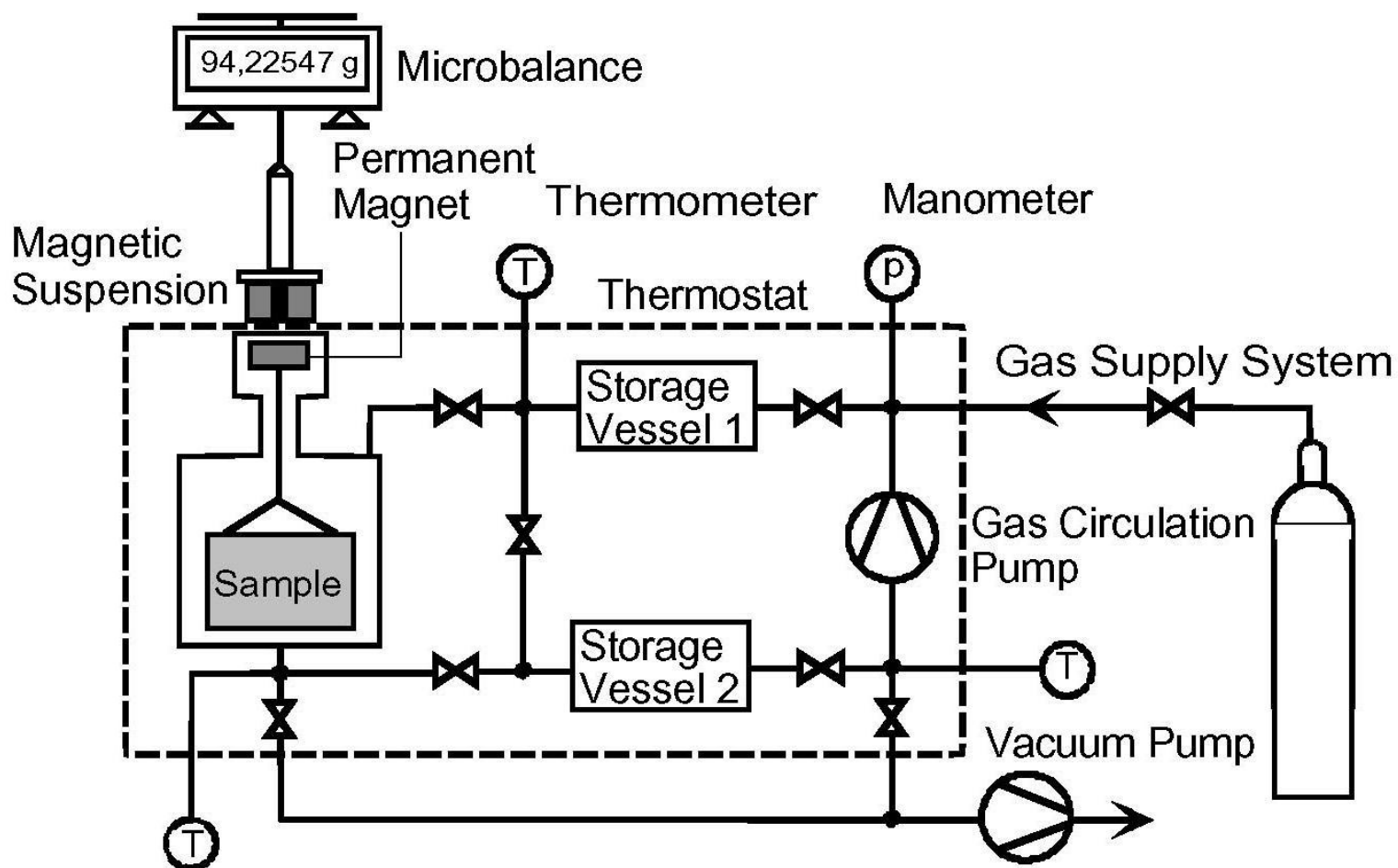
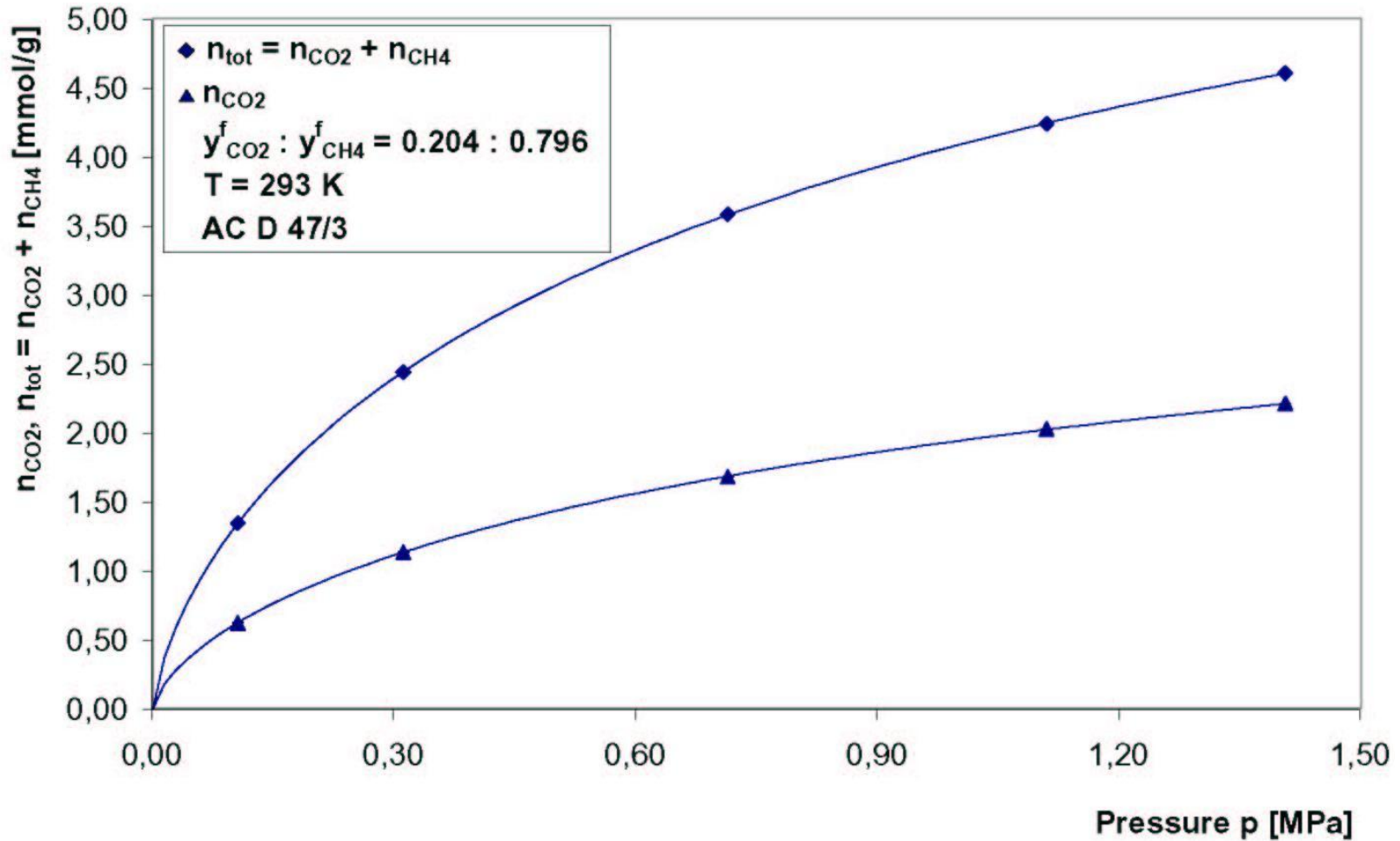**Experimental Setup for volumetric-gravimetric measurements**

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

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

Adsorptive's equation of state $\quad \dfrac{m_1^f}{M_1} + \dfrac{m_2^f}{M_2} = \dfrac{p\ V^* + V^f}{ZRT}$
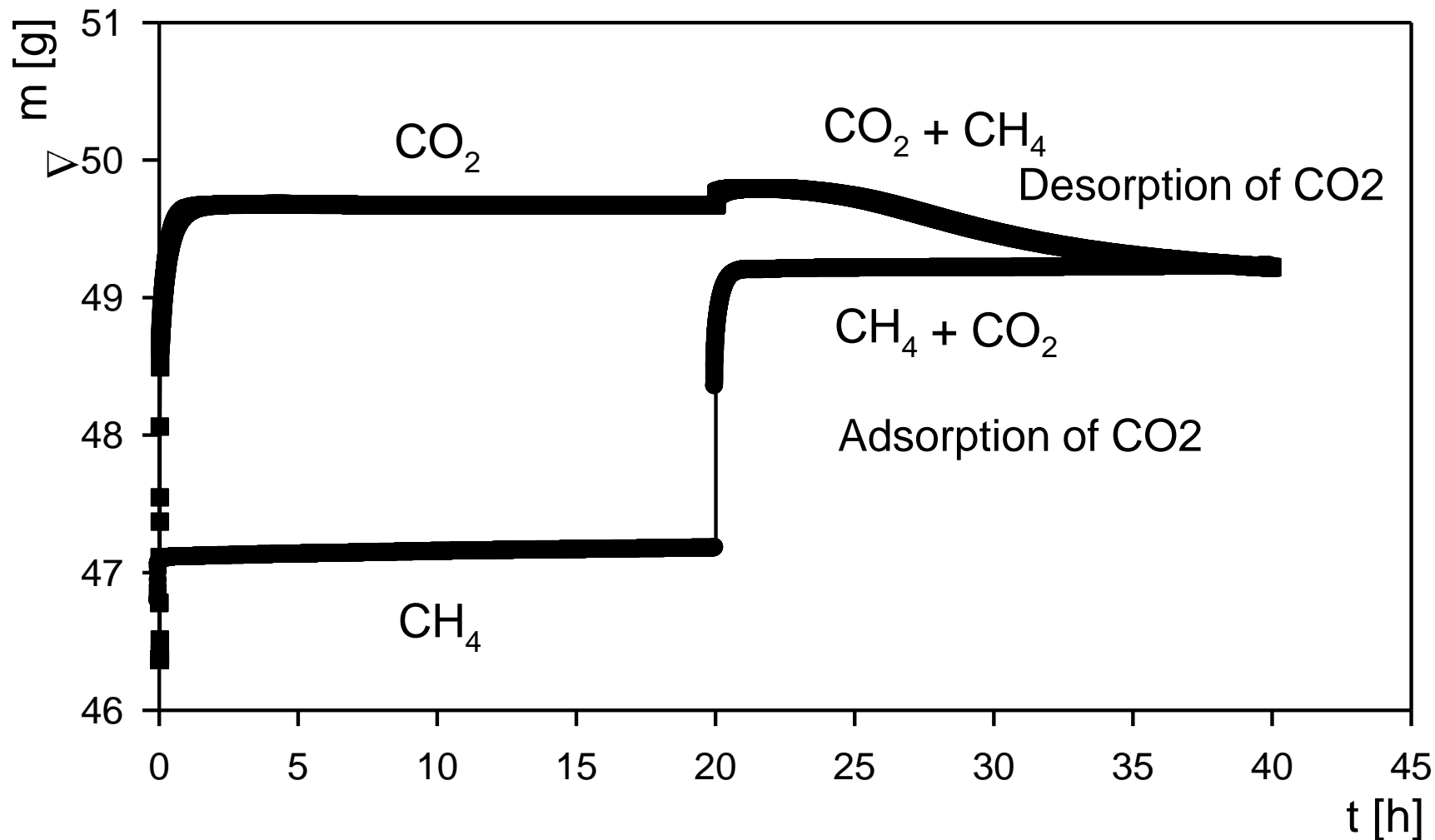
$\rightarrow\ m_1, m_2, m_1^f, m_2^f \ldots V^f = V - \left(1 + \dfrac{m_0^s}{m^s}\right) V^{as} \quad \text{if}\quad M_1 \neq M_2$

**Volumetric-Gravimetric Measurements
of Binary Coadsorption Equilibria**
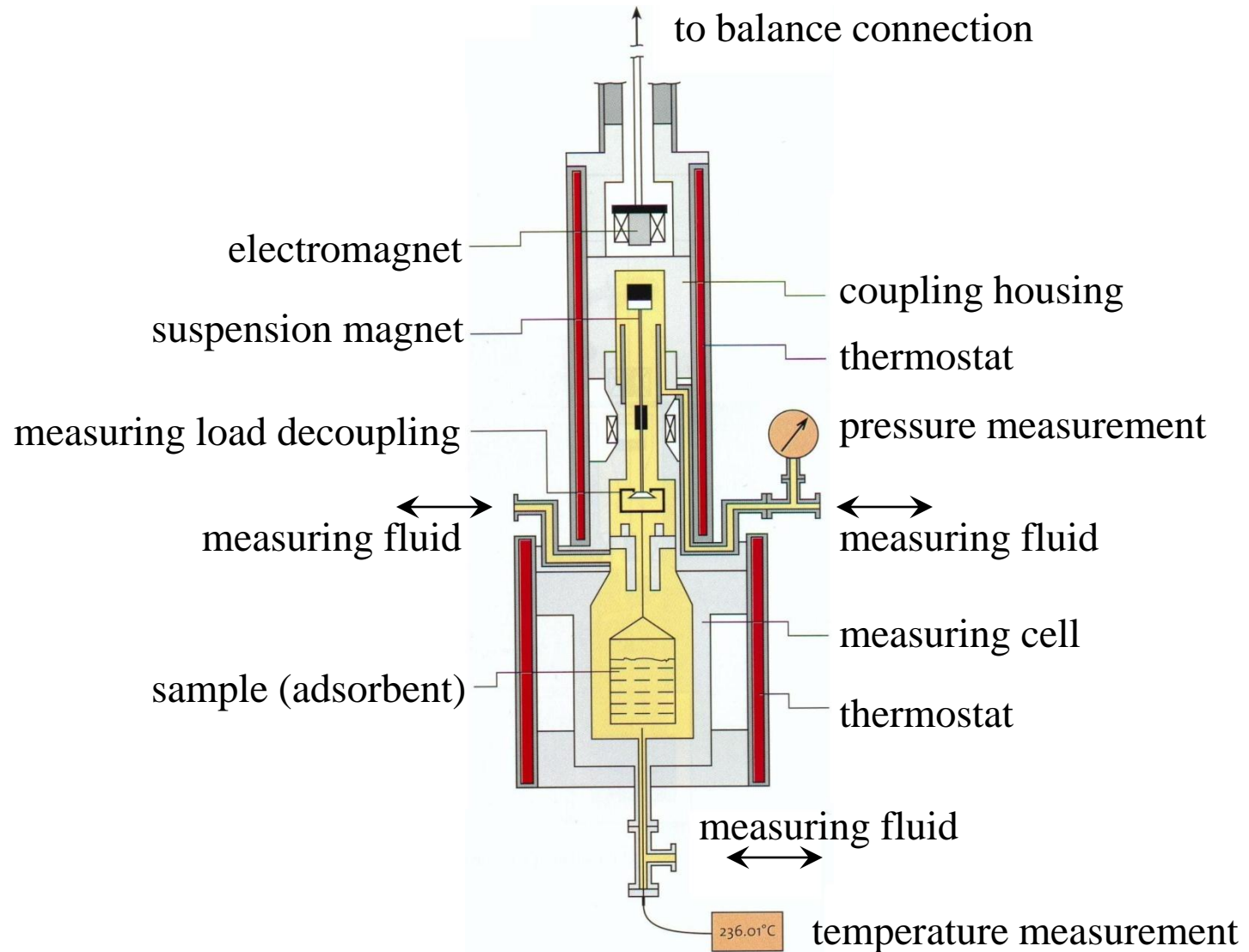
Coadsorption equilibria of CO_2 / CH_4 at $T = 293K$, $y_{CO_2} = 20.4\% \, mol$, $y_{CH_4} = 79.6\% \, mol$ on AC D47/3. Correlation by GAI: $n_i = n_{i_\infty} (bp)^{\alpha_i} / \left[1 + (bp)^{\alpha_i} \right]$, $i = CO_2, CH_4$
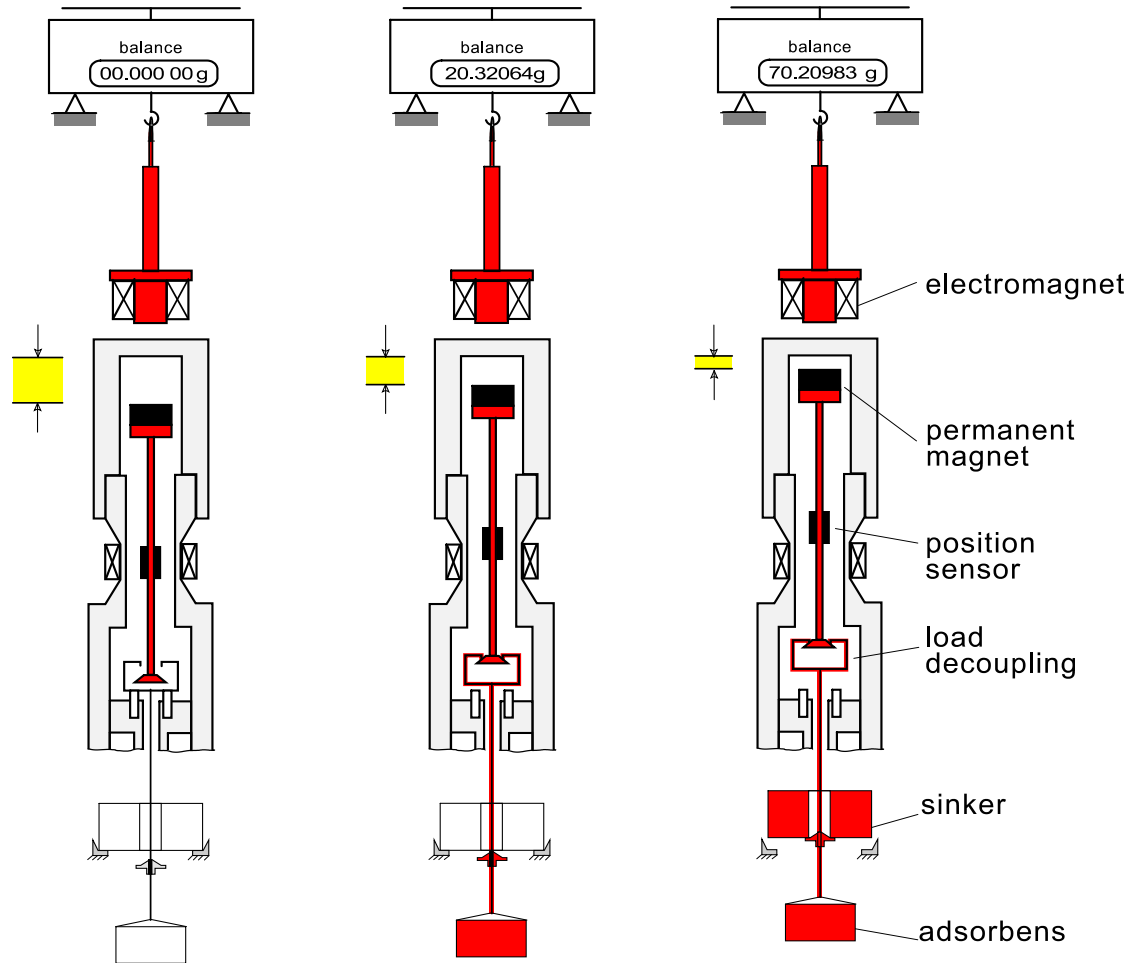
Kinetics of Coadsorption Experiments

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

↑ to balance connection

electromagnet

coupling housing

suspension magnet

thermostat

measuring load decoupling

pressure measurement

measuring fluid

measuring fluid

measuring cell

sample (adsorbent)

thermostat

measuring fluid

236.01°C temperature measurement

Sorption measurement (Rubotherm)

balance
00.000 00 g

balance
20.32064g

balance
70.20983 g

electromagnet

permanent magnet

position sensor

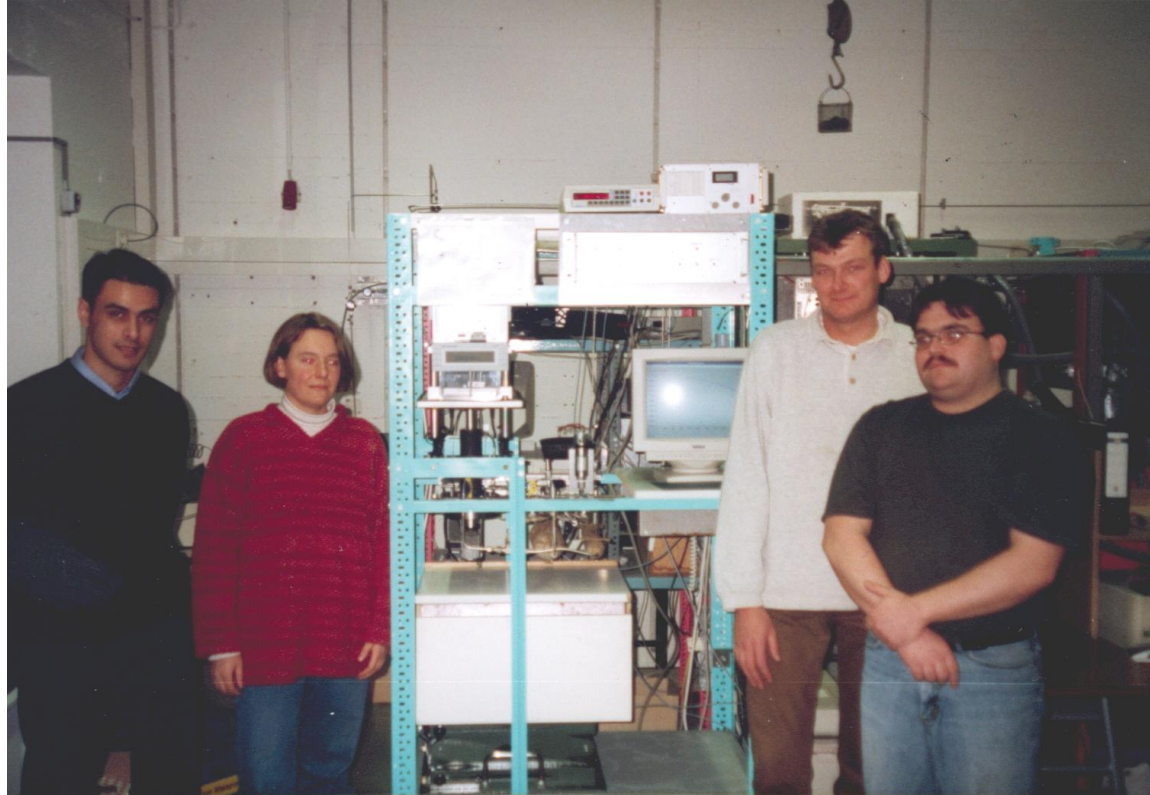load decoupling

sinker

adsorbens

zero point

(tare)

measuring point I
(sorption)

measuring point II
(density)

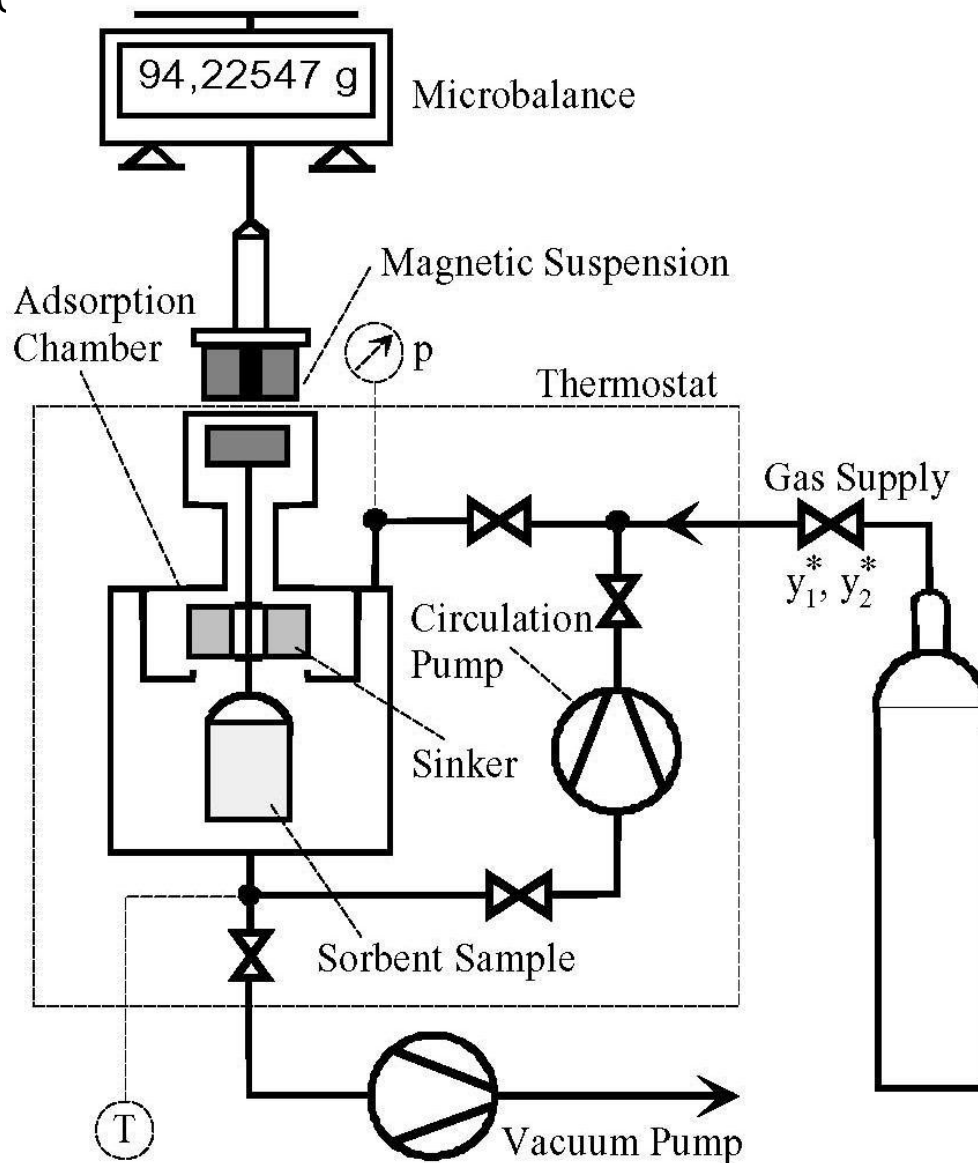**Simultaneous Sorption and Density Measurement (Rubotherm, Bochum, Germany)**

**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**

**Coadsorption Instrument
BEL-Rubotherm, IFT, 2001**

94,22547 g — Microbalance

Magnetic Suspension

Adsorption Chamber

p

Thermostat

Gas Supply

y_1^*, y_2^*

Circulation Pump

Sinker

Sorbent Sample

T

Vacuum Pump

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

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

$$\text{Total gas mass supplied} \quad m^* = m_1^* + m_2^* = m_1^a + m_2^a + m_1^f + m_2^f \tag{2}$$
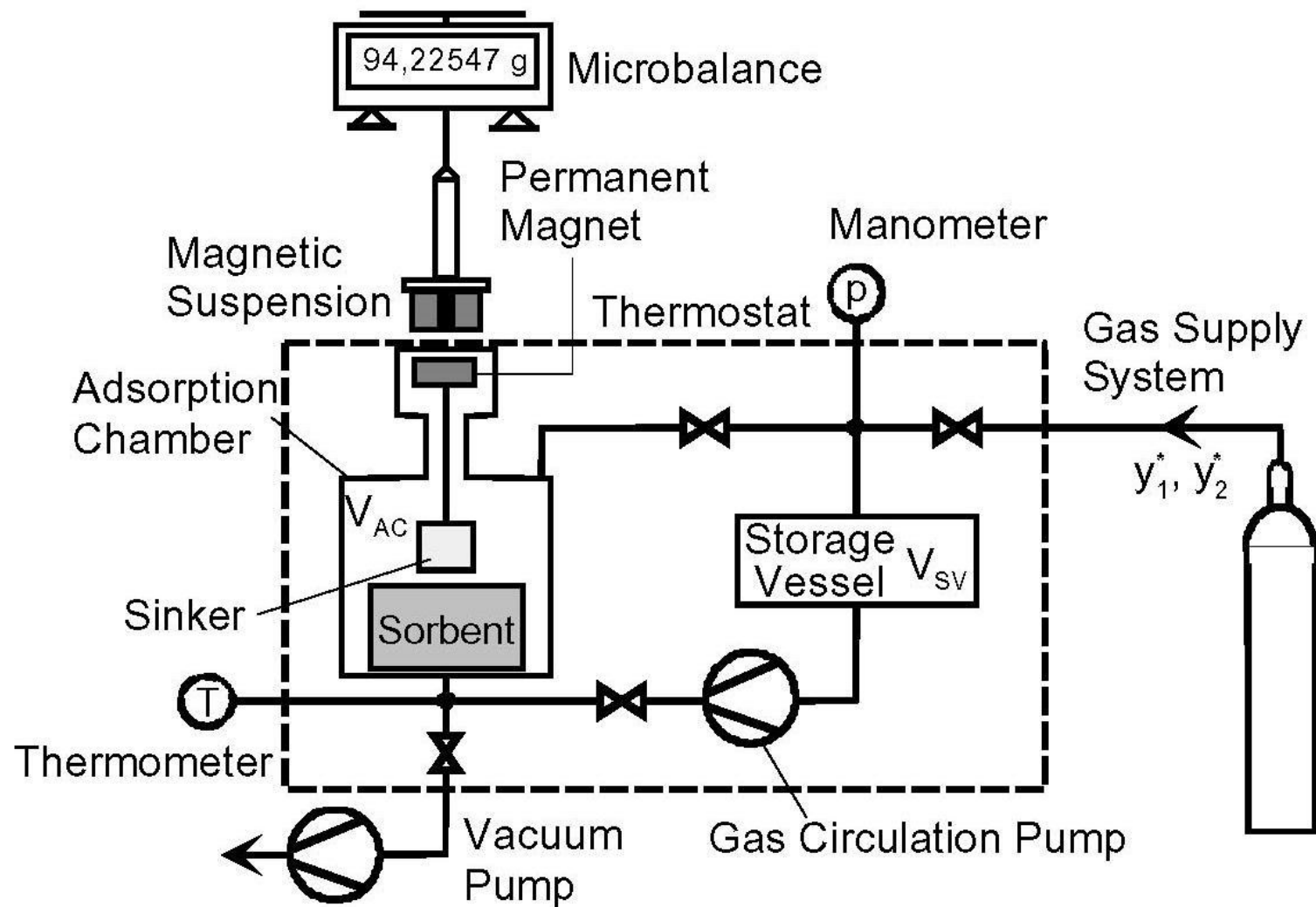
$$m^* = \Omega + \rho^f V^*$$

$$m_i^* = w_i^* m^* \tag{2A}$$

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

$$\frac{m_1^f}{M_1} + \frac{m_2^f}{M_2} = \frac{p \left(V^* - V^{as} \right)}{R\,T\,Z\left(p, T, w_i\right)} \tag{4}$$

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

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

DGMs / Theory

94,22547 g — Microbalance

Permanent Magnet

Manometer

Magnetic Suspension

Thermostat

Adsorption Chamber

Gas Supply System

y_1^*, y_2^*

V_{AC}

Storage Vessel V_{SV}

Sinker

Sorbent

T — Thermometer

Vacuum Pump

Gas Circulation Pump

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

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

EOS
$$m_i^* = \frac{y_i^* \, p^* \, V_{SV}}{R\,T\,Z^*}\,M_i \qquad Z = Z\left(p^*,T,y_i^*\right) \qquad (2)$$

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

$$\frac{\dfrac{m_1^f}{M_1} + \dfrac{m_2^f}{M_2} = \dfrac{p\left(V^* - V^{as}\right)}{R\,T\,Z\left(p,T,w_i\right)}}{w_i = \dfrac{m_i^f}{m_1^f + m_2^f} \qquad i = 1,2} \qquad (4)$$

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

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

DVMs / Theory

CH$_4$/N$_2$ (9/91) adsoption on AC Norit R1 at T=298K
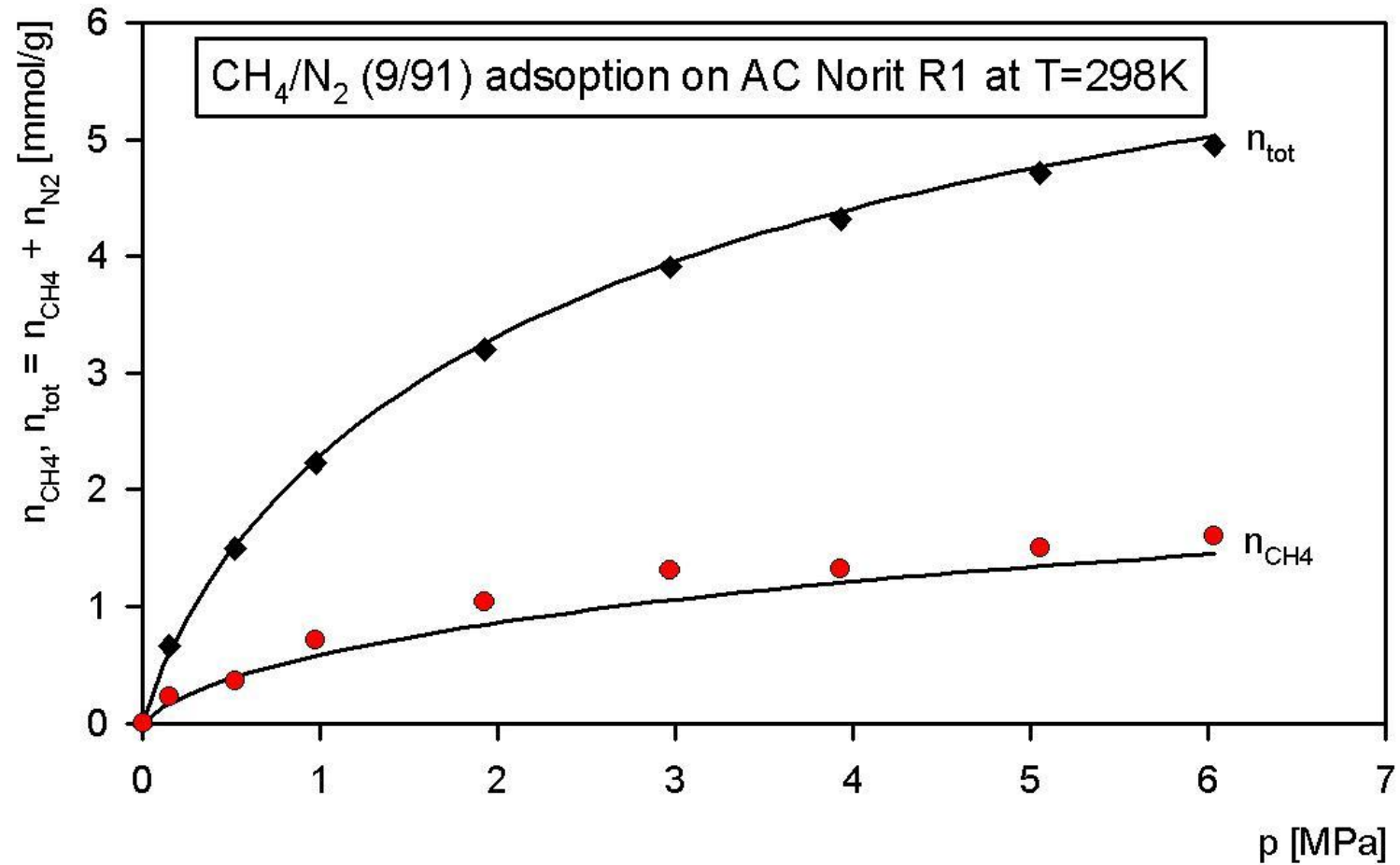
Prediction of binary adsorption data with the 2-sites Al

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

Gravimetrische Messung von Diffusionskoeffizienten (D)
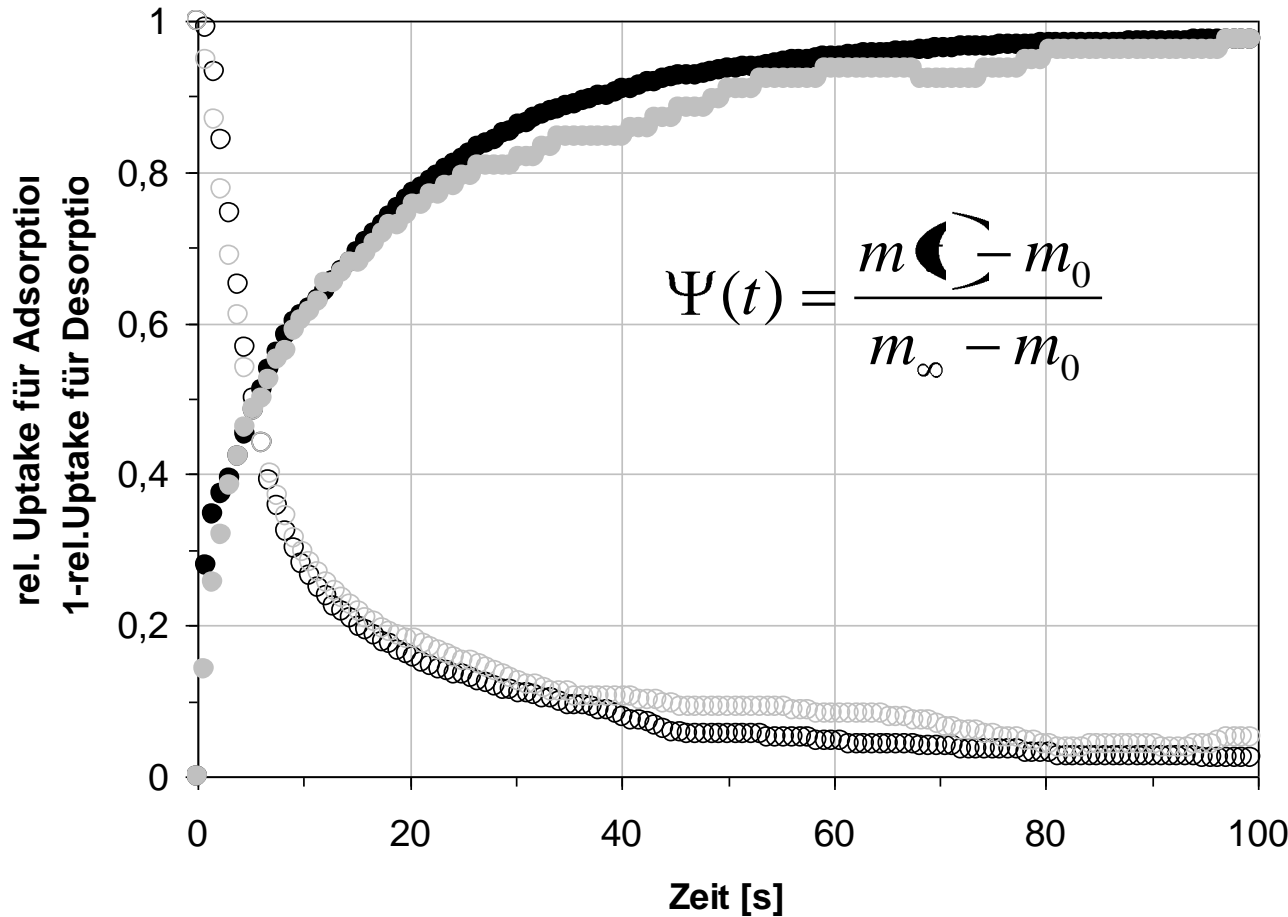

$$\Psi(t) = \frac{m(t) - m_0}{m_\infty - m_0}$$

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.

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

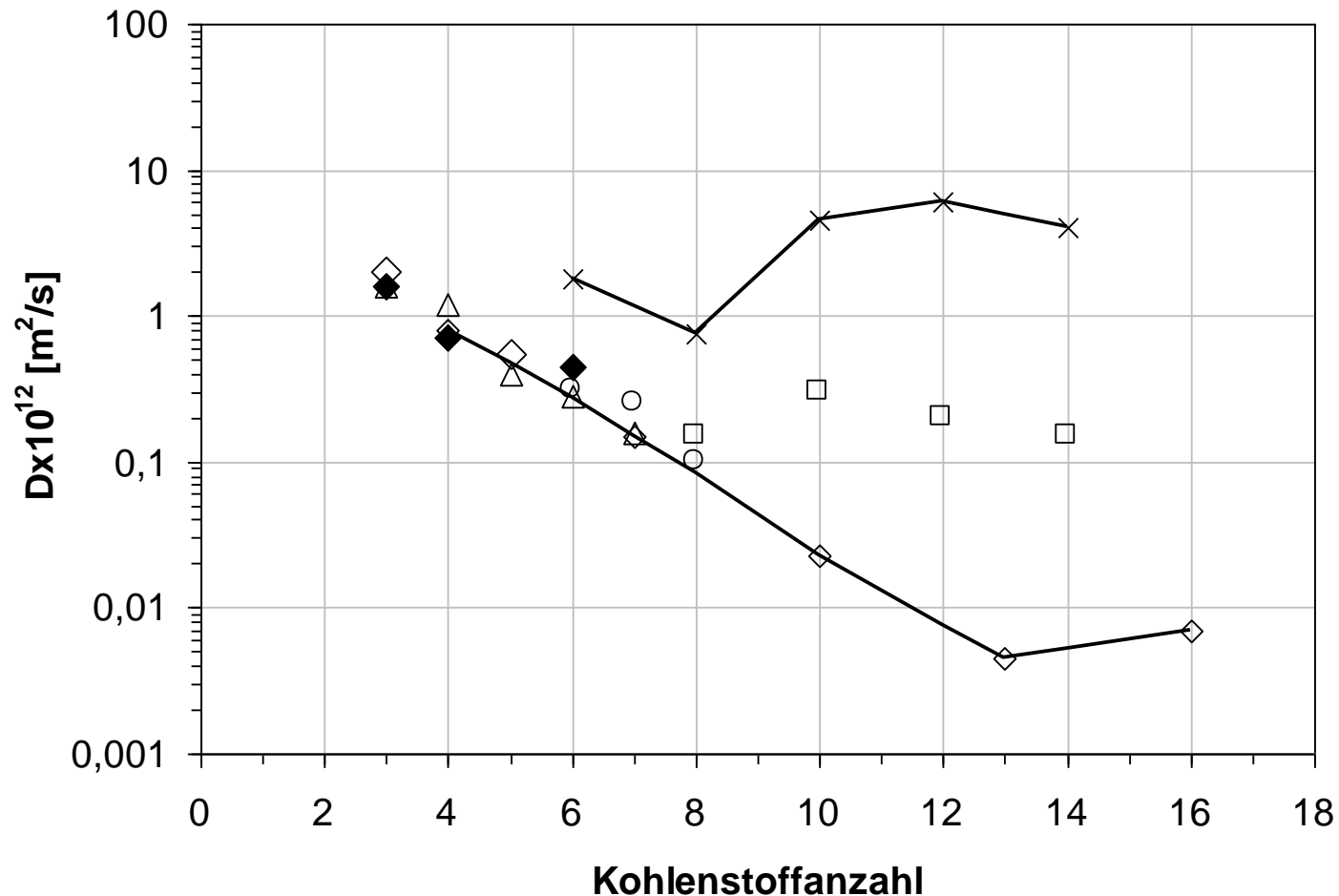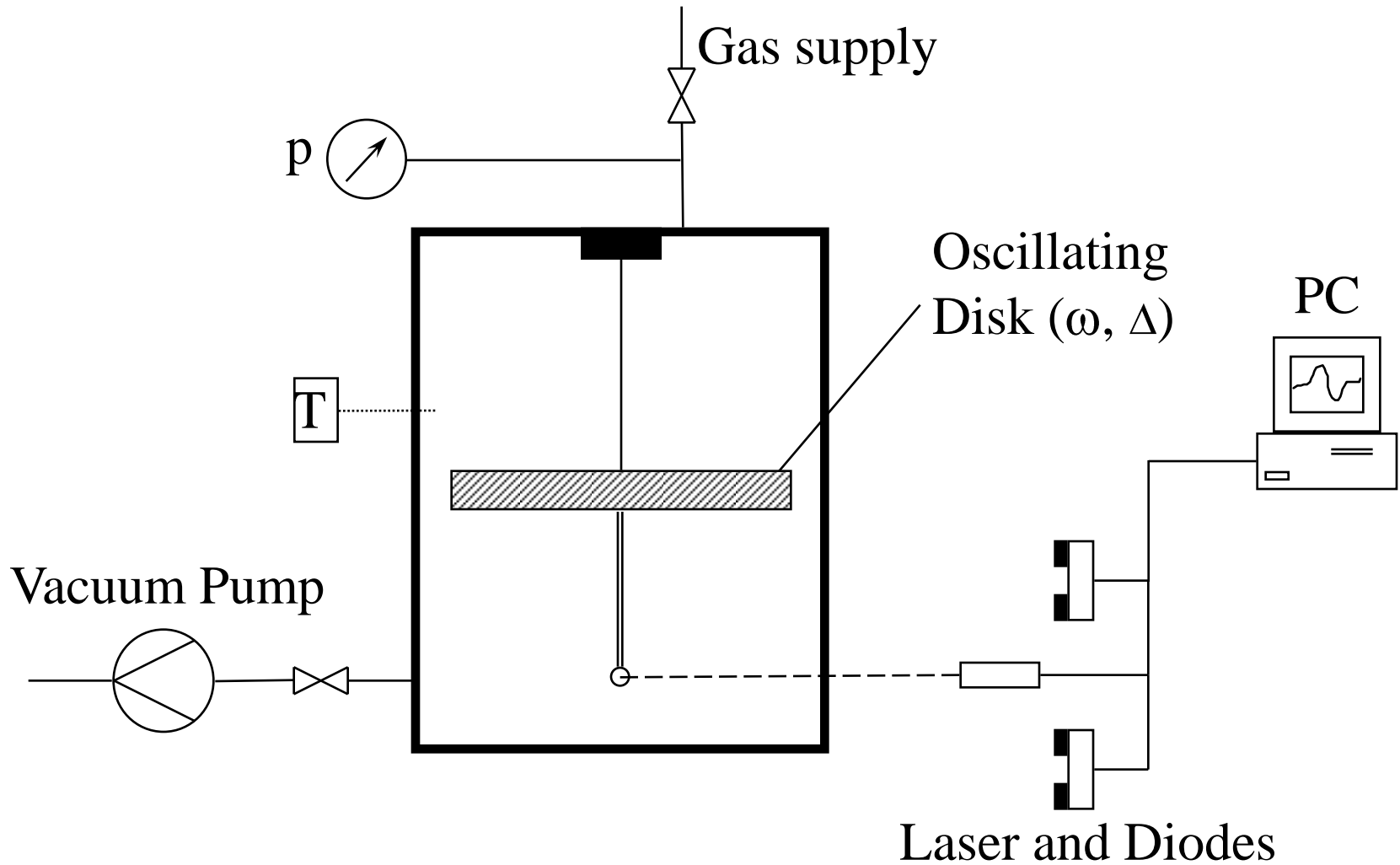# Gravimetrische Messung von Diffusionskoeffizienten

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

Gas supply

p

Oscillating
Disk (ω, Δ)
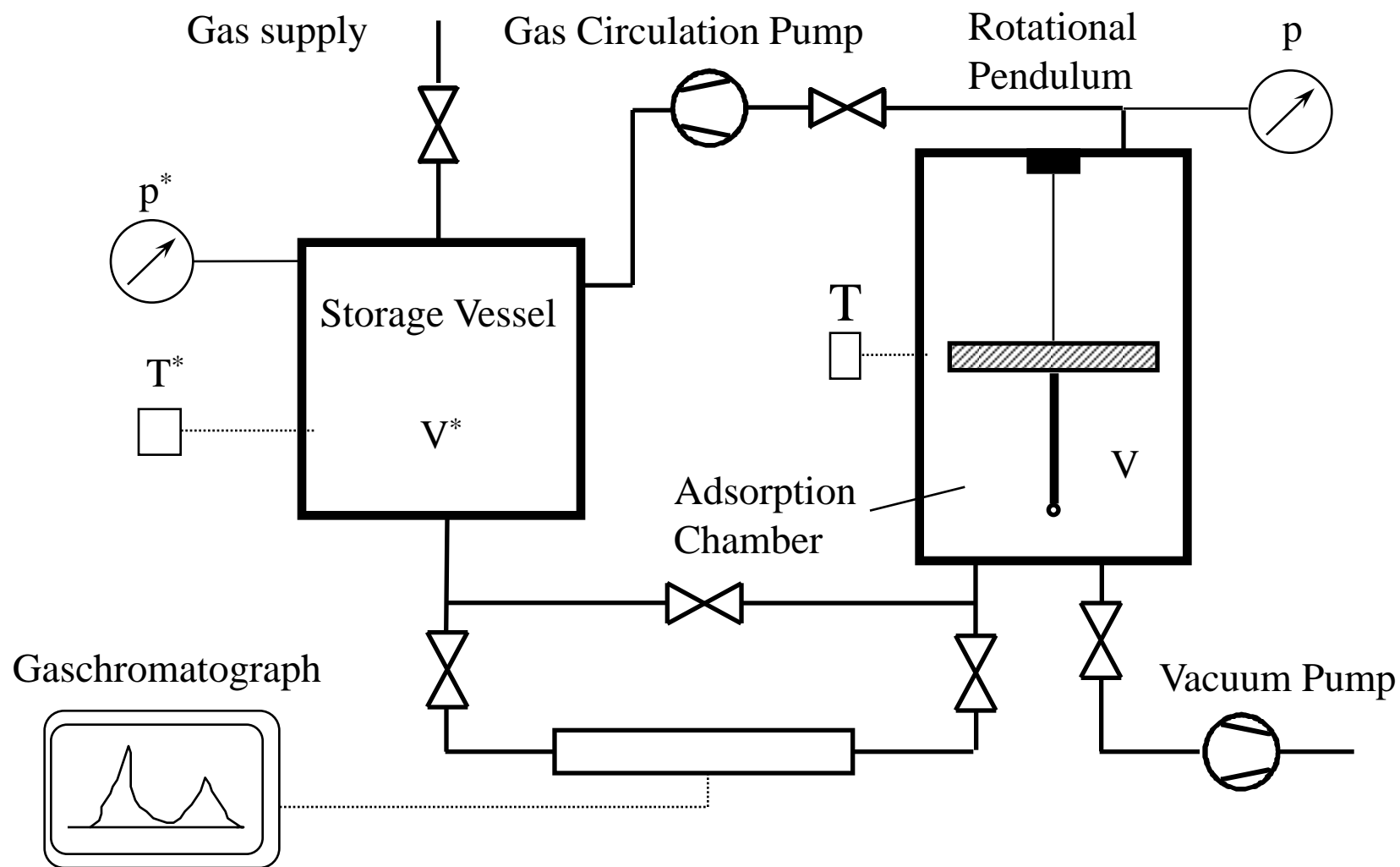
PC

T

Vacuum Pump

Laser and Diodes

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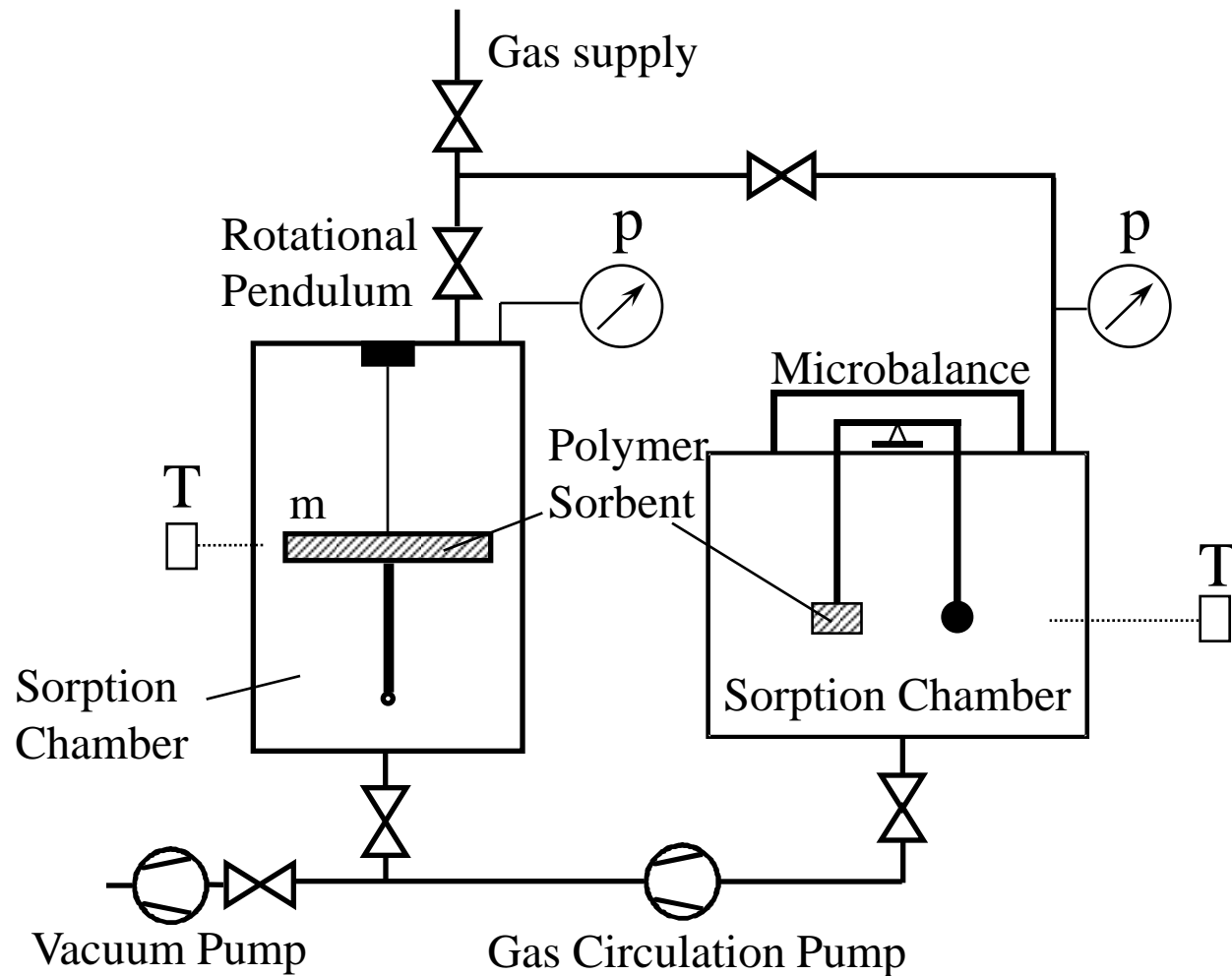of Gas Adsorption Equilibria**

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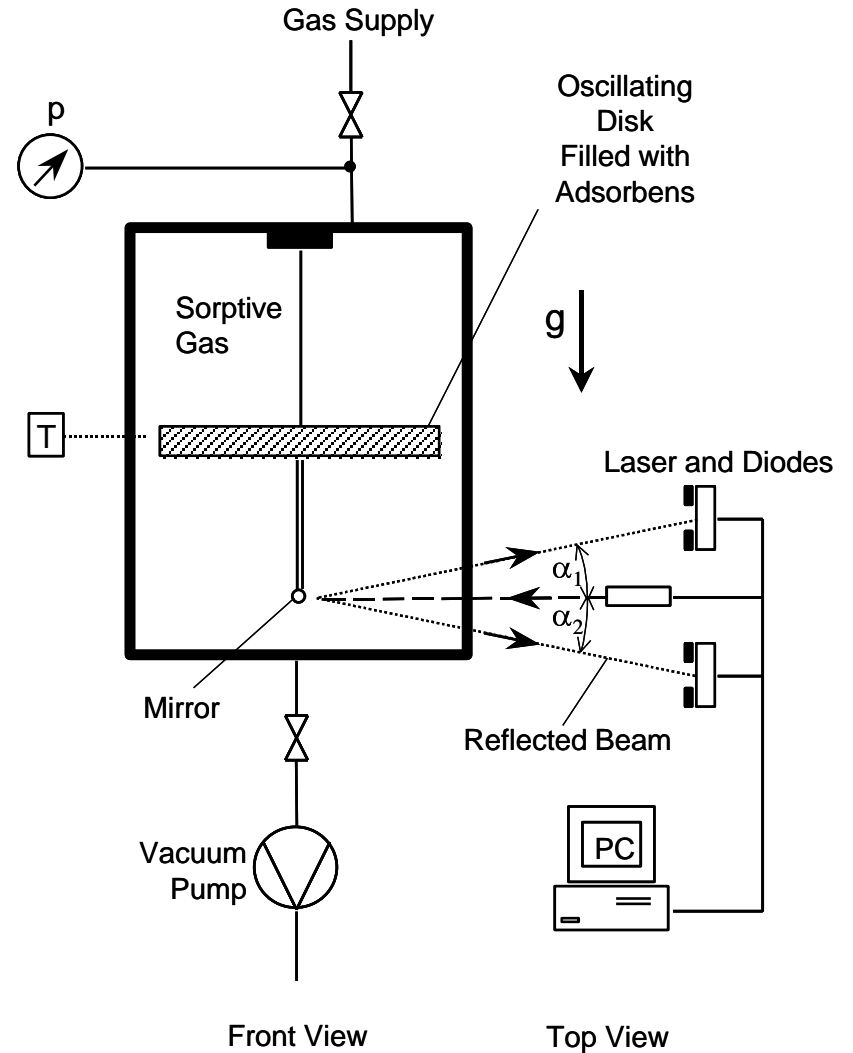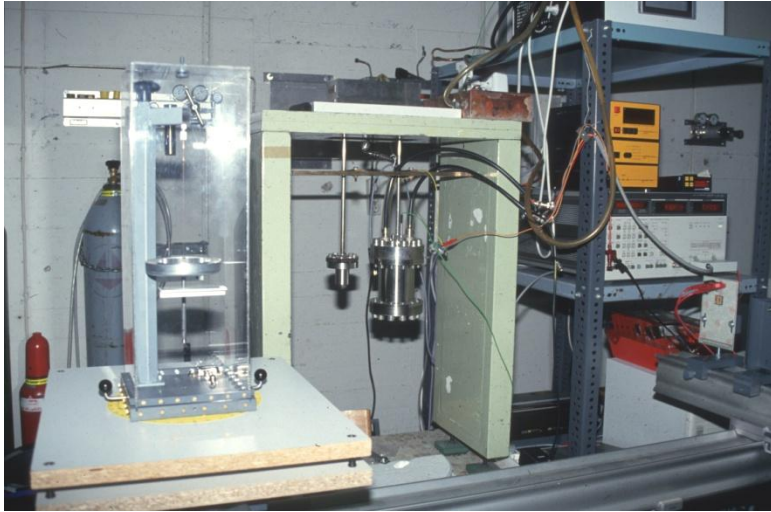

Experimental Setup for oscillometric measurements of gas adsorption equilibria using a rotational pendulum.

Gas supply

Gas Circulation Pump

Rotational
Pendulum

p

p^*

Storage Vessel

T^*

V^*

T

Adsorption
Chamber

V

Gaschromatograph

Vacuum Pump

Experimental Setup for oscillometric-volumetric measurements

Gas supply

Rotational
Pendulum

p

p

Microbalance

Polymer
Sorbent

T

m

T

Sorption
Chamber

Sorption Chamber

Vacuum Pump

Gas Circulation Pump

**Experimental Setup for oscillometric-gravimetric measurements**

Training instrument for
oscillometric,
volumetric,
gravimetric and
dielectric
gas adsorption measurements .
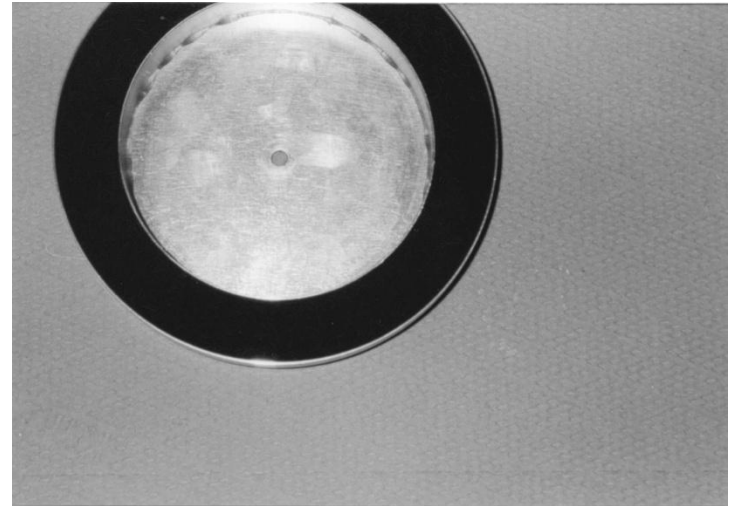
Ring-slit of pendulum
(R_i=3.75cm, R_a=5.5cm)
filled with activated carbon
powder (Norit R1 Extra).

Oscillometric – Gravimetric - Volumetric Measurements

Gas Supply

p^*

Storage Vessel

T

Pump

p

Sorbents

T

Microbalance

p

T

Sorbents

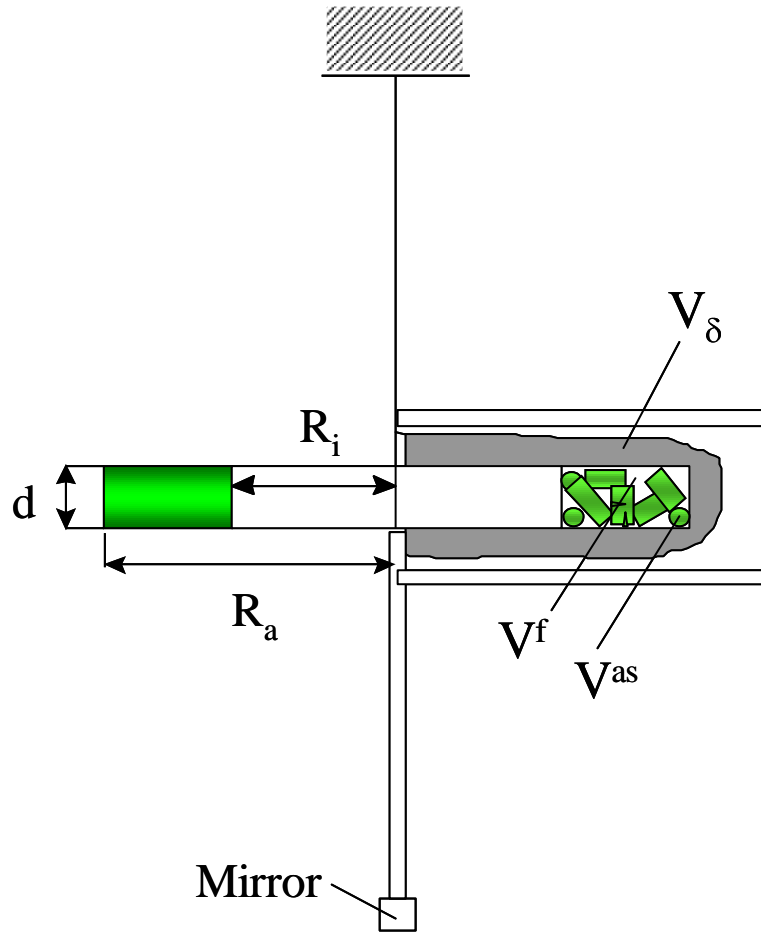ω Δ
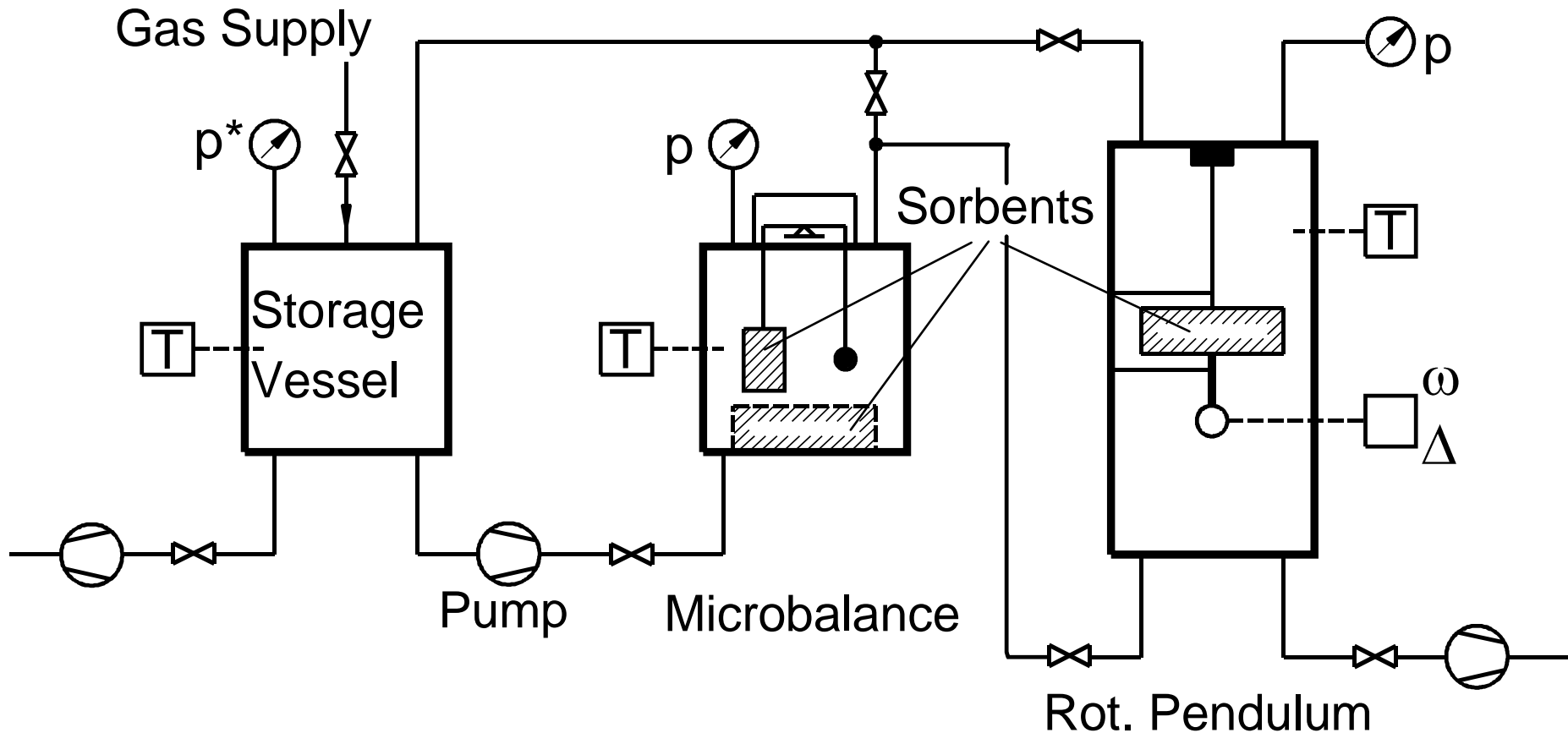
Rot. Pendulum

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.
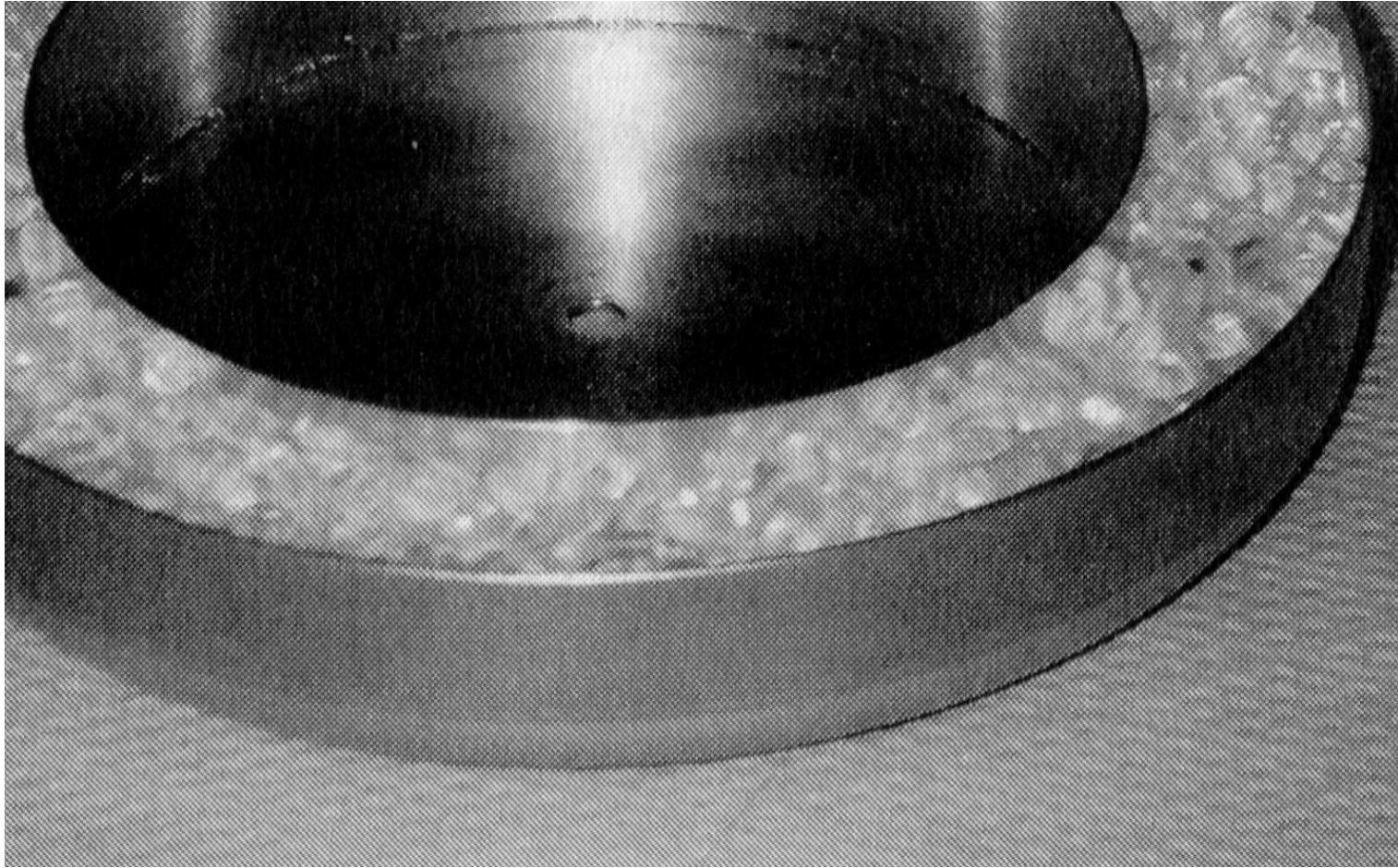
Rotational pendulum and ring slit filled with polycarbonate pellets

Theory

$$\text{(1)} \quad V^f + V^{as} = \frac{1}{\rho^f}\left[\Omega_{osc} + \Omega_{gra}\right] - V_\delta$$

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

$$V_\delta ... non-sorbing \quad pellets$$

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

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

V_δ

R_i

d

R_a

V^f

V^{as}

Mirror

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

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

Oscillometric Measurements of Gas Adsorption Equilibria. Theory*

Ideal Pendulum m^s, m $\qquad$ Physical Pendulum m^*, m^s, m

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

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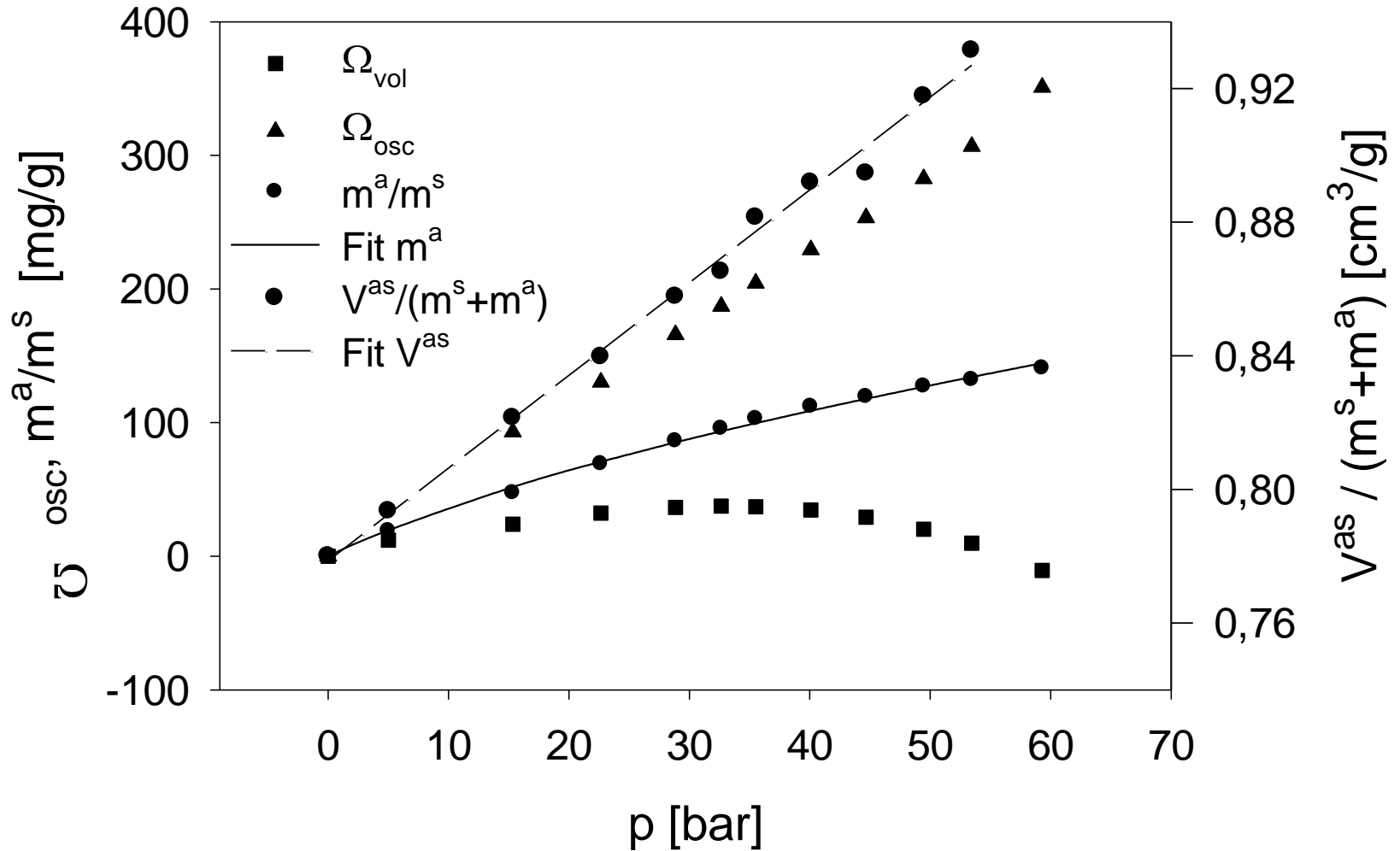
ω_0, Δ_0 ... pendulum and adsorbent m^*, m^s , vacuum

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.
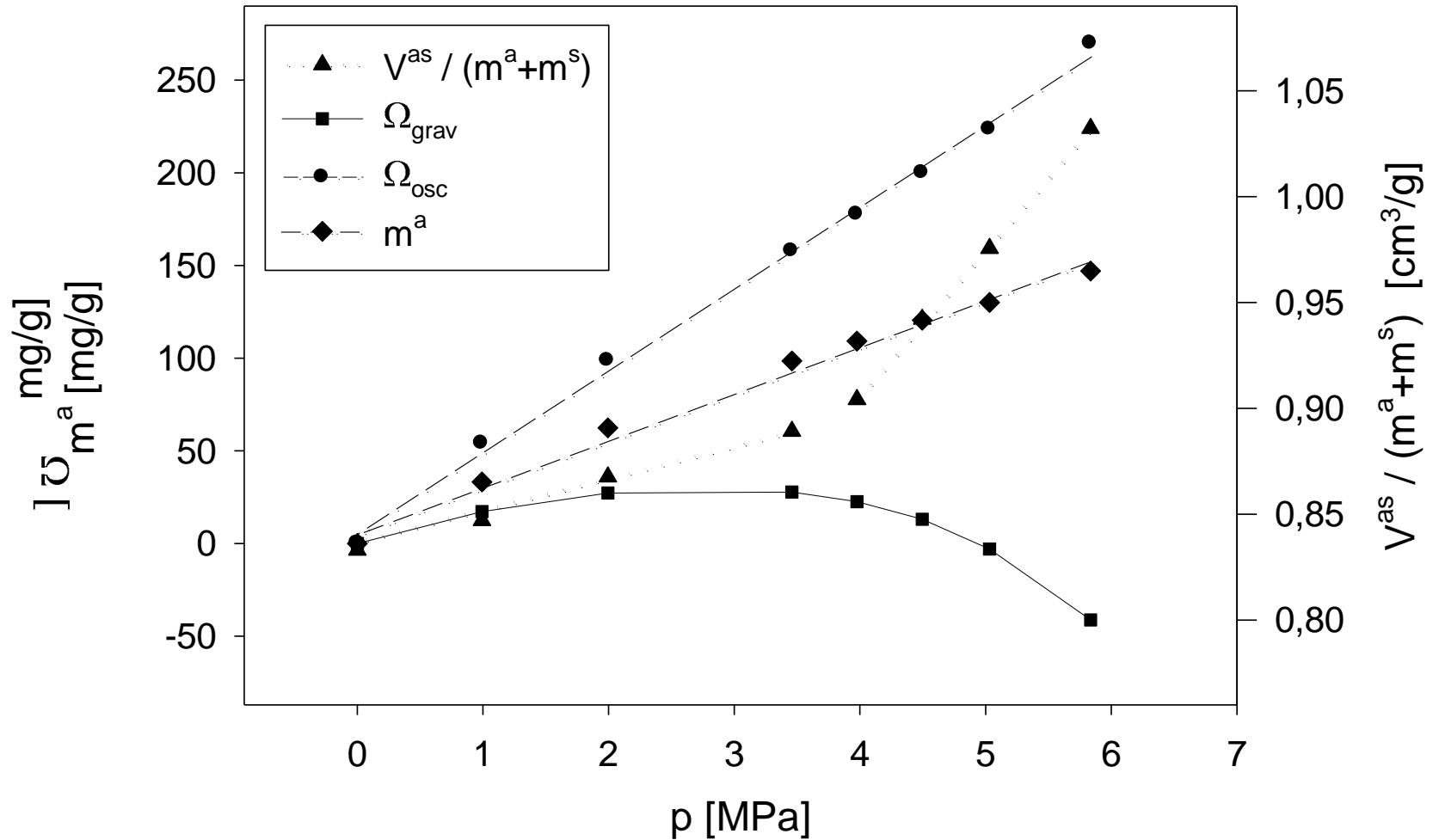
Swelling and sorption isotherm of polycarbonate/CO$_2$ at 293 K.

Swelling of volume (V^{as}) and sorption isotherm (m_a) of CO_2 on polymethylmethacrylate Makrolon 2400 (PMMA, Bayer) at 308 K.
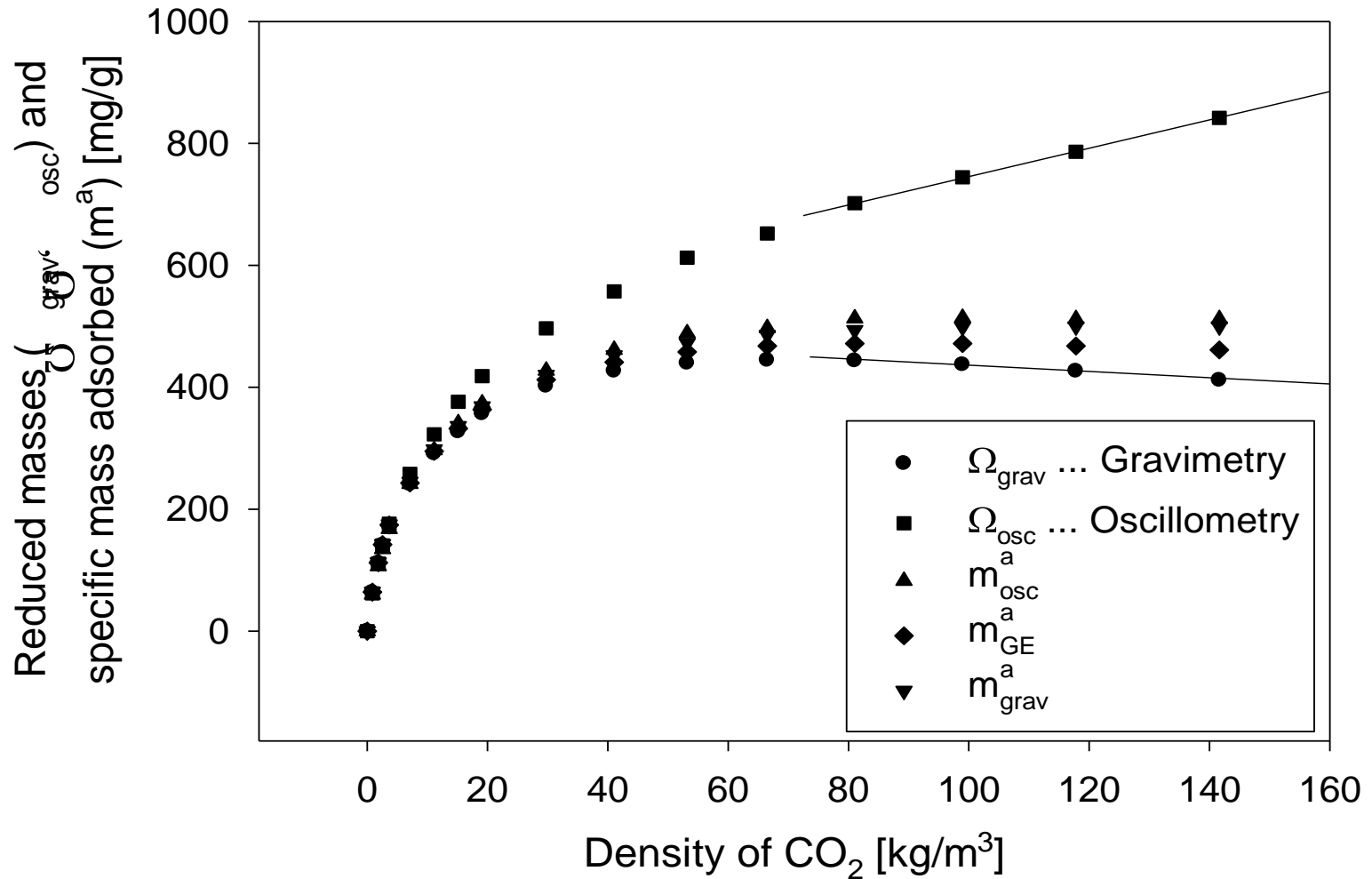
Reduced masses resulting from oscillometric and gravimetric adsorption measurements (Ω_{osc}, Ω_{grav}) of CO_2 on activated carbon (Norit R1 Extra) at 293 K. Gibbs excess masses (m^a_{GE}) and absolute masses adsorbed (m^a_{osc}, m^a_{grav} -data).

$V = 0.0035\ p + 0.86$

$V = 0.0022\ p + 0.86$

V 308 K
V 318 K
Fit
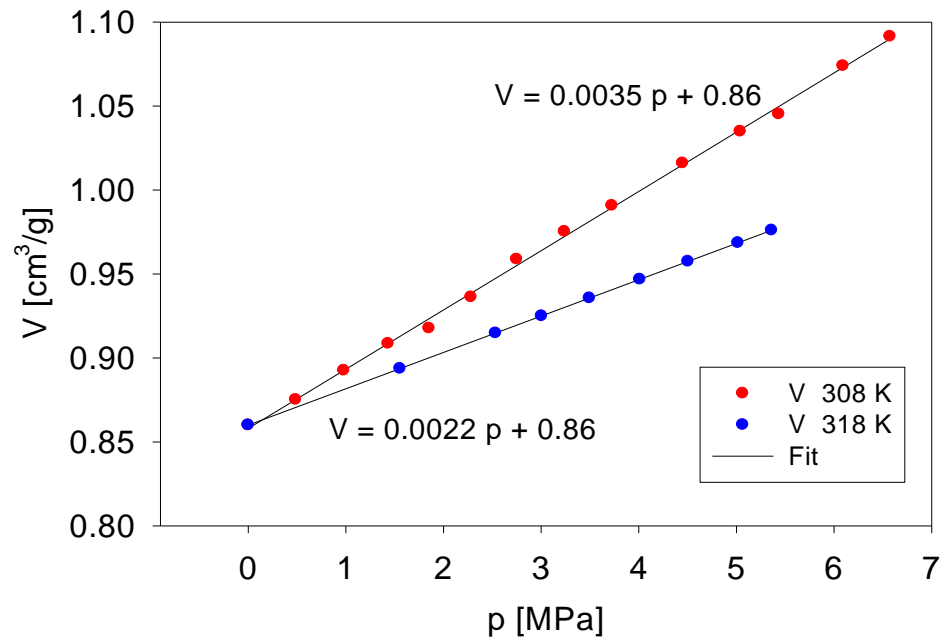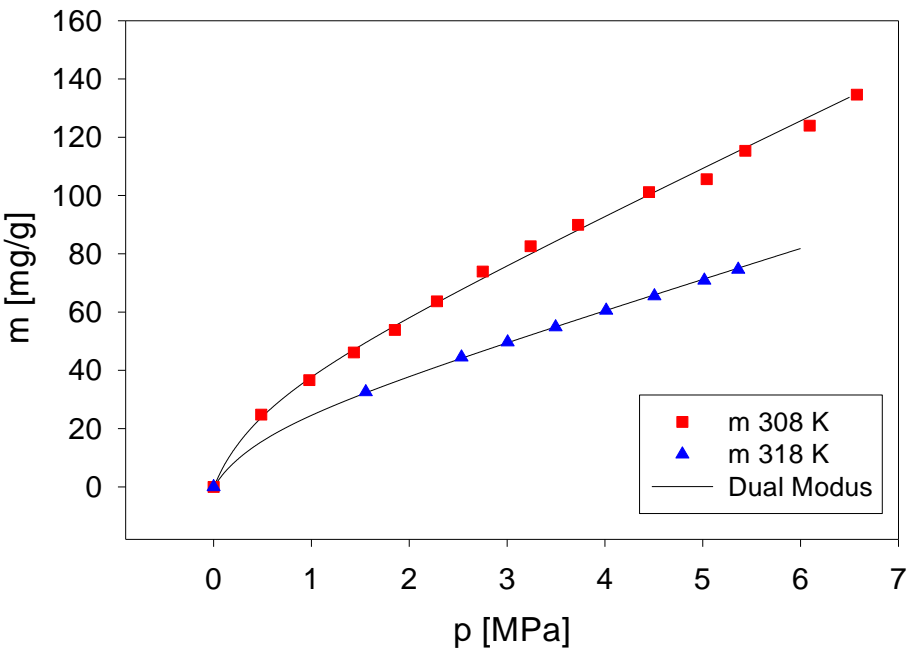
Swelling isotherms of polycarbonate/CO_2 at T = 308 K and T = 318 K.

m 308 K
m 318 K
Dual Modus

Sorption isotherms of polycarbonate/CO_2
at T = 308 K and T = 318 K.

Gas Supply   Gas Circulation Pump   Capacitor   p

p^*

Storage Vessel

V^*

T^*

Sorbent

Impedance
Analyzer

m^s

T

IA

Adsorption
Chamber

Gas Chromatograph

Vacuum Pump

$$V, M \quad m_{MG} = m^* - \left(V^* - V^{as} \right) \varrho^f(p,T), \quad V^{as} \cong V_{He}$$

$$DE \qquad \Omega_{DE} = \alpha(p,T) m_{MG}$$
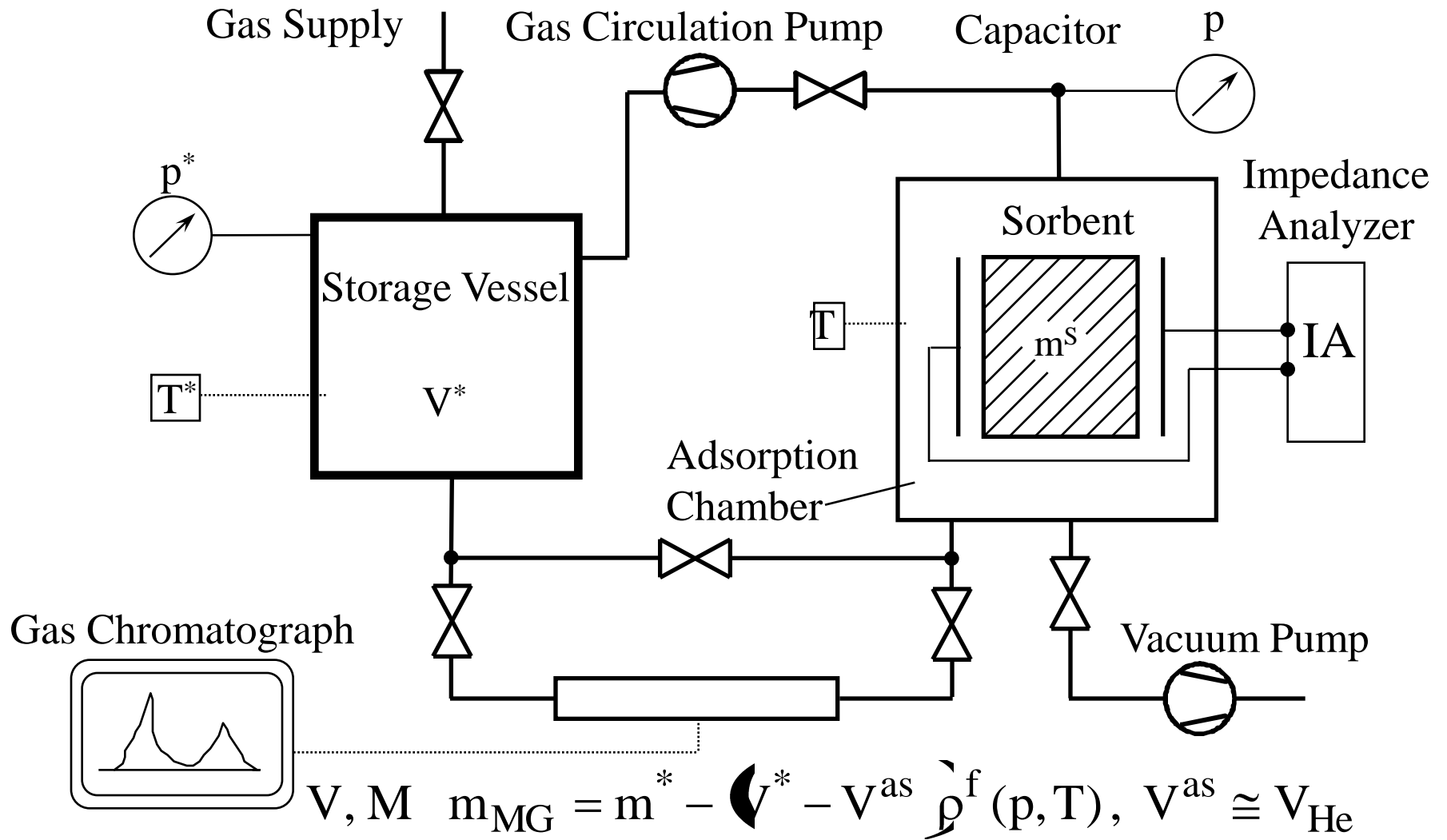
Experimental setup for volumetric-dielectric measurements
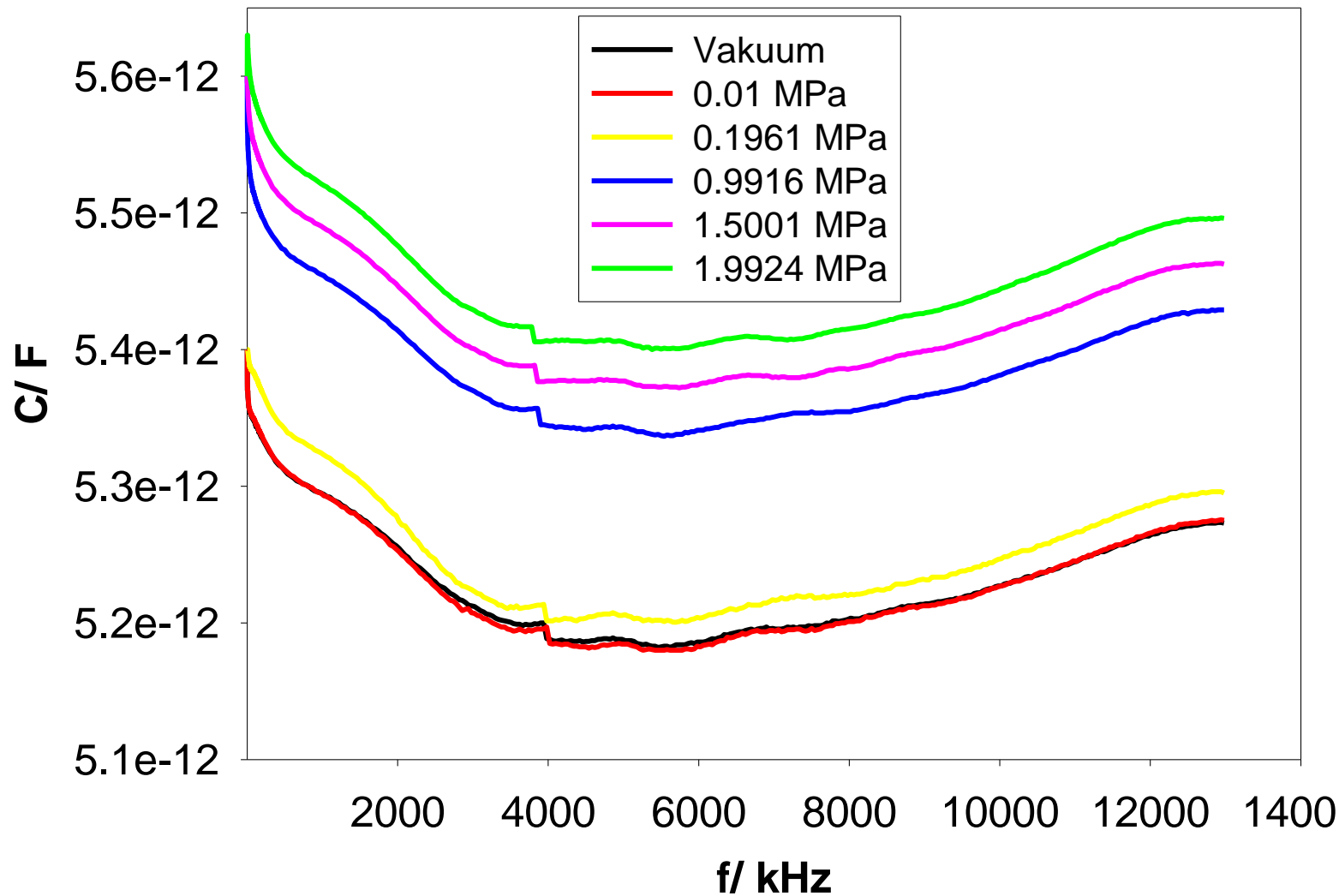
Impedance spectra of CO_2 on zeolite (DAY), T=298K
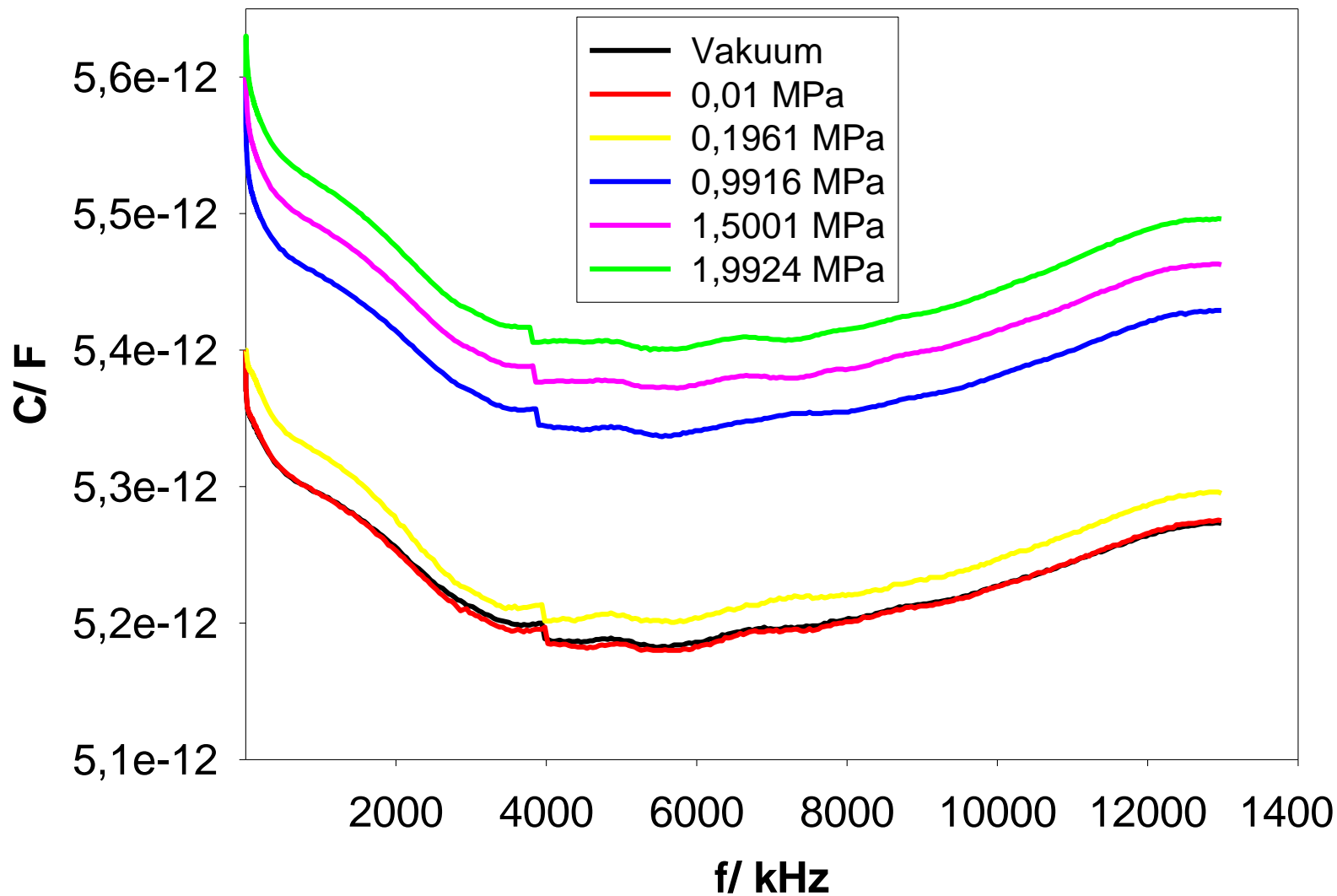
Impedance spectra of CO$_2$ on zeolite (DAY), T=298K
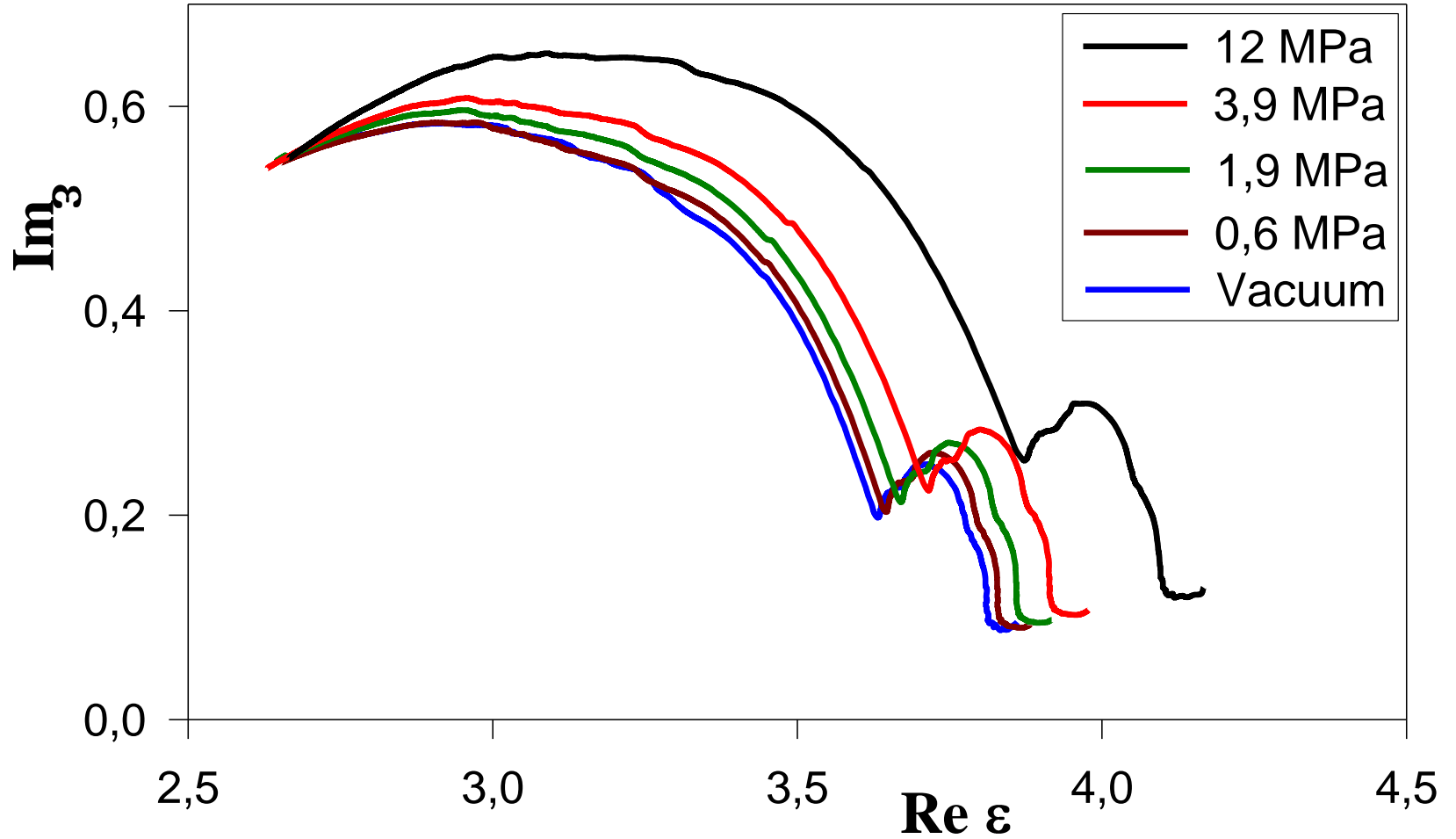
Cole-Cole-Plot for system CO / MS 13X, T=298K
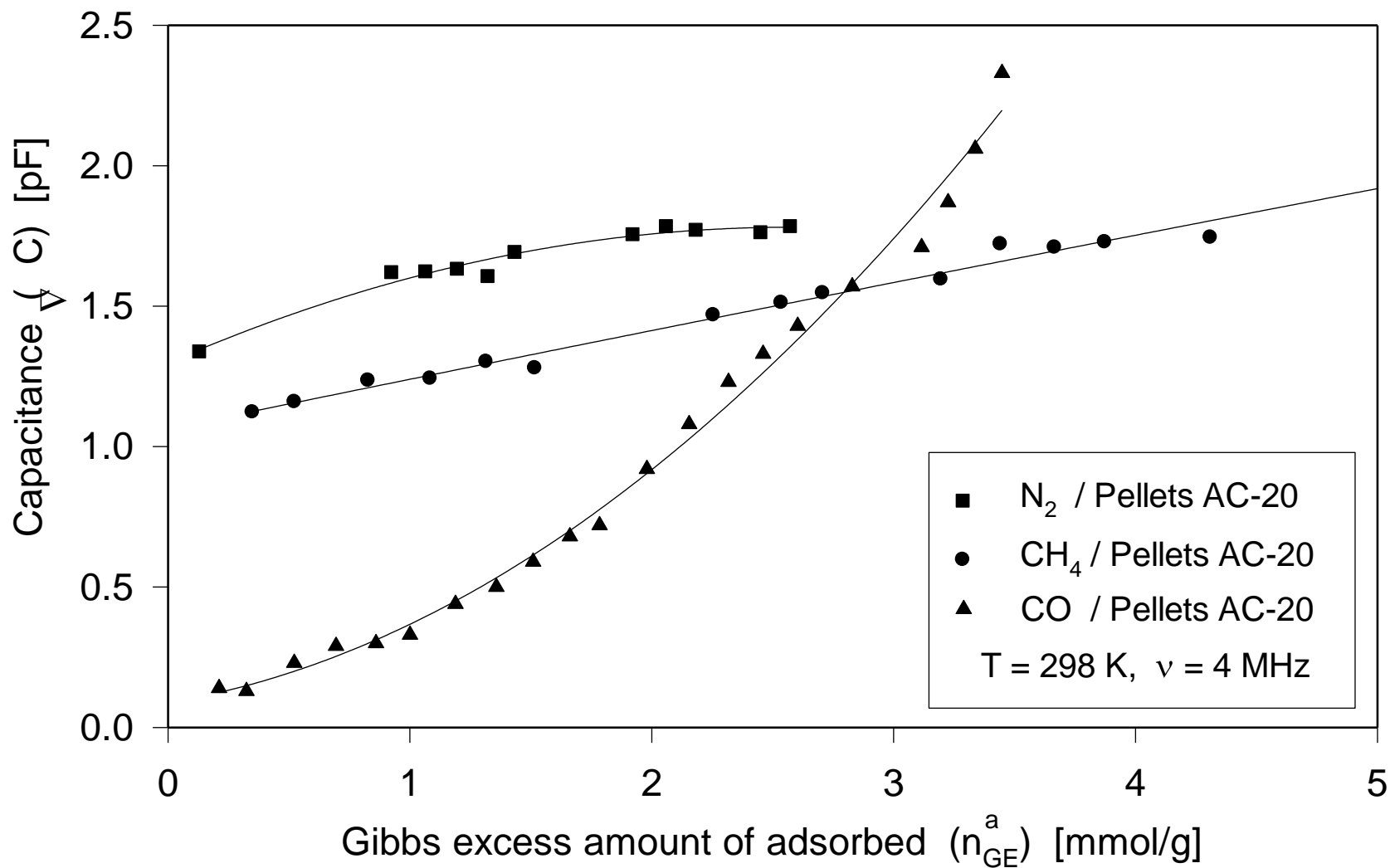
Change of the dielectric capacity (ΔC) of AC-20 pellets upon adsorption of gases (N$_2$, CH$_4$, CO) at 298 K, ν = 4MHz. Gas pressures (p $\leq$ 4MPa).
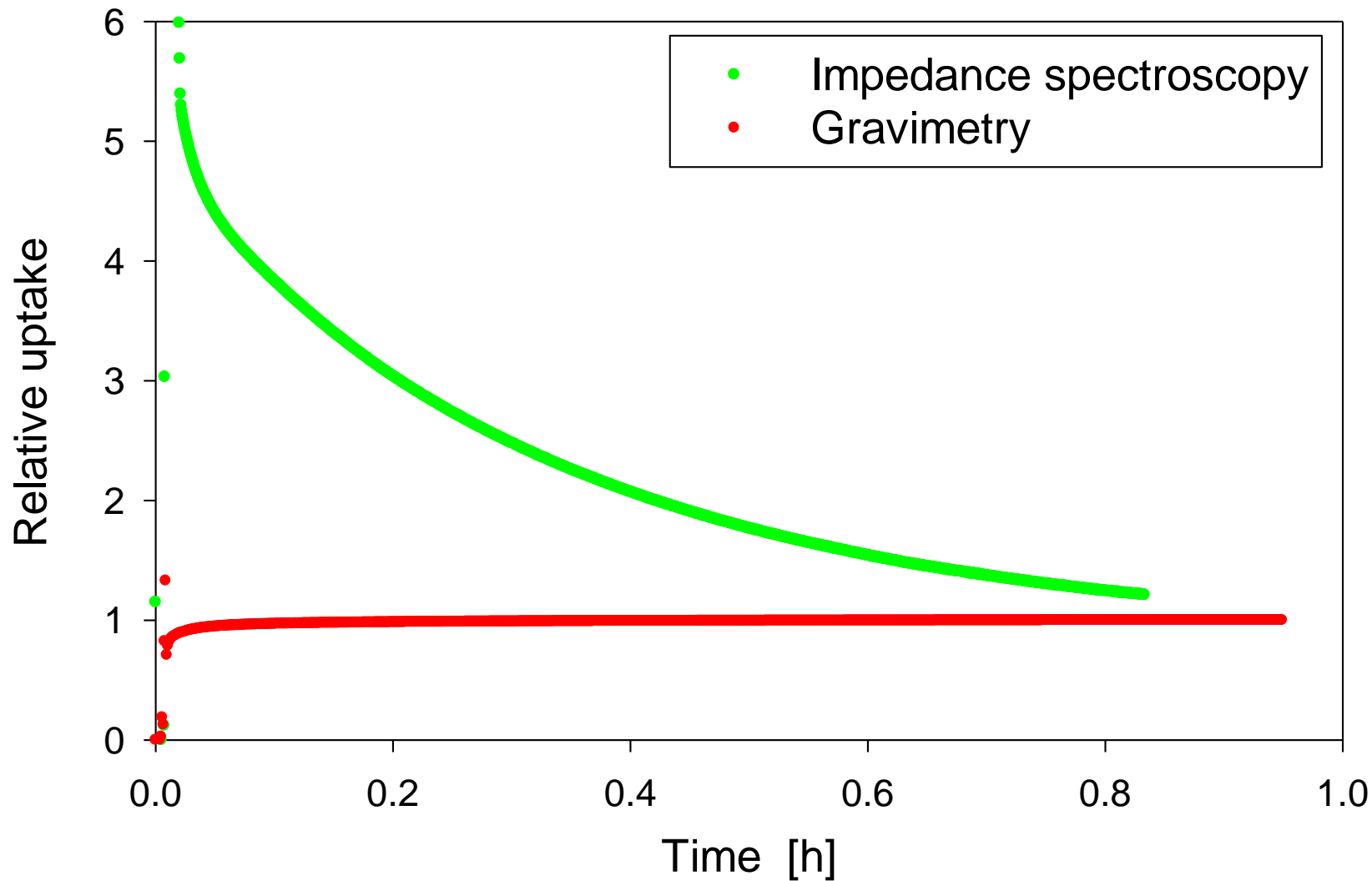
Uptake curves of H$_2$S on MS 13X, T=298K
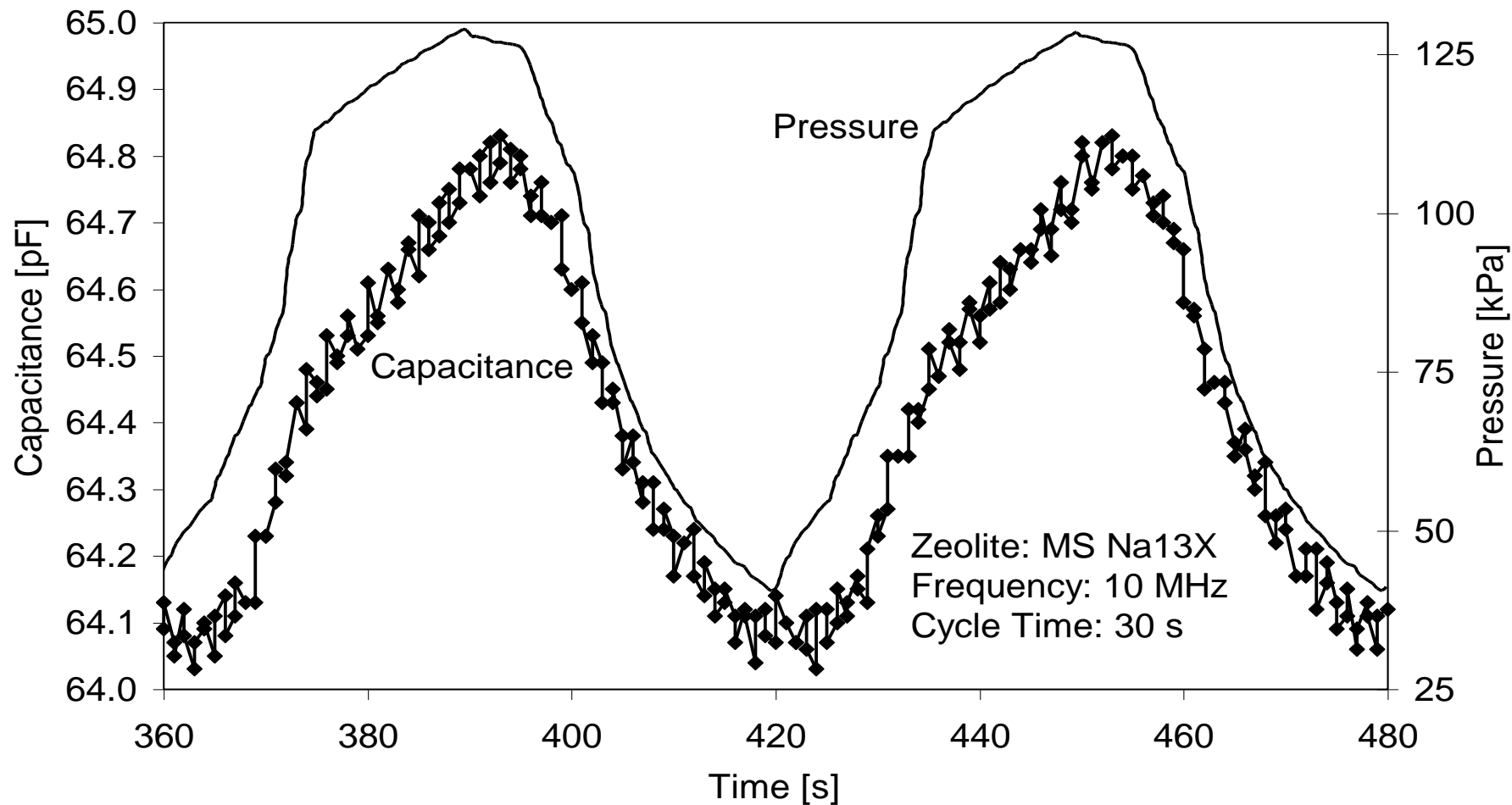
Combined manometric (p) and dielectric (ε_r) measurements of ad- and desorption of N_2 on MSNa13X (UOP) at 293K.
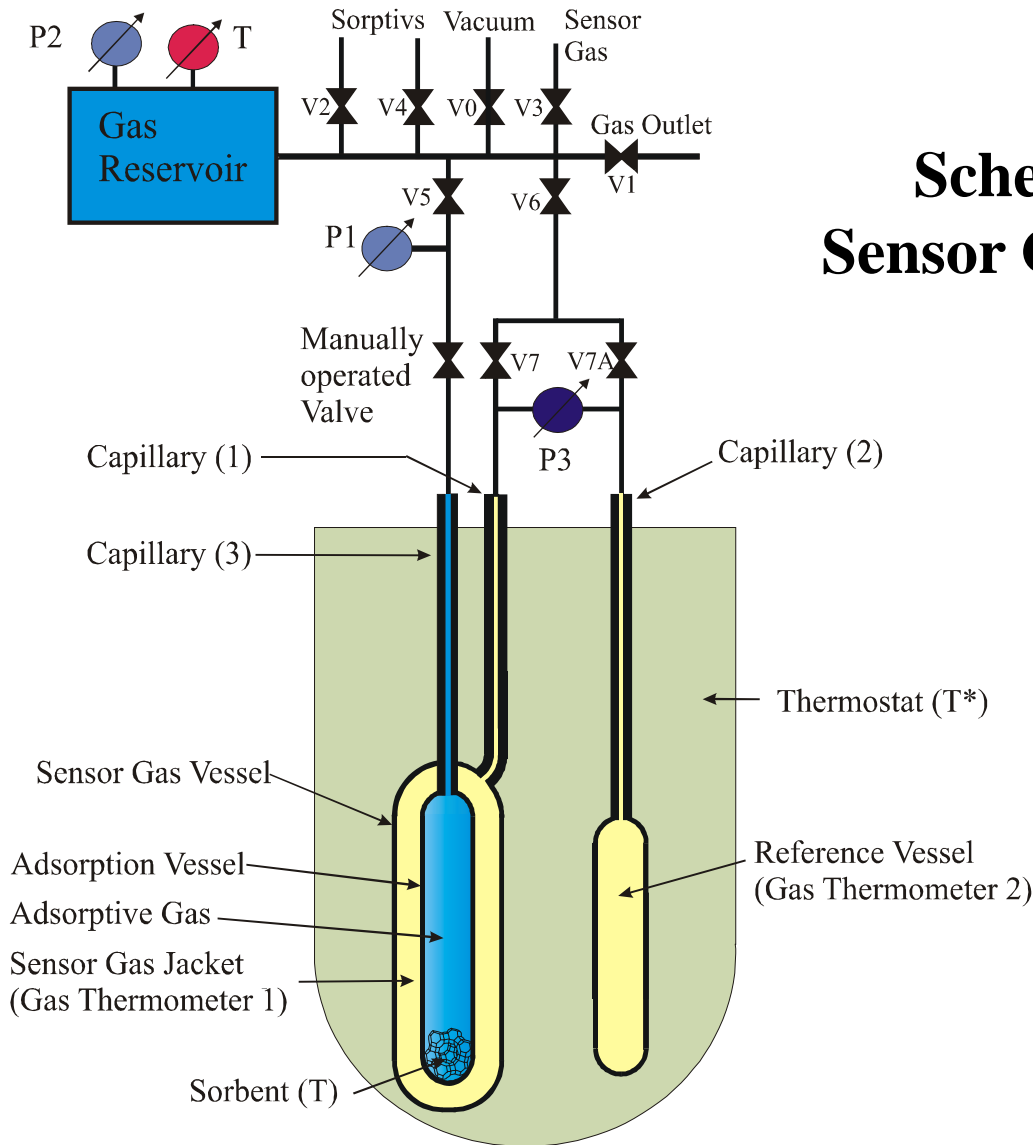
**Schematic diagram of a
Sensor Gas Calorimeter (SGC)**
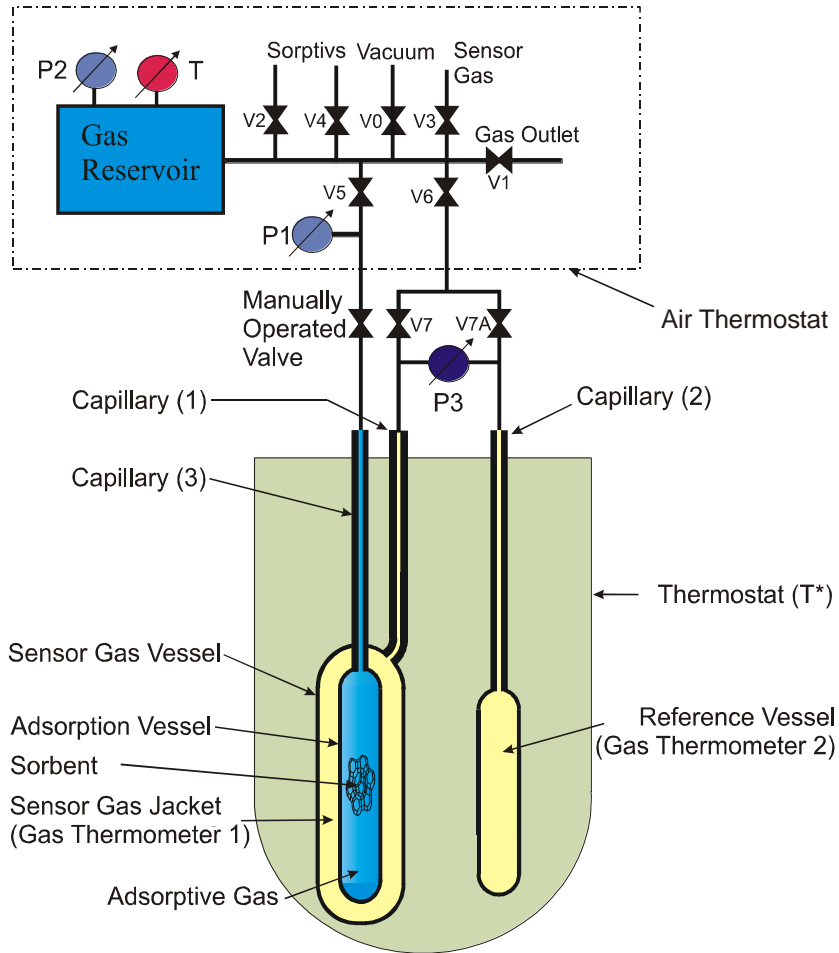
Schematic diagram of a sensor gas calorimeter (SGC)
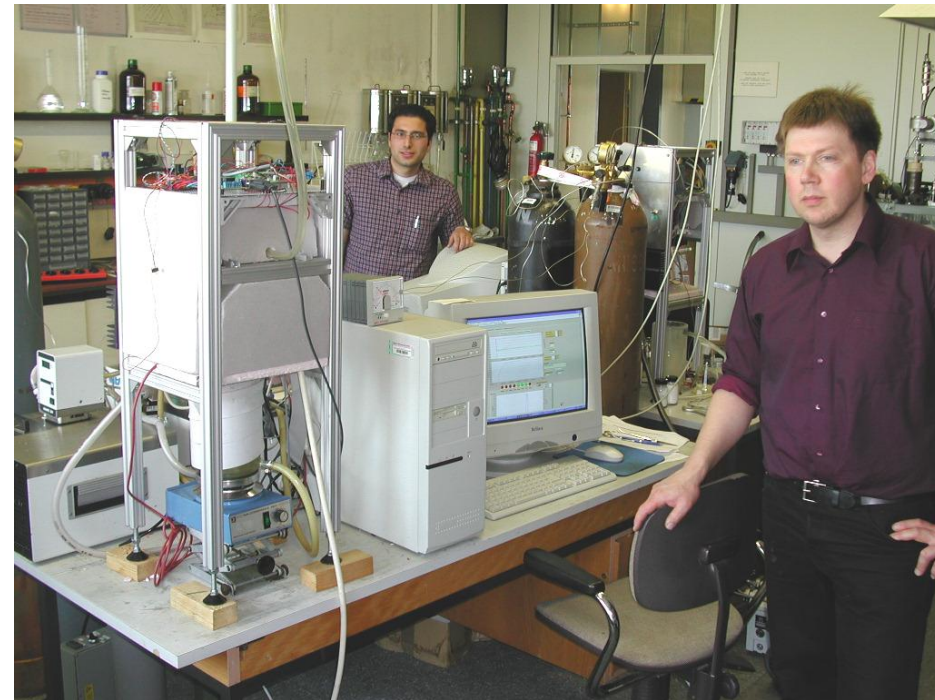
Sensor gas calorimeter (SGC) for simultaneous measurements of adsorption isotherms and enthalpies. © IFT, University of Siegen, 2003.
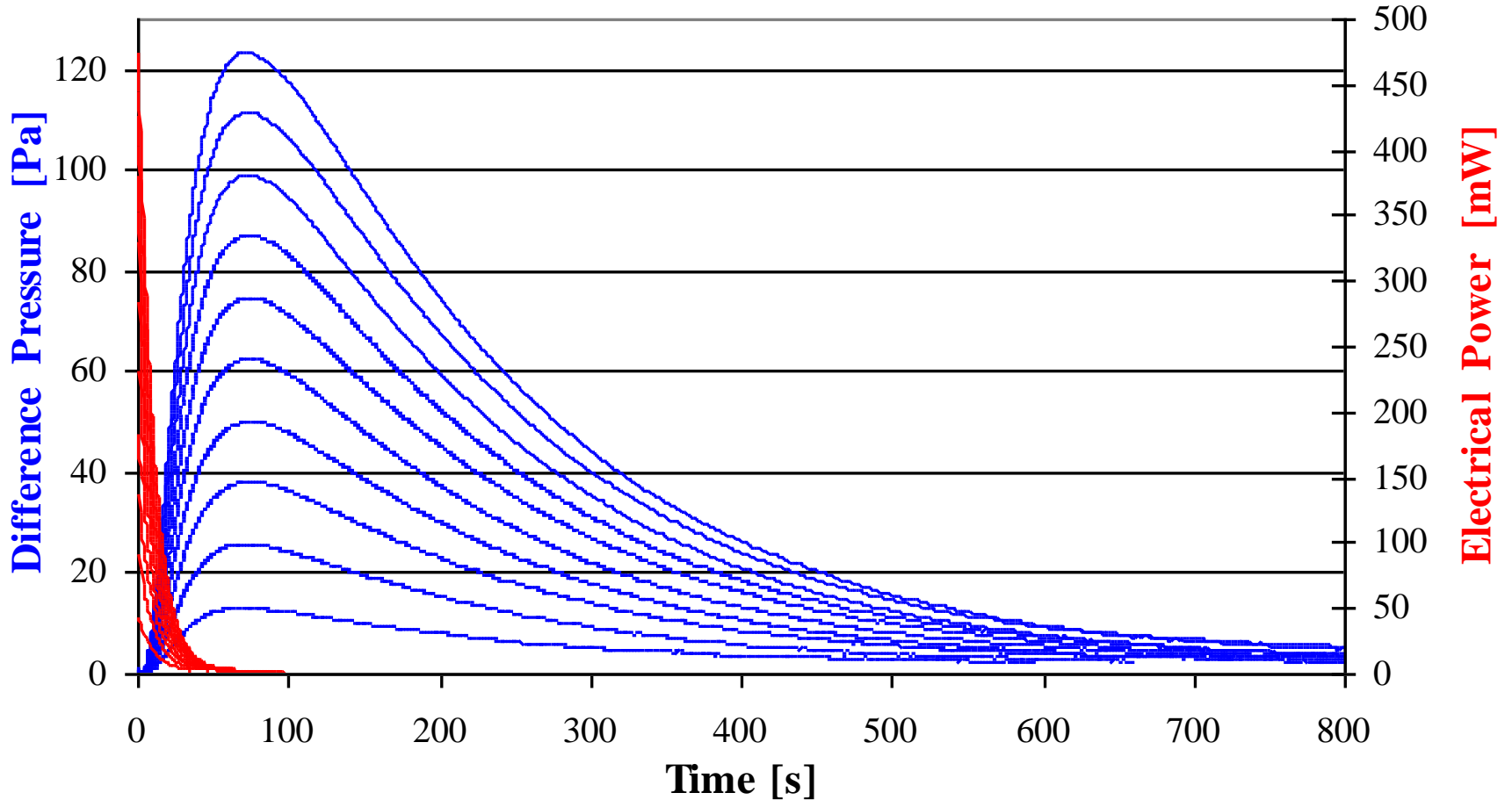
Calibration experiments in the SGC 0.5J to 5J
Sensor gas N$_2$ (1.6bar), T=298K, τ=10s
Ohm's heat release (red lines) $\rightarrow$ Pressure signal (blue lines)

Timescale for Electrical Power Axis [s]

Difference Pressure
Electrical Power

Difference Pressure $\Delta p(t)$ [Pa]

Electrical Power [mW]

Timescale for Difference Pressure Axis [s]
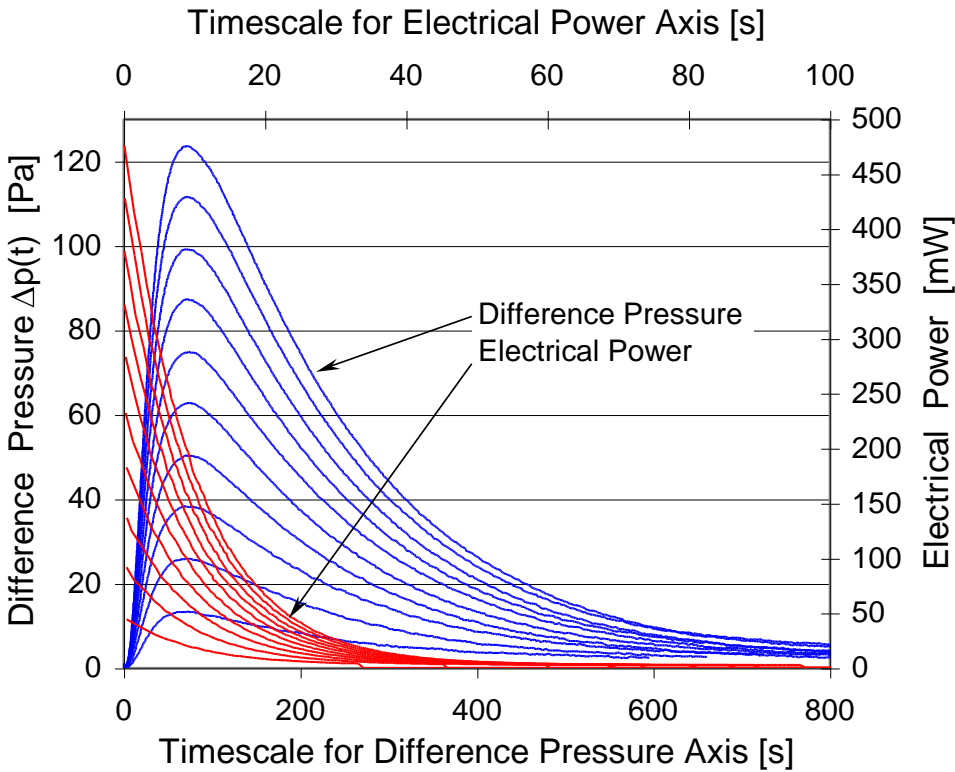
**Calibration experiments of the SGC.
Ohm's heat : Q= (0.5, 1.0 ... 5.0)J
Sensor gas: N$_2$, p*=0.15MPa,
T*=298K**

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

$$A \equiv A^* + 0.525 \text{ kPas} = 6.211\frac{\text{kPas}}{\text{J}} \cdot Q$$

$$R^2 = 0.9993$$

Reduced Peakarea A* [kPa s]

Ohm's Heat Q [J]
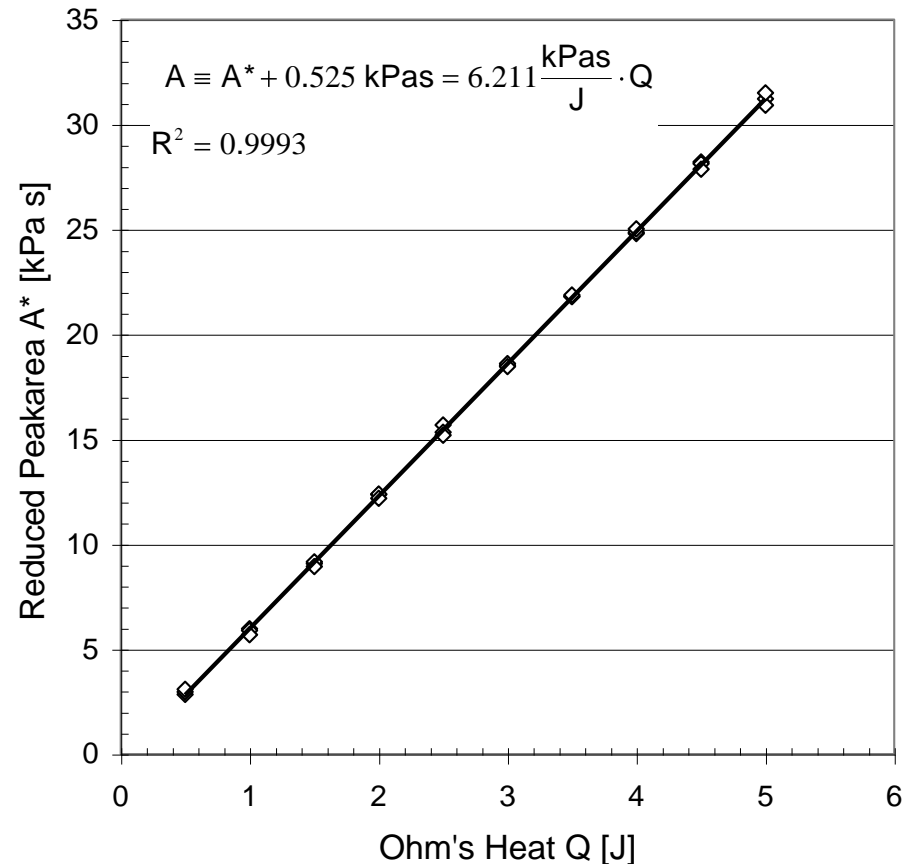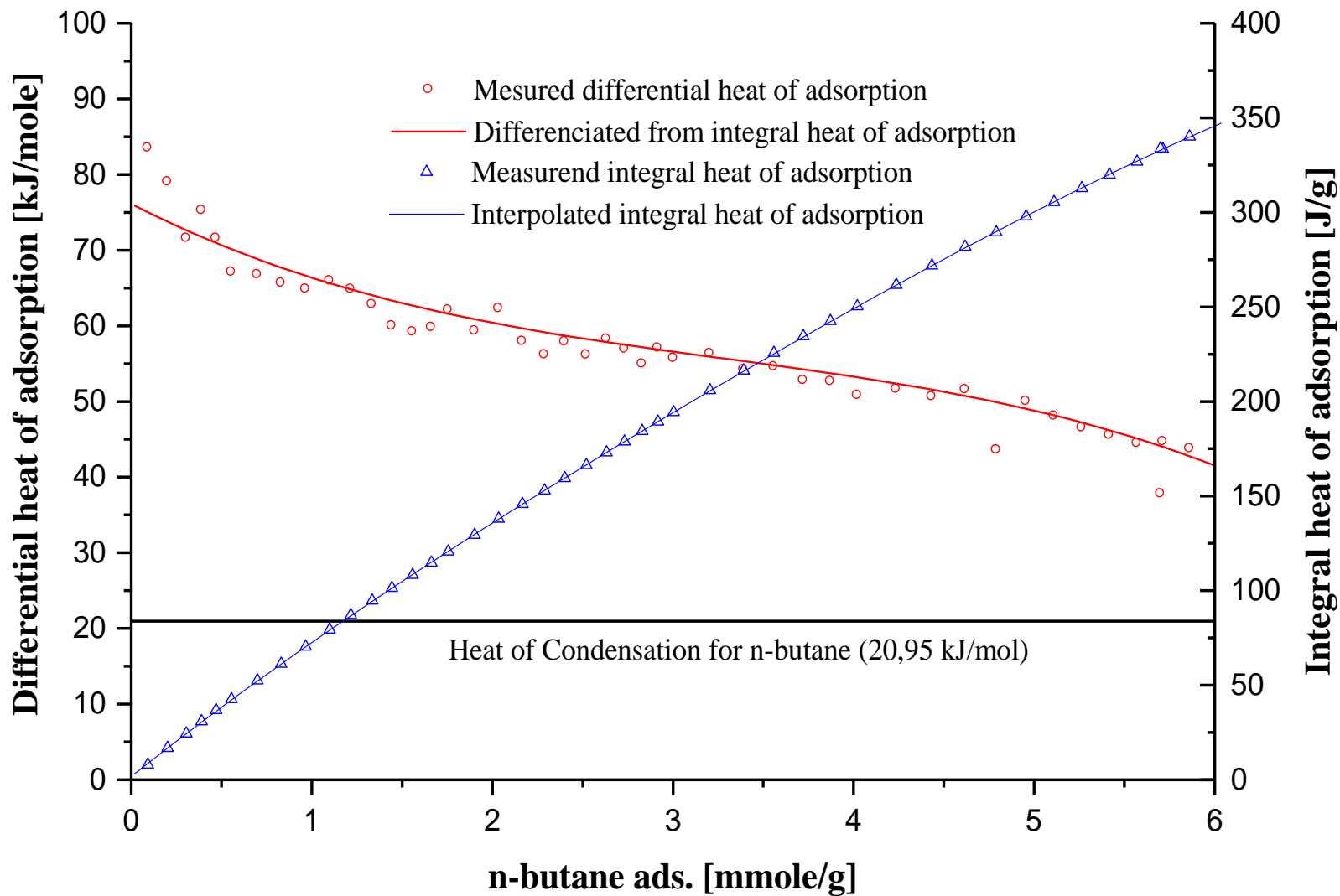
Differential and integral heat of adsorption for activated carbon AC BAX 1500 / n-butane (C₄H₁₀) at 298K
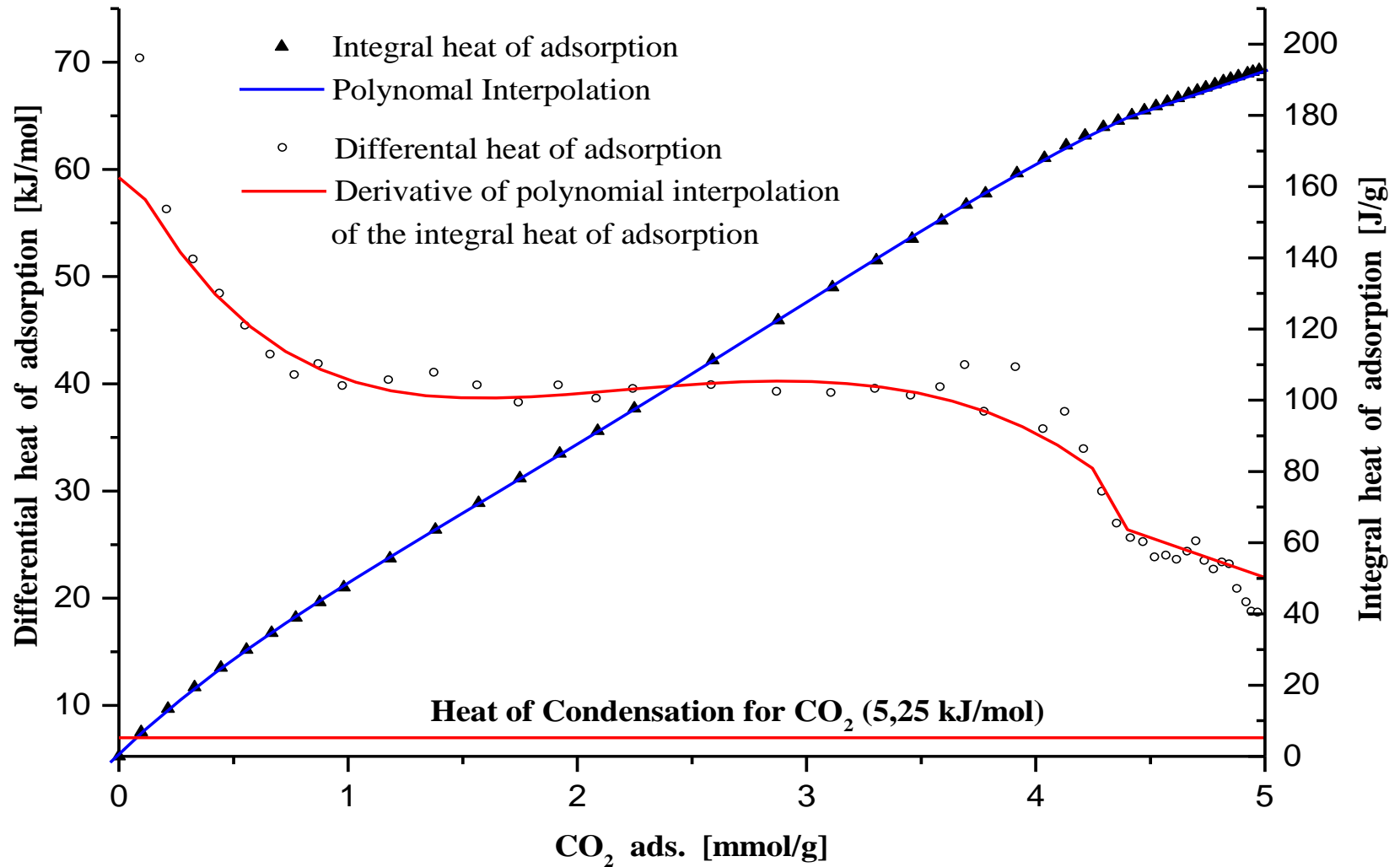
Heat of adsorption for CO_2 / Na13X, T=298K

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	Purpose
Volumetry/Manometry	Characterization of porous solids
Gravimetry	Equilibria, Kinetics, Gas Density
	Process Control
Oscillometry	Swelling Material
Dielectric Permittivity	Industrial Process Control

Gas Mixtures (N=2)

Volumetric-Densimetric M.	Equilibria, Process Control
(2-sites Magnetic Balance)	

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)   Verwendung von Wasserstoff

> 50 M t   95%   Herstellung von

> 500 G Nm3   Ammoniak
                                                                         Methanol
> 17   T SCFT/YR   Raffinerieprodukte (CW)
   (1m3 = 35.315 CFT)

                                                                5%   Nahrungsmittelindustrie
                                                                         Chemie
Welthandelsmenge: 5% WJP   Elektronik
                                                                         Metallurgie

SCFT: Standard Cubic Foot   Verkehr !?

Erzeugung wasserstoffreicher Gase(1)

Methode	Jahresproduktion (2006) / G Nm3	
	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
Summe	~ 500	~18

Erzeugung wasserstoffreicher Gase(2)

1.Reformierung Methan

$CH_4 + H_2O => CO + 3H_2$

$CO + H_2O => CO_2 + H_2$
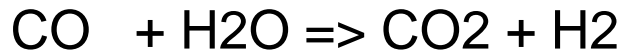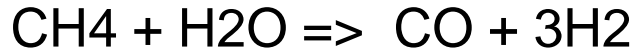
Reformergas (SMROG)*
	% mol
H2	70 - 80
CO2	15 - 25
CO	1 - 3
N2	Spuren

Sättigungszustand Wasserdampf
p= (4-30) bar, T= (20-40) C

*Steam-Methane-Reformer-Off-Gas
** Refinery – Off – Gas

2.Raffineriegas (ROG)**
   Kopfprodukt bei
   Trennkolonnen für Erdöl

H2, CH4, C2H6, C3H8

	% mol
H2	65 - 90
CH4	3 - 20
C2H6	4 - 8
C3H8	1 - 3
N2	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 CH4,
                                               < 200 ppm N2

Brennstoffzelle (PEM)   < 30 ppm CO

Elektronik   < 10 ppb N2, O2, CH4, CO, HCs

Nahrungsmittelindustrie   3.1 – 5.5 (%Vol H2)

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

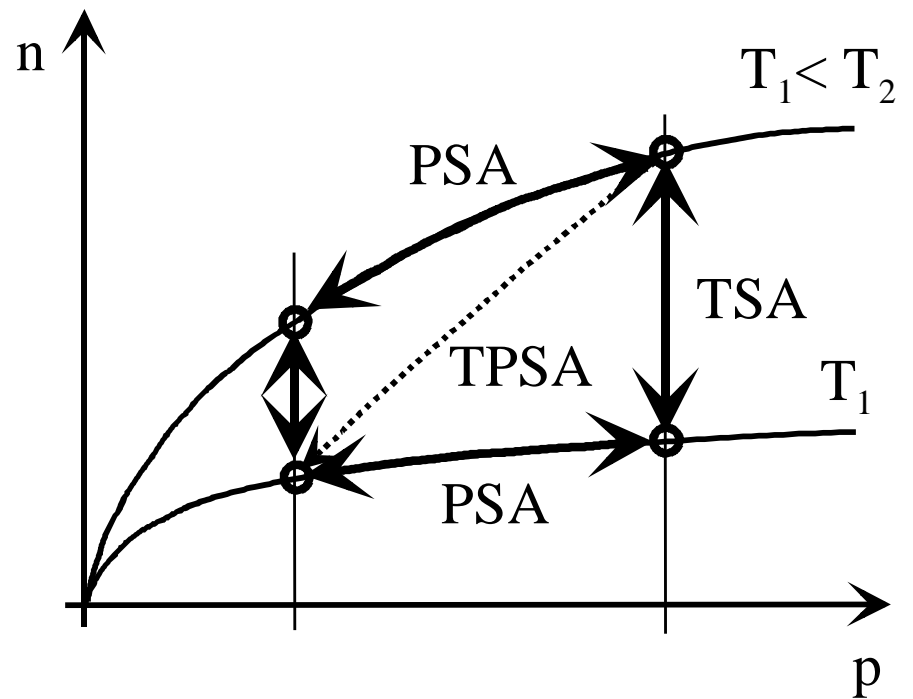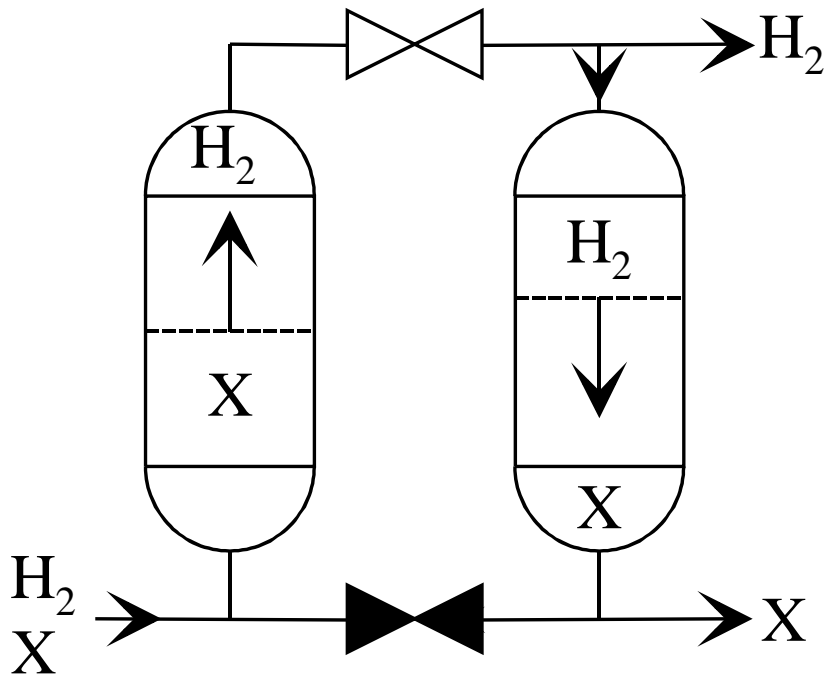## Production Cost Hydrogen ($ / kg) (USA, 2006)
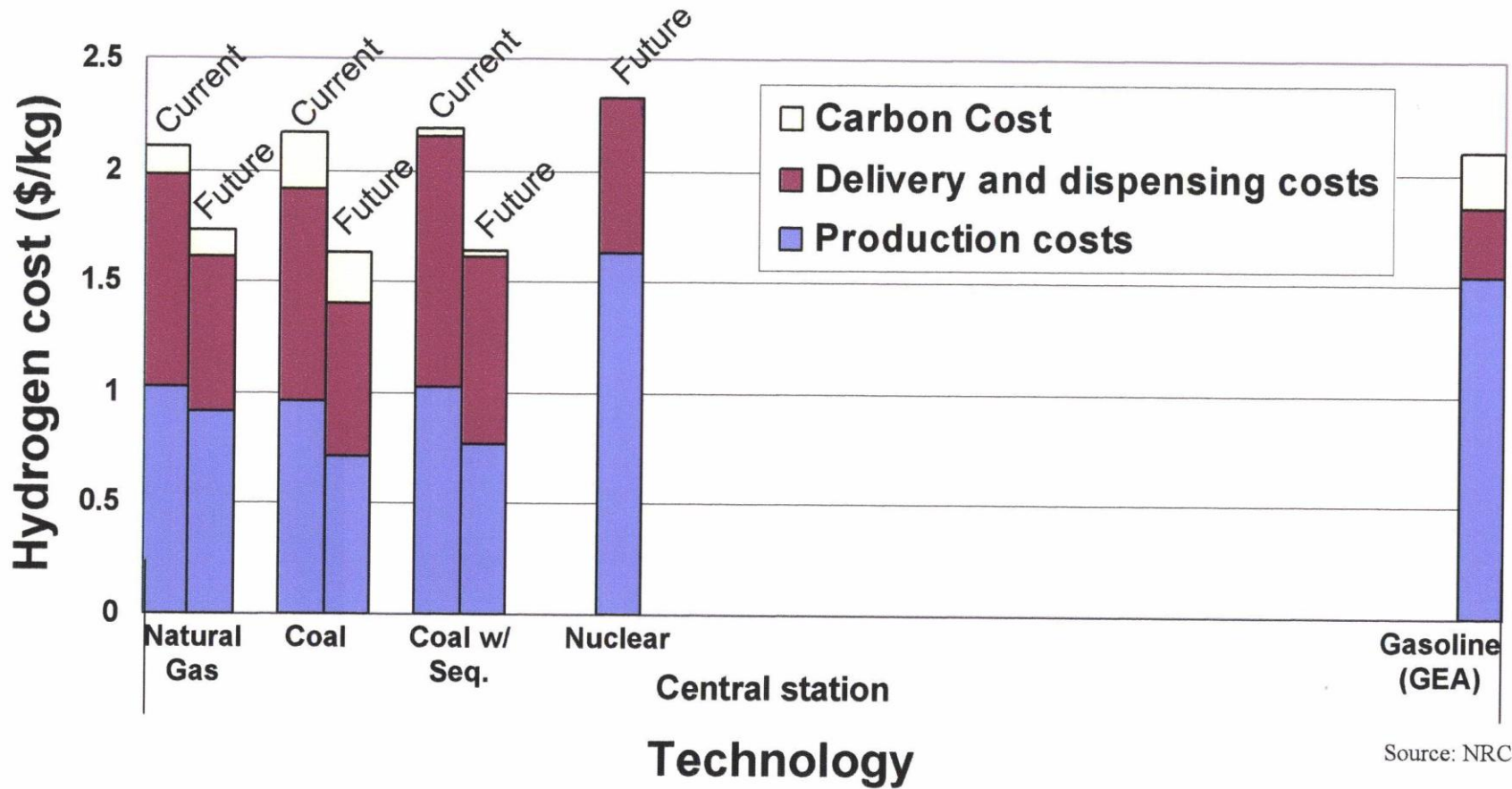
GEA = Gasoline Efficiency Adjusted – scaled to hybrid vehicle efficiency

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[*)]

H_2 (T_C)

R
H
T

(1)

H_2

(2)

N_2

H_2 (T_H)

(3)

H_2

(4)

N_2

N_2
H_2

N_2
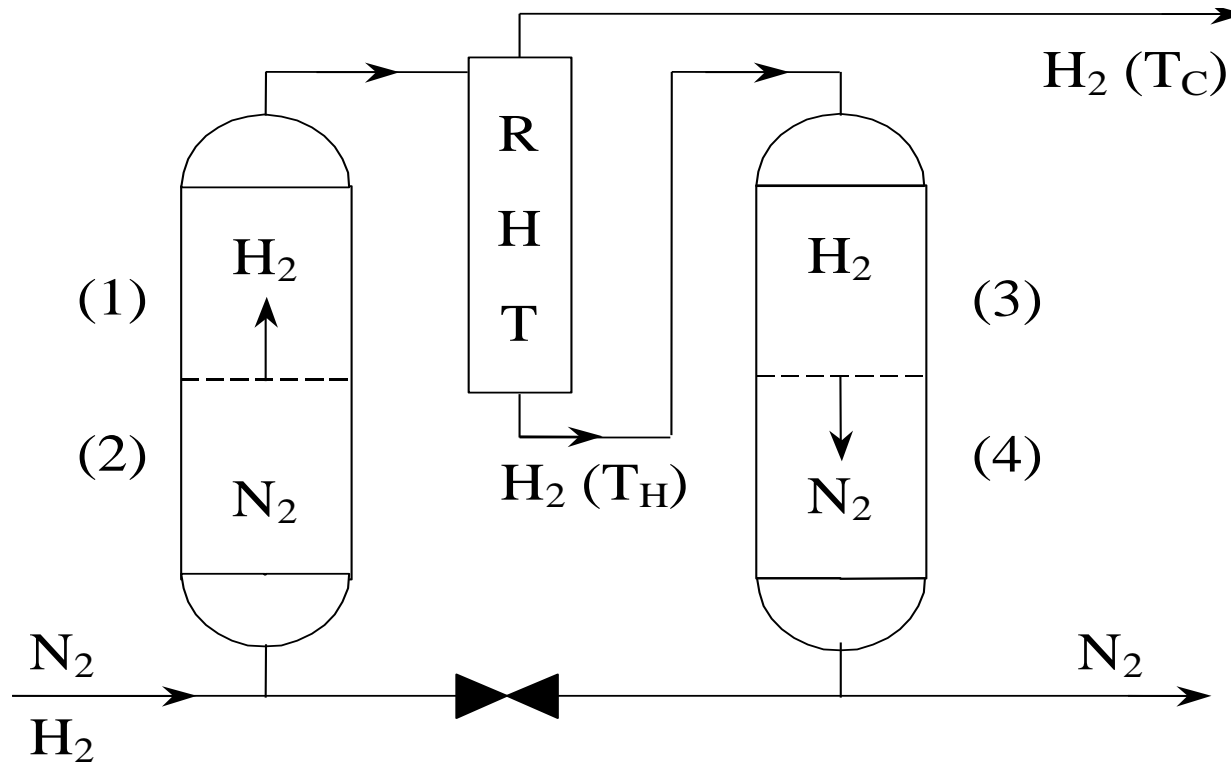
1) Pressurization   3) Blowdown
2) Adsorption   4) Purge with hot product gas

SURVEY OF US PATENTS ON H$_2$ PSA PROCESSES
Total No. of Patents (1978 - 2005) = 273
Awarded to 73 Corporations Around the World
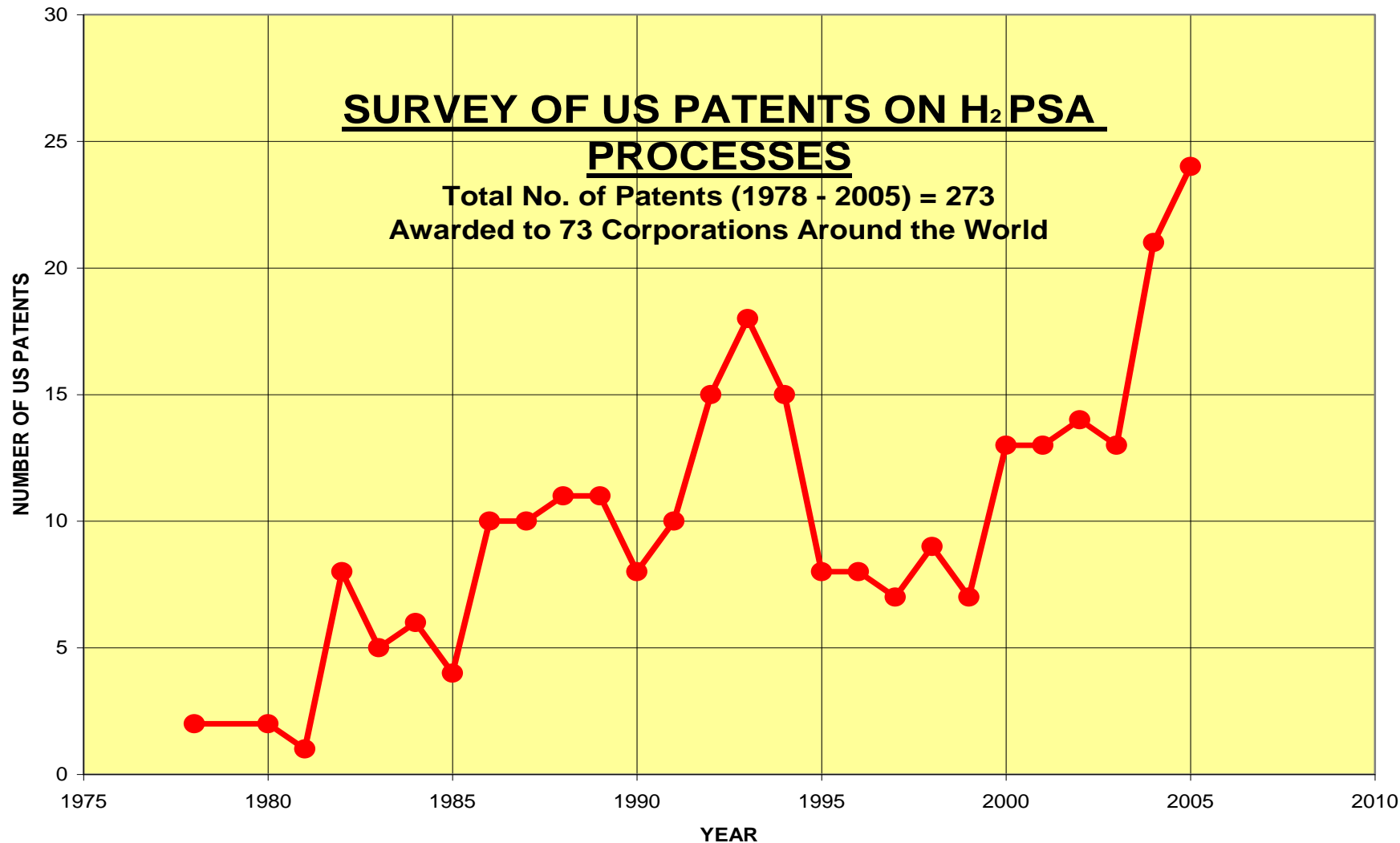
Druckwechseladsorption mit LOFIN-Schaltung

Product H$_2$

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

1   **2**   **3**   **4**
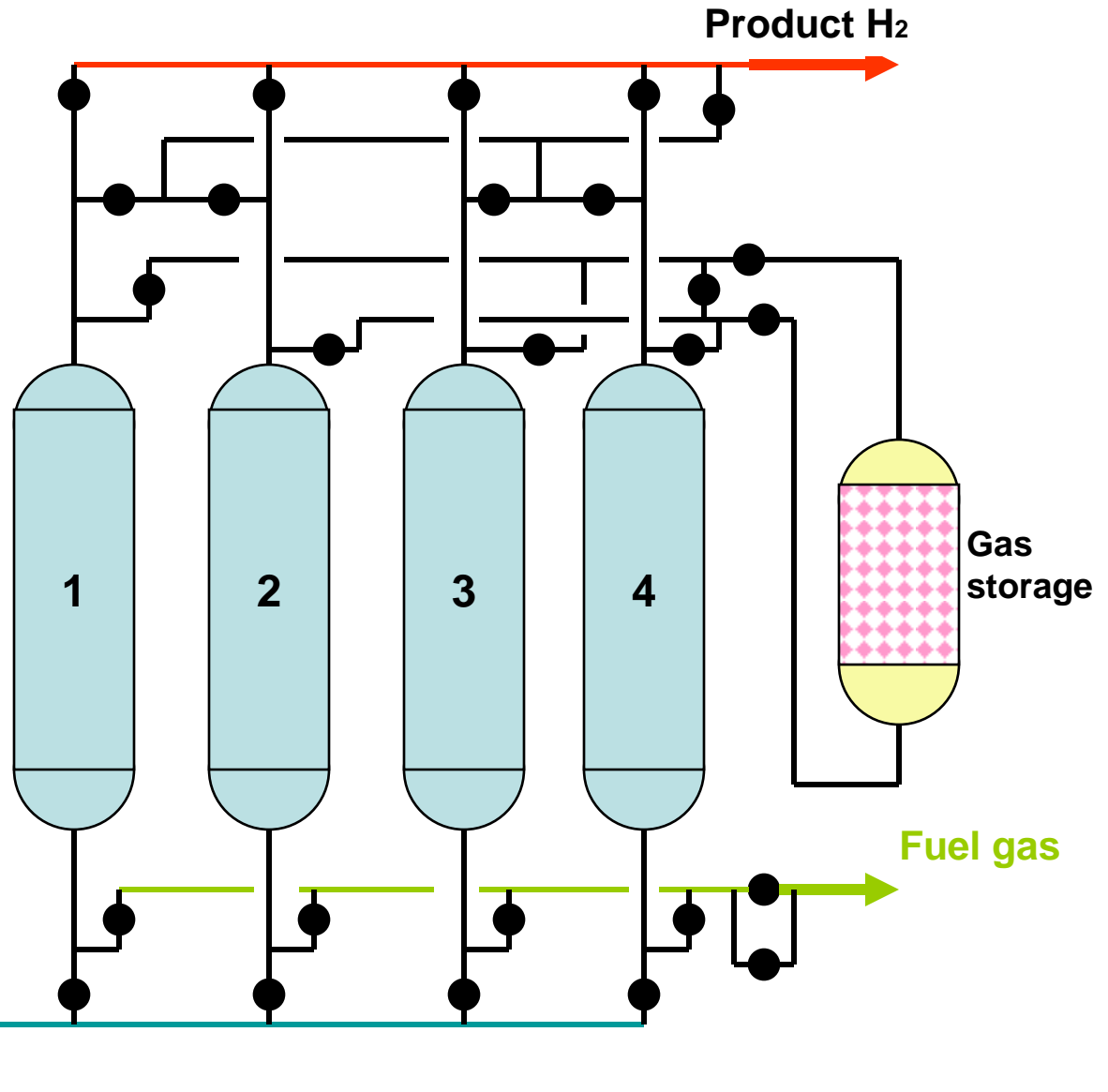
Gas storage

Fuel gas

Crude H$_2$ feed gas

Sorbentien für Druckwechsel-Adsorptionsprozesse
Geschichtete Festbettadsorber

Sorbens   Störkomponente

<u>Reformergas</u> (SMROG)

Aktivtonerden (Al_2O_3) H_2O
Aktivkohlen CO_2
A-Zeolithe   CO, CH_4, N_2

<u>Raffineriegas</u> (ROG)

Aktivtonerde H_2O
Silikagele C_3 H…
Aktivkohle CH_4, C_2H_6…

Zukünftige Entwicklungstrends der PSA-Technologie

Rasche Druckwechselprozesse (t < 1min) (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.
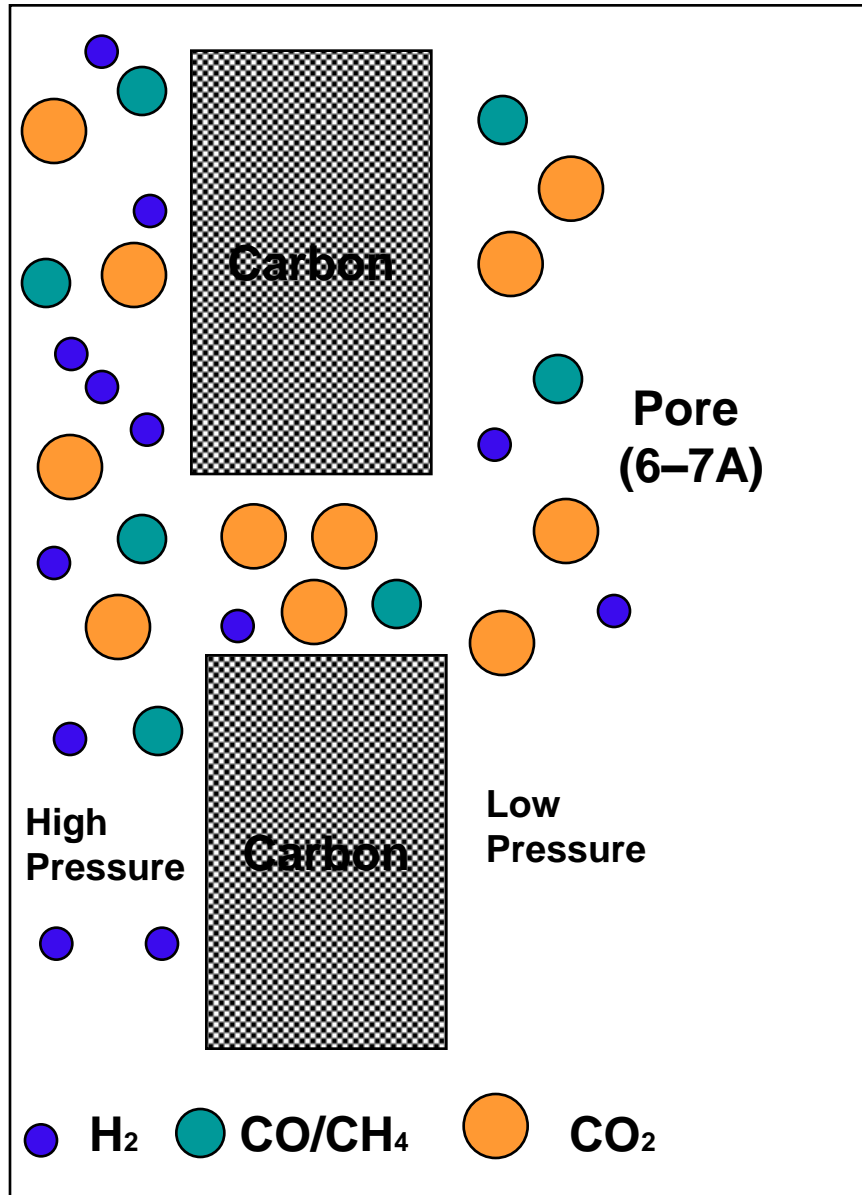
Oberflächenselektive Membranen

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

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