Gas Adsorption Equilibria Measurements and Correlations

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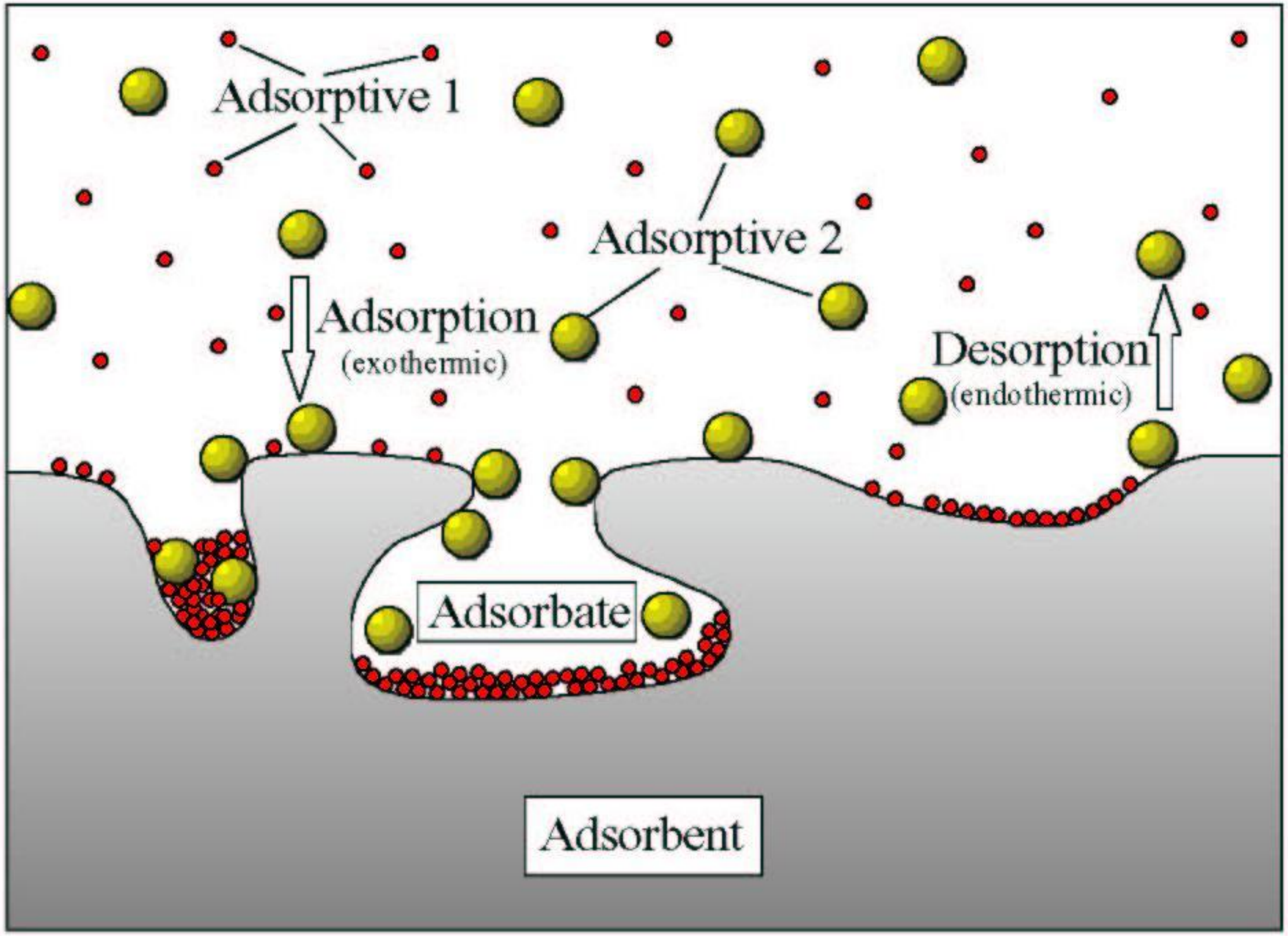
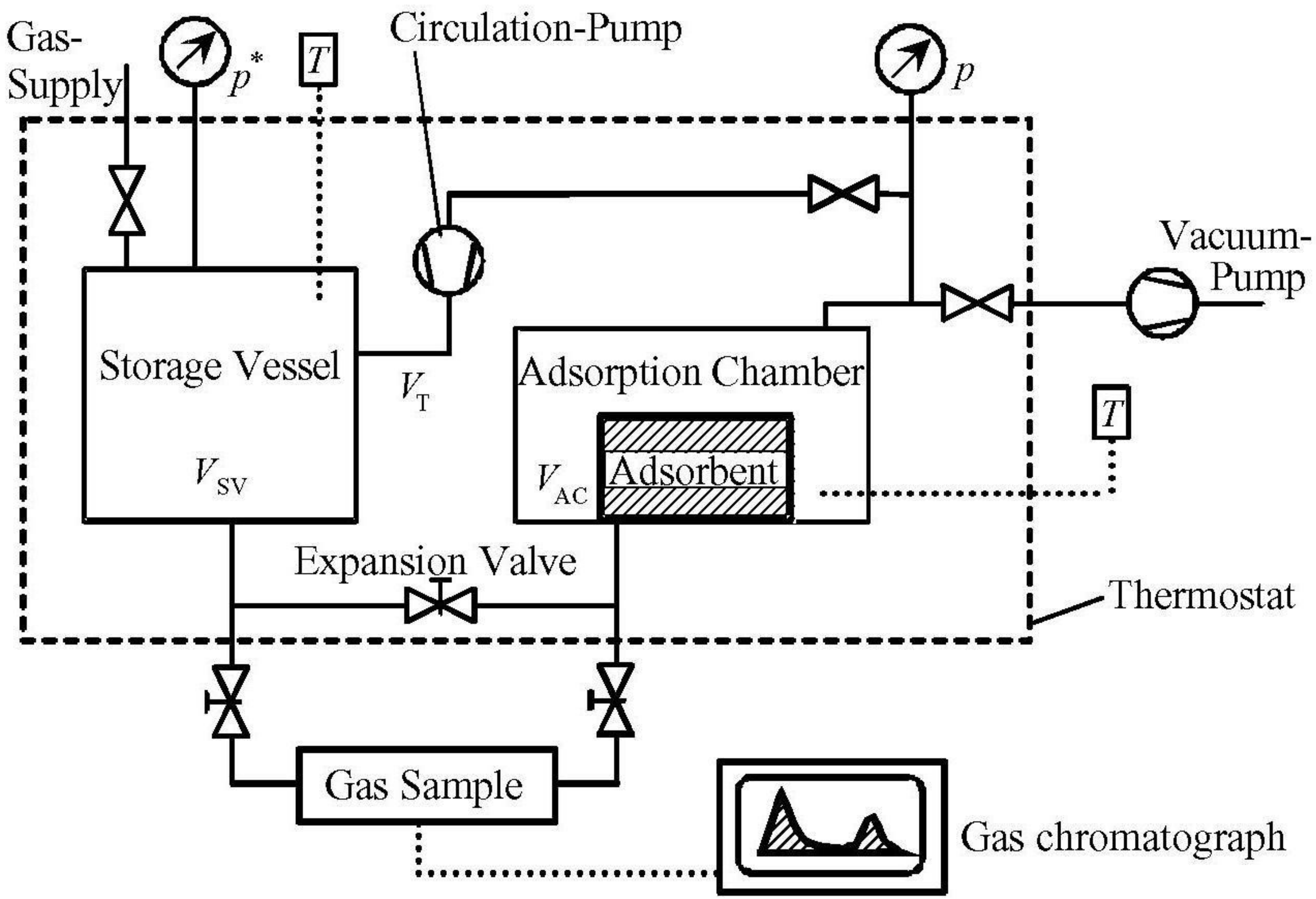

Adsorptive 1
Adsorptive 2
Adsorption
(exothermic)
Desorption
(endothermic)
Adsorbate
Adsorbent

Adsorption

Gas Mixture Sorption

Measurement Methods

	M	G	O	SP	CHR	D	C
Manometry (M)		++	+	0	++	++	0
Gravimetry (G)	2		+	0	+	+	0
Oscillometry (O)	1, V	1, V		0	0	0	0
Spectroscopy (SP)	(2)	(2)	1, V		–	–	AMA
Chromatography (CHR)	≥2	≥2	≥2*	–		–	–
Densimetry (D)	2	2	1, V	–	–		–
Calorimetry (C)	(1)	(1)	(1)	1	–	–	



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

Mass balances $m_i^* = m_i^f + m_i \qquad i = 1 \ldots N$ (1)

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

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

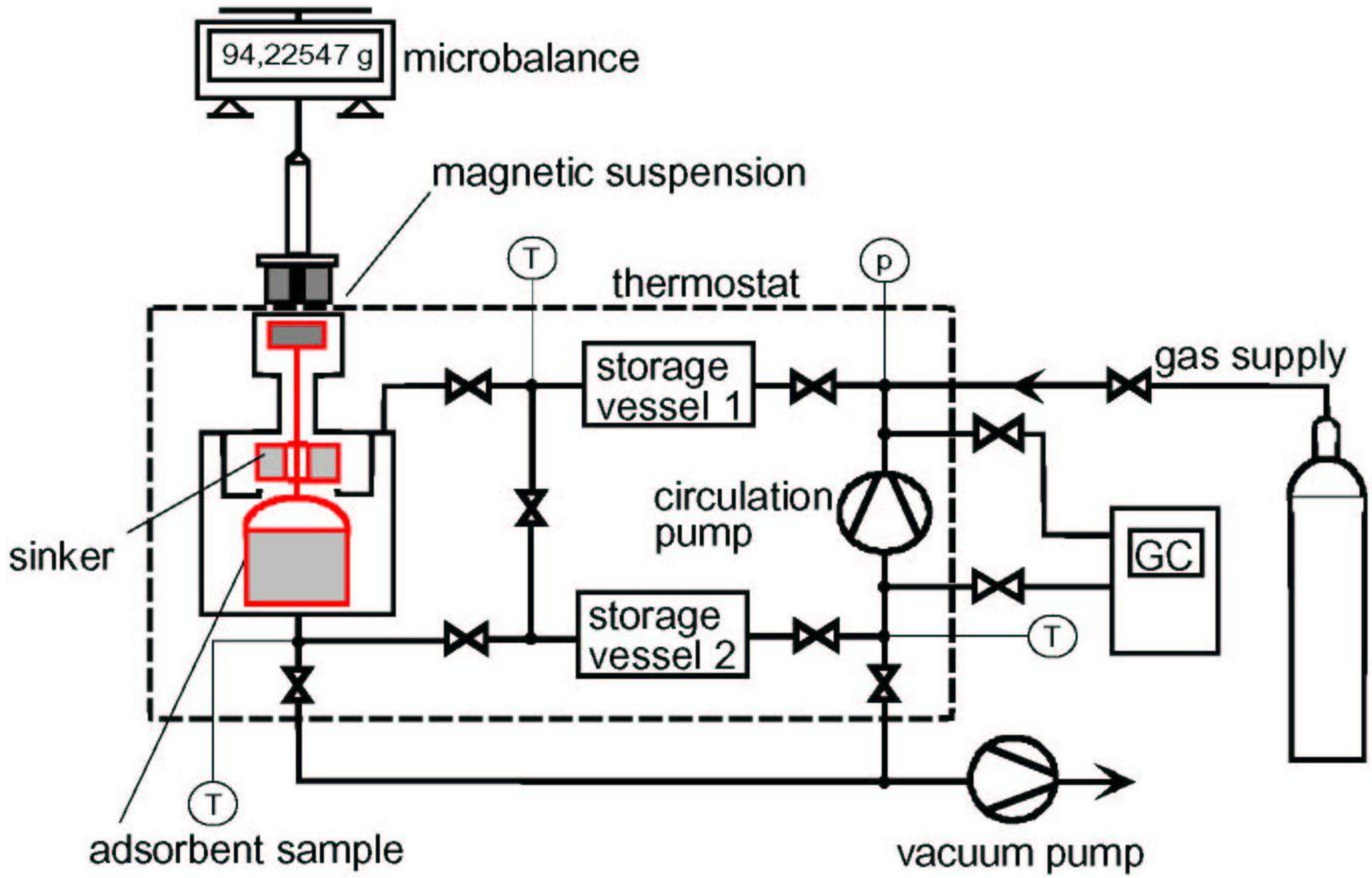
$$(1-3): \underline{\Omega_i = m_i - \rho_i^f V^S} \qquad (4)$$

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

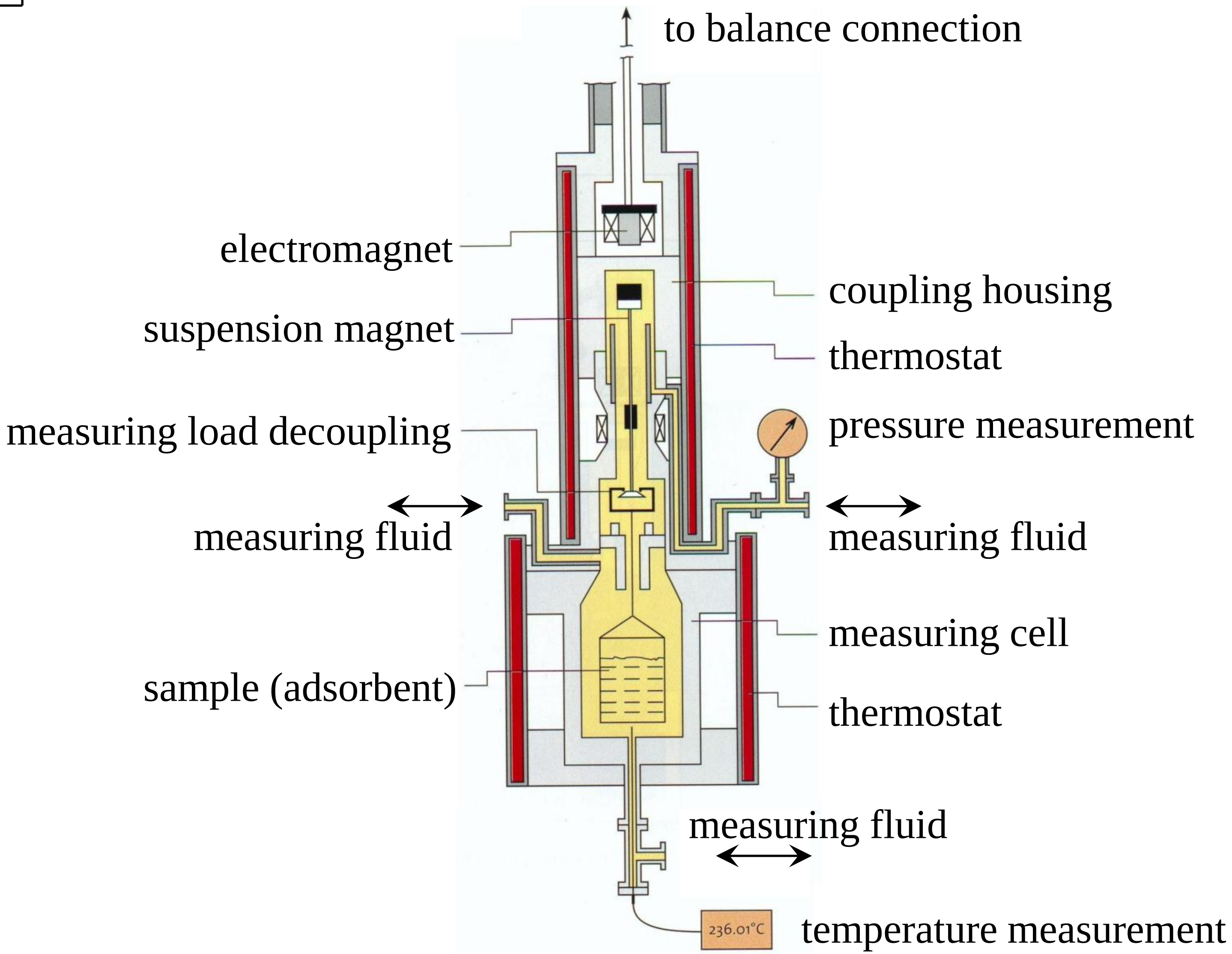
$$\rho_i^f = w_i \rho^f \; T, p, w, \ldots w_N \;, \qquad w_i : GC$$

$m_i \ldots$ Gibbs excess mass

Volumetry / Manometry

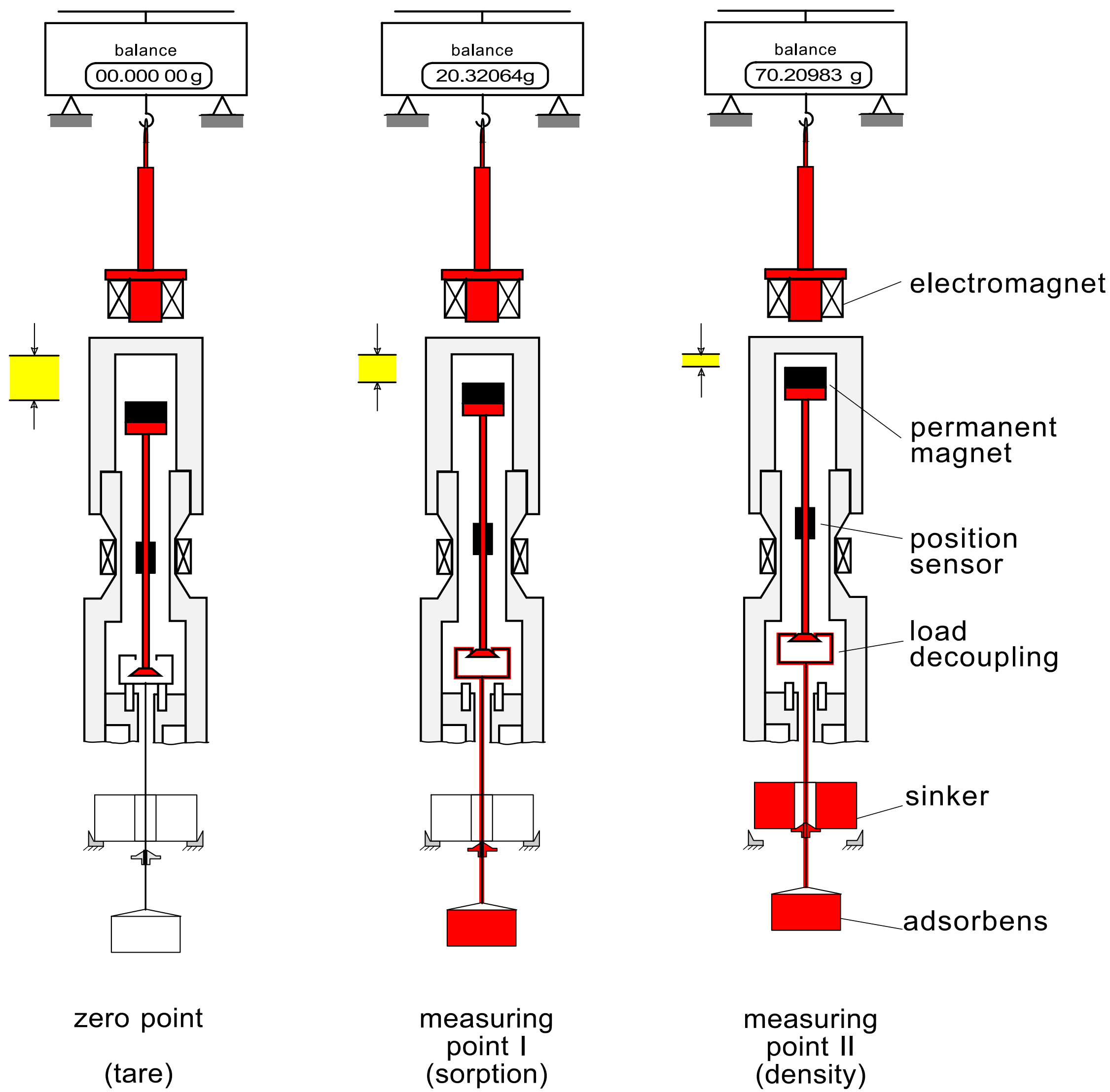


Schematic diagram of volumetric-gravimetric-chromatographic installation with magnetic suspension balance

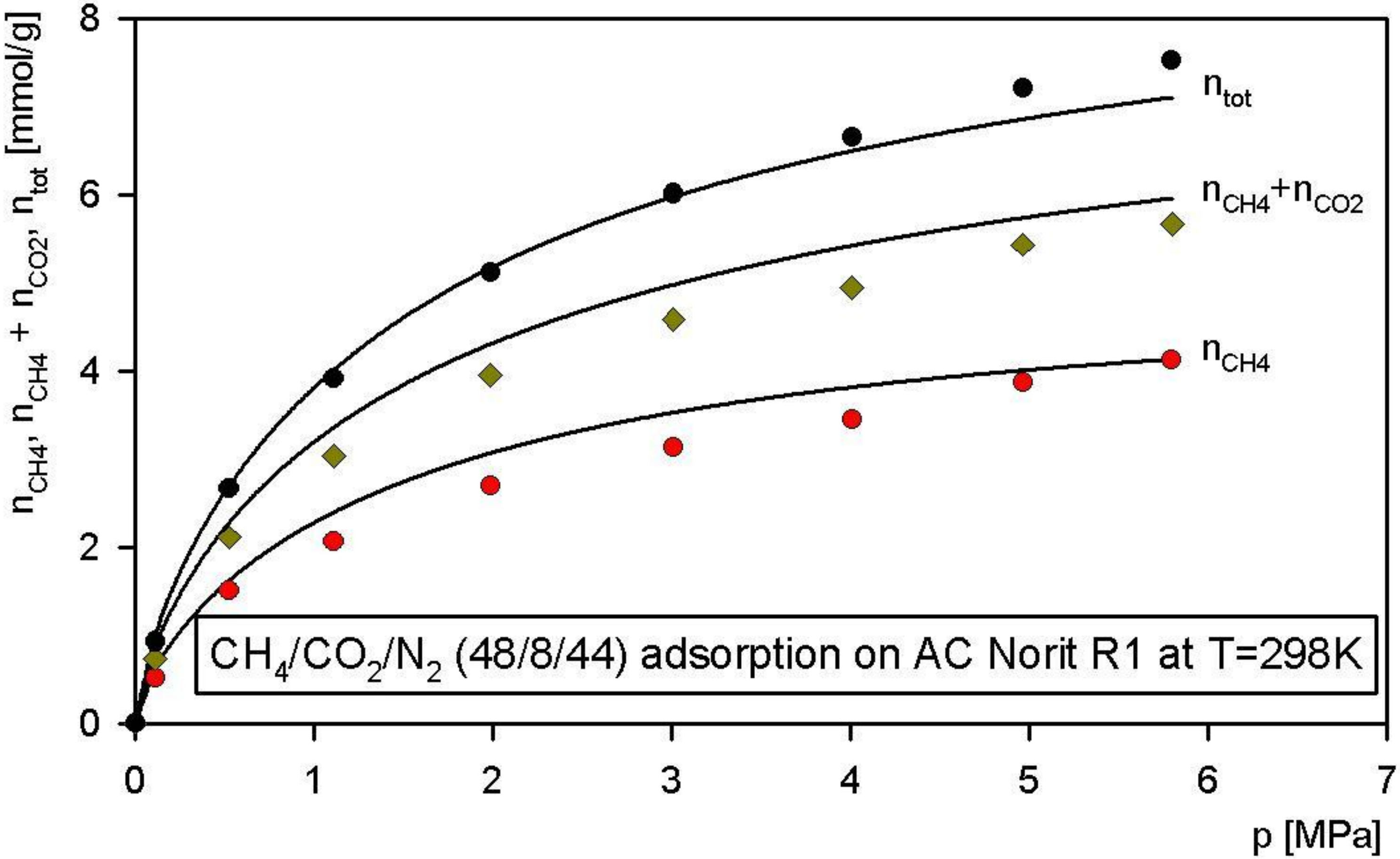


Sorption measurement (Rubotherm)

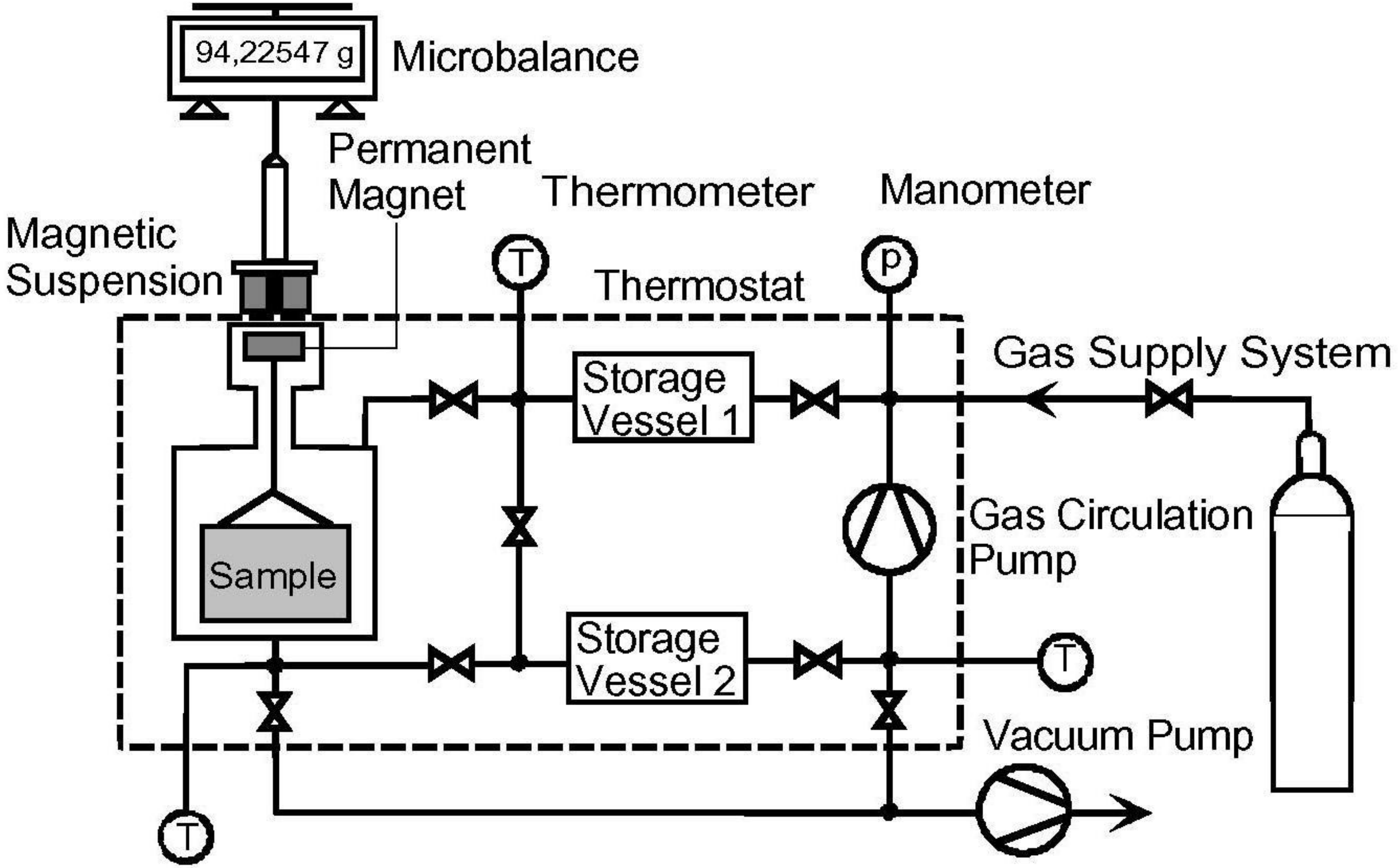
Simultaneous Sorption and Density Measurement (Rubotherm, Bochum, Germany)



Magnetic-Suspension-Balance Instrument (12/96)



Prediction of tenary adsorption data with the 2-sites AI



Experimental Setup for volumetric-gravimetric measurements

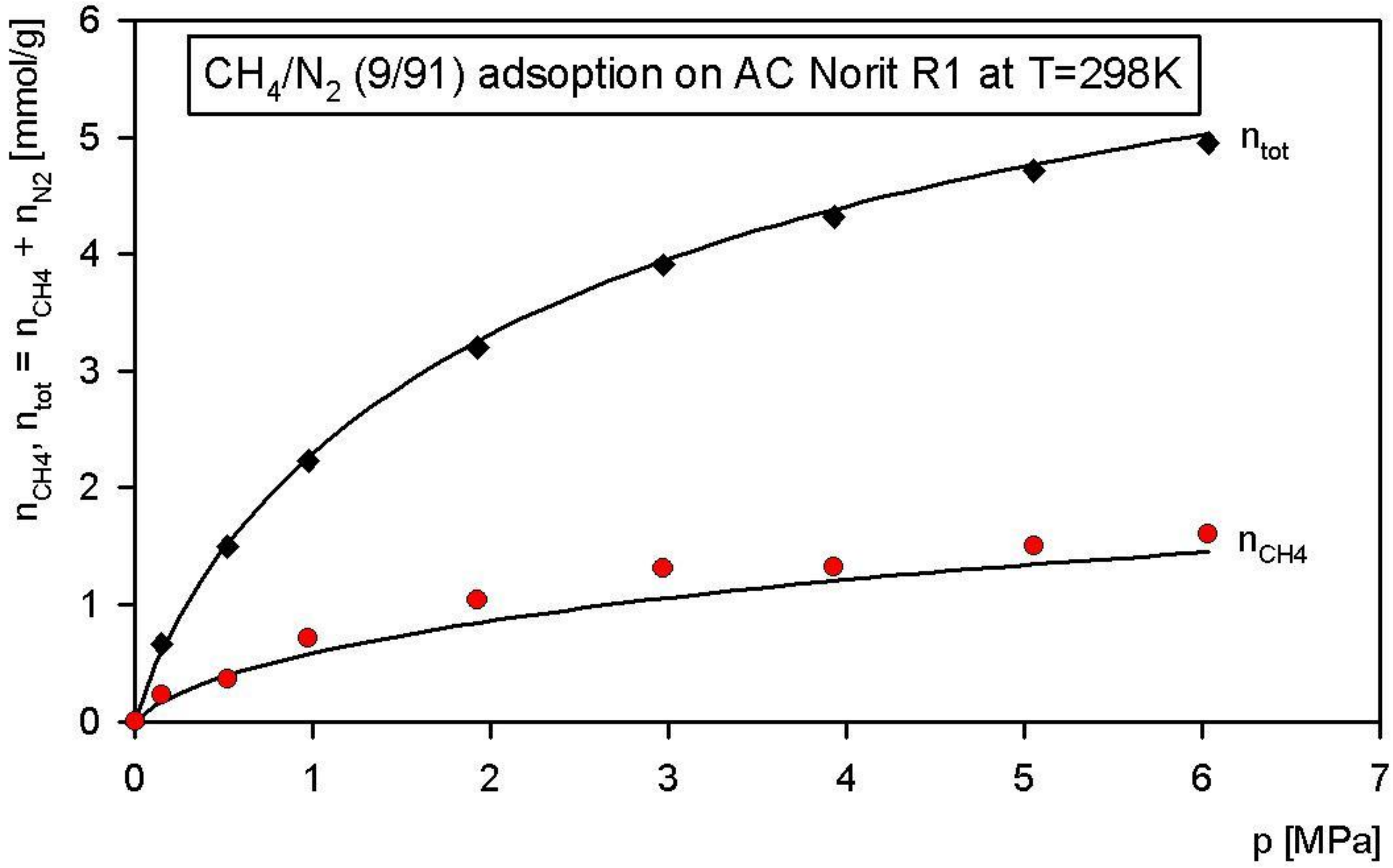
Mass balances $$m_i^{*} = m_i^{f} + \left(1 + \frac{m_0^{s}}{m^{s}}\right) m_i \qquad i = 1, 2$$

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 $$\frac{m_1^{f}}{M_1} + \frac{m_2^{f}}{M_2} = \frac{p \;\; V^{*} + V^{f}}{Z R T}$$

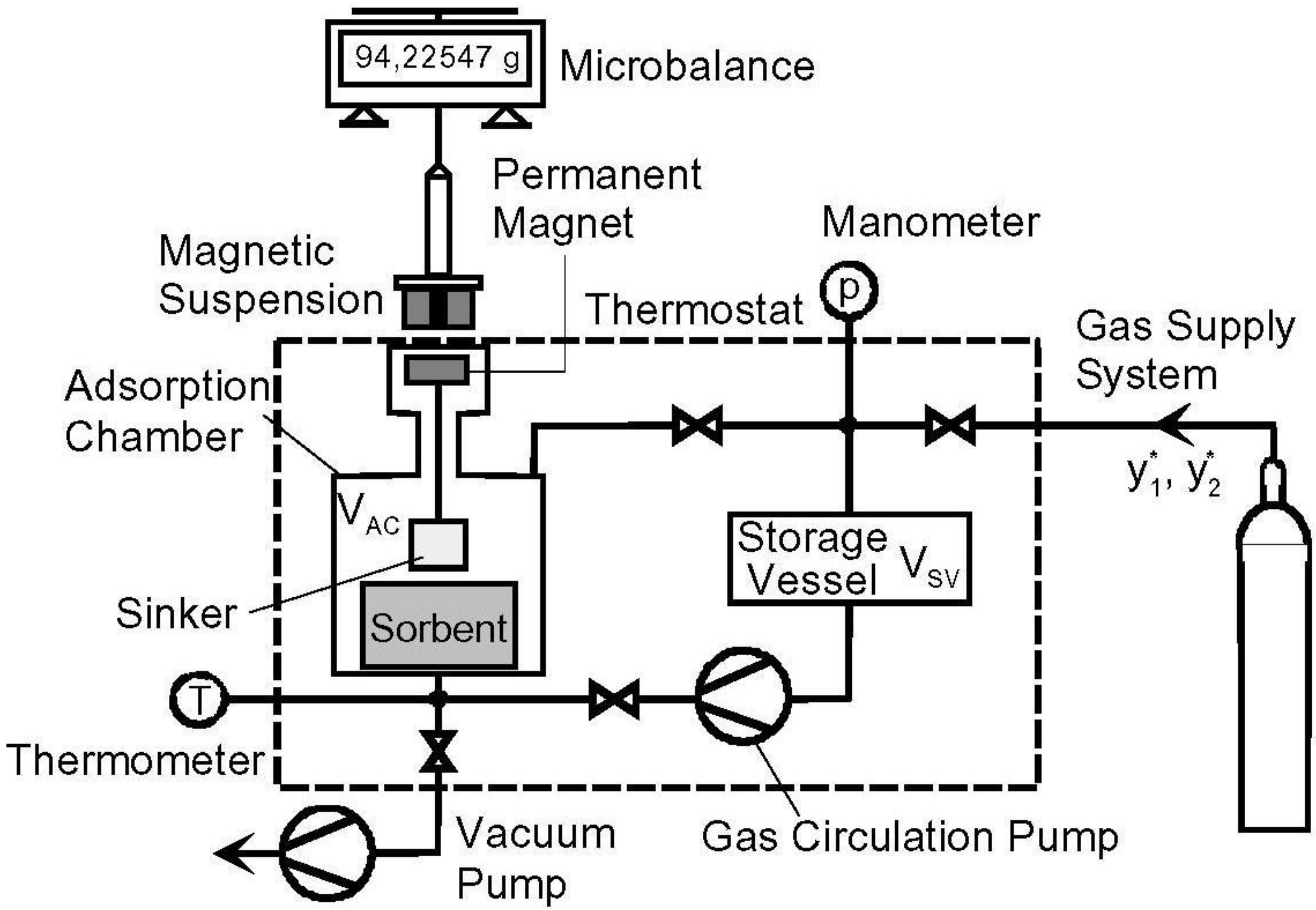
$$\rightarrow \; m_1, m_2, m_1^{f}, m_2^{f} \ldots V^{f} = V - \left(1 + \frac{m_0^{s}}{m^{s}}\right) V^{as} \quad \text{if} \quad M_1 \neq M_2$$

Volumetric-Gravimetric Measurements of Binary Coadsorption Equilibria



Prediction of binary adsorption data with the 2-sites AI

Coadsorption Instrument
BEL-Rubotherm, IFT, 2001



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

Instrument for DVMs of binary coadsorption equilibria using a MSB (2) (Rubotherm AG, Bochum)

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

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

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

Sorptive gas masses (m_1^f, m_2^f)

$$m_1^f + m_2^f = \rho^f (V^* - V^{as}) \qquad (3)$$

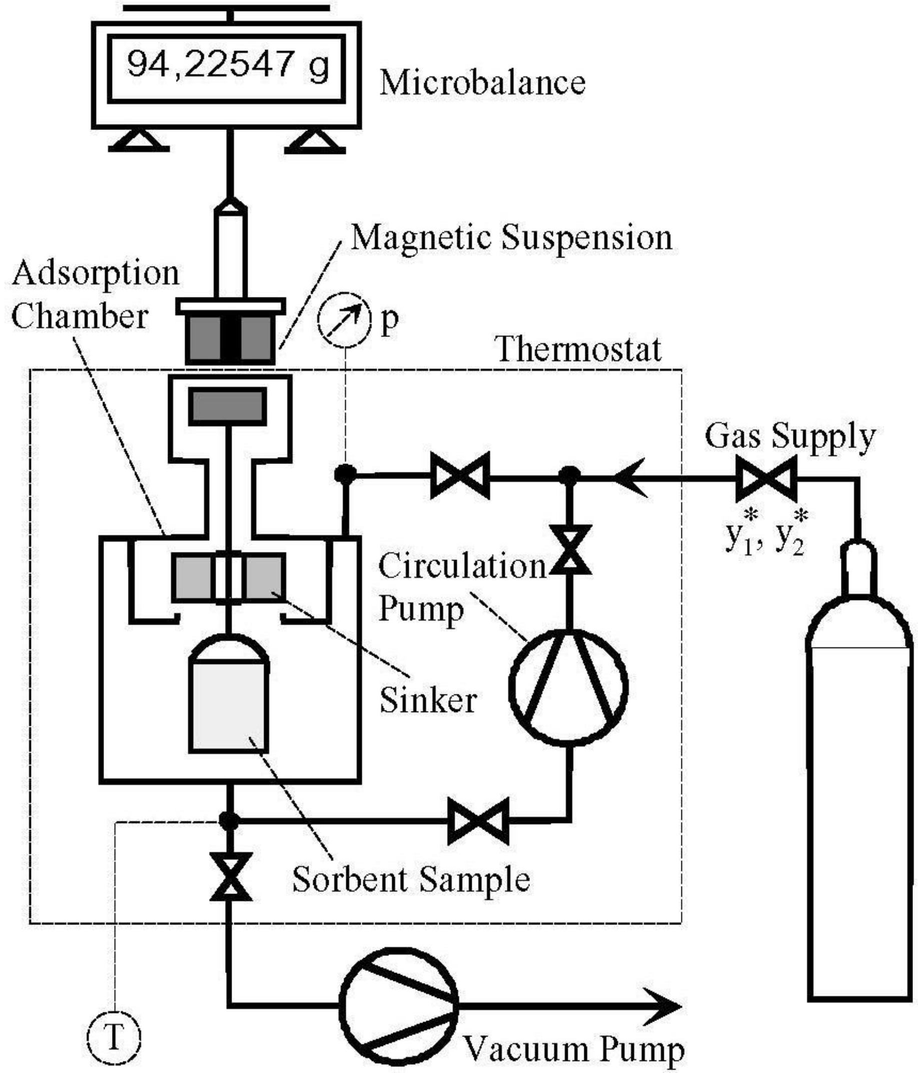
$$\frac{m_1^f}{M_1} + \frac{m_2^f}{M_2} = \frac{p(V^* - V^{as})}{R T Z(p, T, w_i)} \qquad (4)$$

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

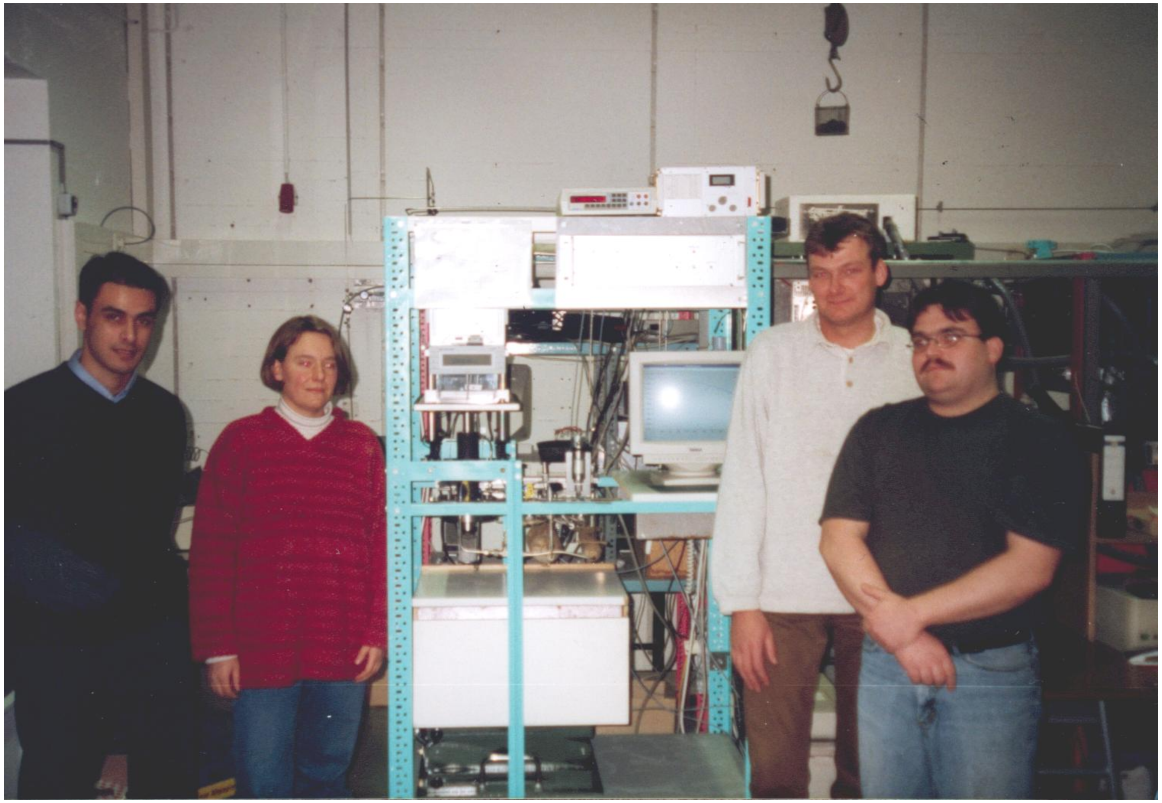
$$(1-4) \quad V^{as} = V_{He}^s \qquad (5)$$

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

DVMs / Theory



Installation for DGMs of Binary Coadsorption Equilibria of Premixed Gases (y_1^*, y_2^*)



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

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

Total gas mass supplied $$m^* = m_1^* + m_2^* = m_1^a + m_2^a + m_1^f + m_2^f \qquad (2)$$

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

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

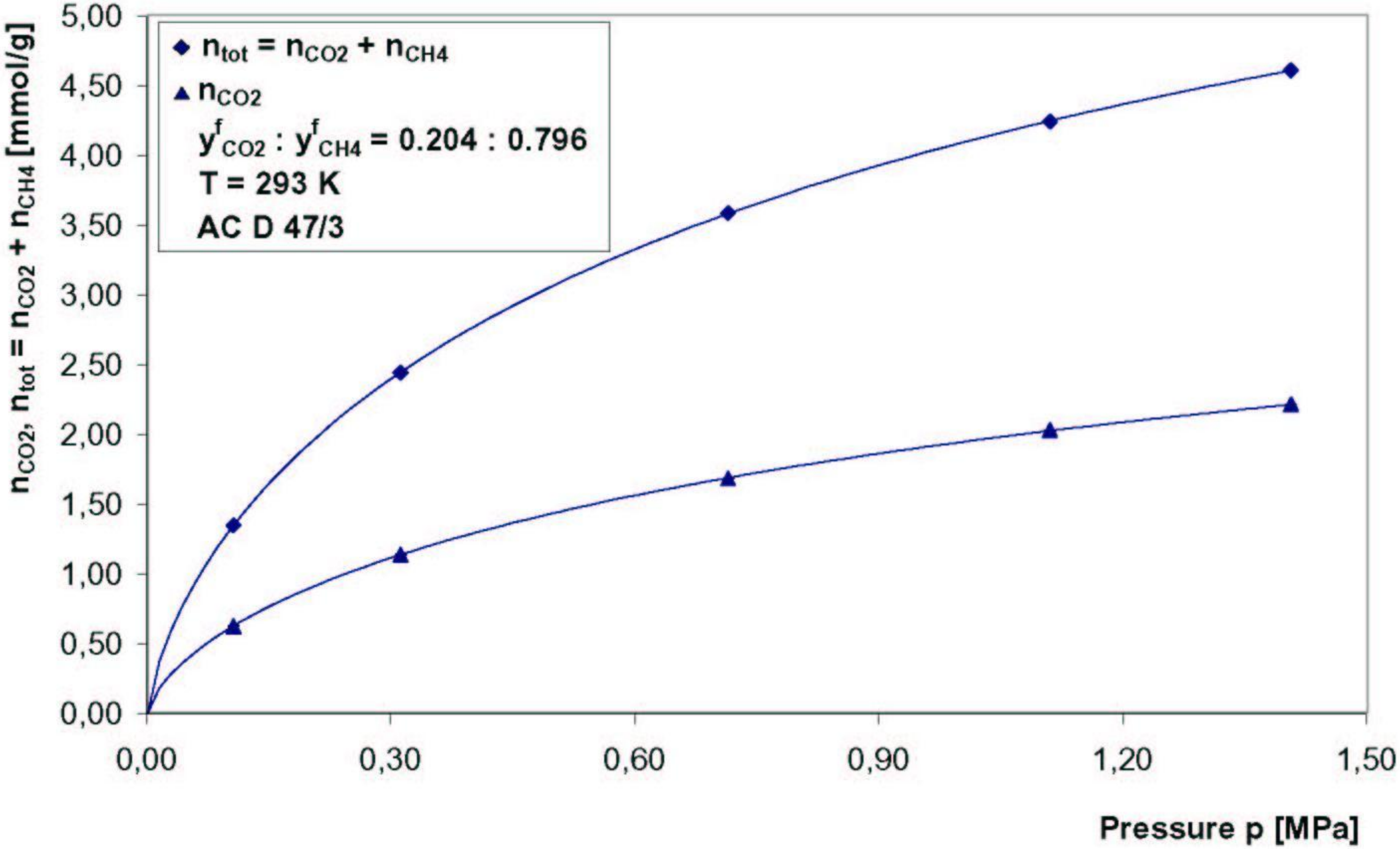
Sorptive gas masses $$m_1^f + m_2^f = \rho^f \;\; V^* - V^{as} \qquad (3)$$

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

(1, 2A, 3, 4) $$V^{as} = V^s_{He} \qquad (5)$$

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

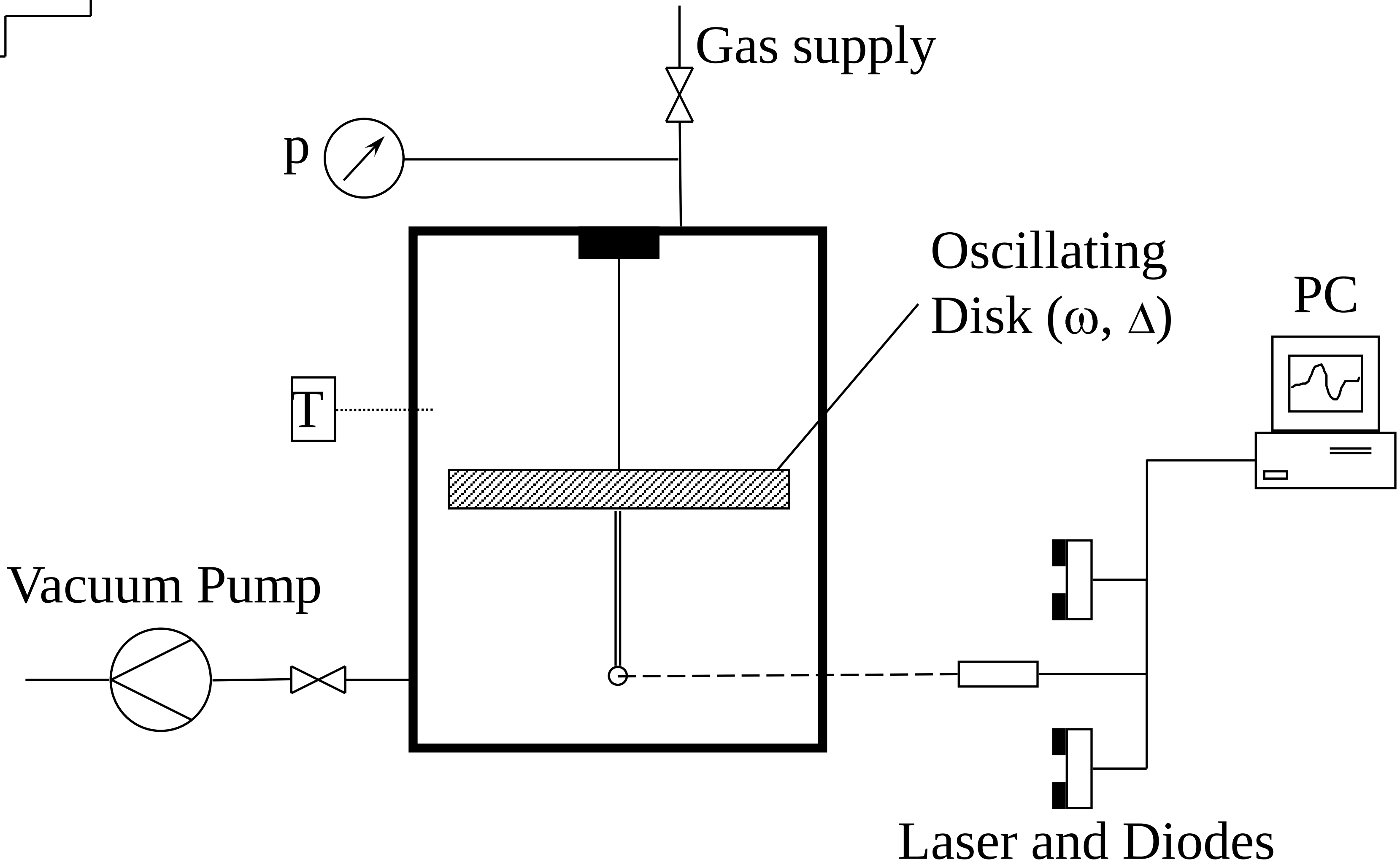
DGMs / Theory



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: $n_i = n_{i_\infty}(bp)^{\alpha_i} / \left[1+(bp)^{\alpha_i}\right]$, $i = CO_2, CH_4$

Comparison of experimental pros and cons of densimetric-gravimetric measurements (DGMs) and densimetric-volumetric measurements (DVMs) of binary gas adsorption equilibria without analyzing the sorptive phase.

Criterion	DGMs	DVMs
1. Equipment needed	Magnetic suspension balance (3 positions)	Spring balance (quartz), microbalance, magnetic suspension balance (2 positions)
2. Operation	sophisticated	fairly simple
3. Automation	sophisticated	fairly simple
4. Kinetics	can be observed	hardly observable
5. Activation of sorbent	inside the instrument i. e. controllable	outside the instrument i. e. often changed during transportation of sorbent to the instrument
6. Amount of sorbent needed	small (> 0.1 g)	large (5 g – 100 g)
7. Wall adsorption	neglectable	may cause serious errors or uncertainties
8. Uncertainties of measurements	add up in pressure step-up experiments	add up more rapidly in pressure step-up experiments
9. Thermostatization	easily achievable	achievable, but takes more time



Experimental Setup for Oscillometric Measurements of Gas Adsorption Equilibria

Ideal Pendulum m^s, m

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

Physical Pendulum m^*, m^s, m

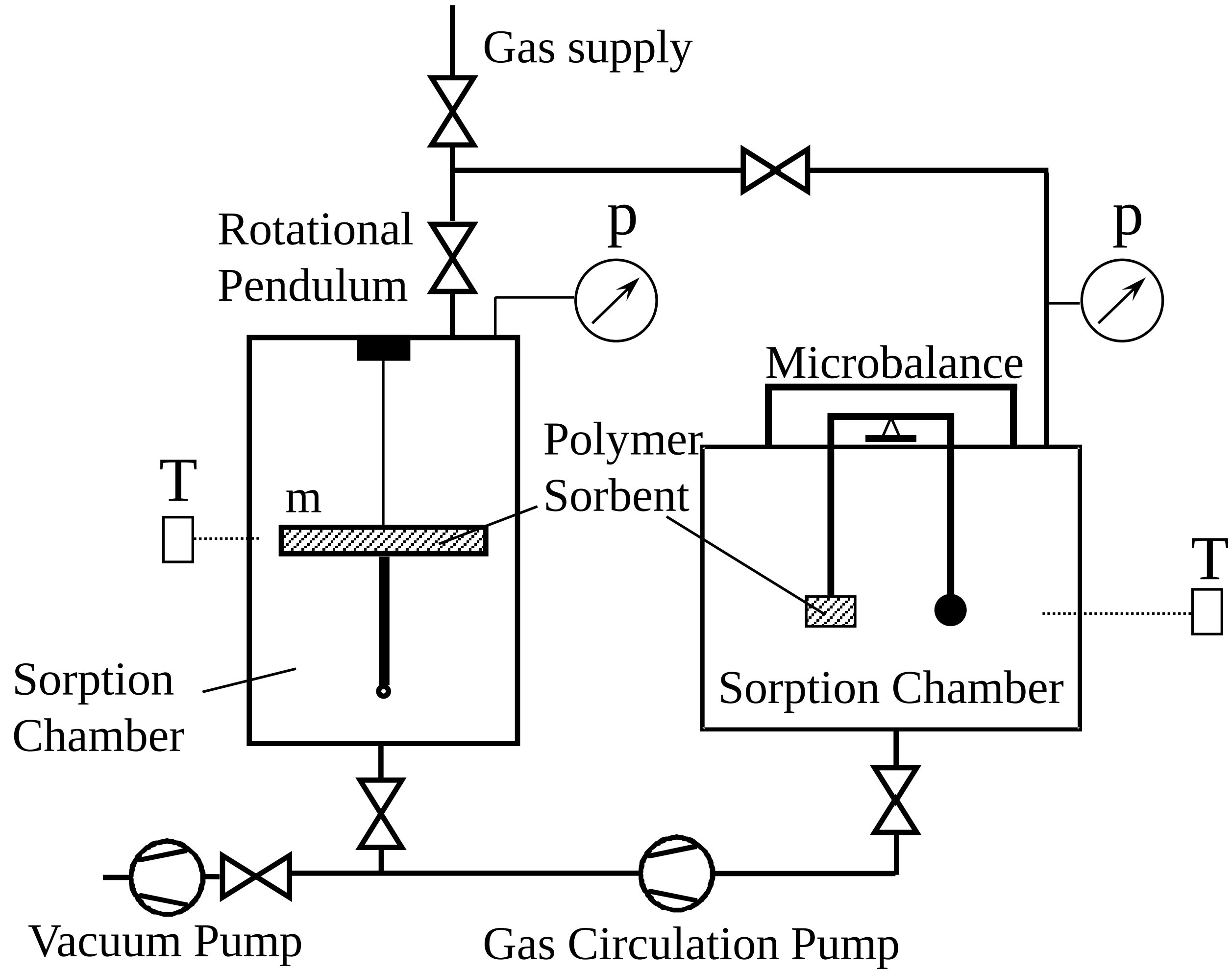
$$\frac{m}{m^s} = \frac{\frac{1+\Delta_0^2}{1+\Delta_E^2}\left(\frac{\omega_0}{\omega_E}\right)^2 - 1}{1-\frac{\Delta_0\omega_0}{\Delta^*\omega^*}}$$

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

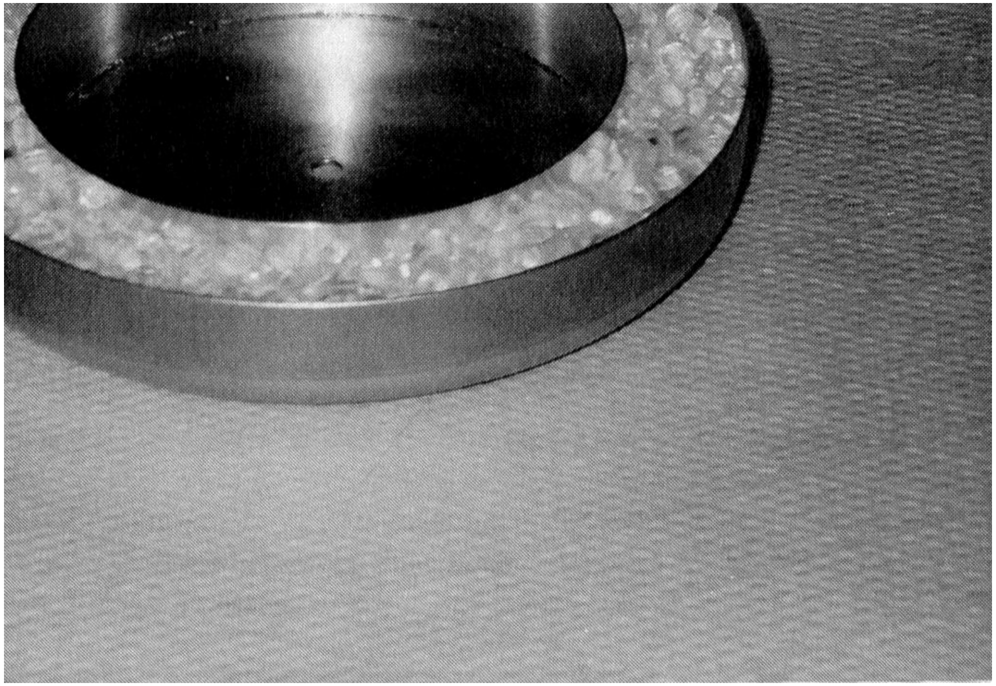
ω_0, Δ_0... pendulum and adsorbent m^*, m^s, vacuum

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

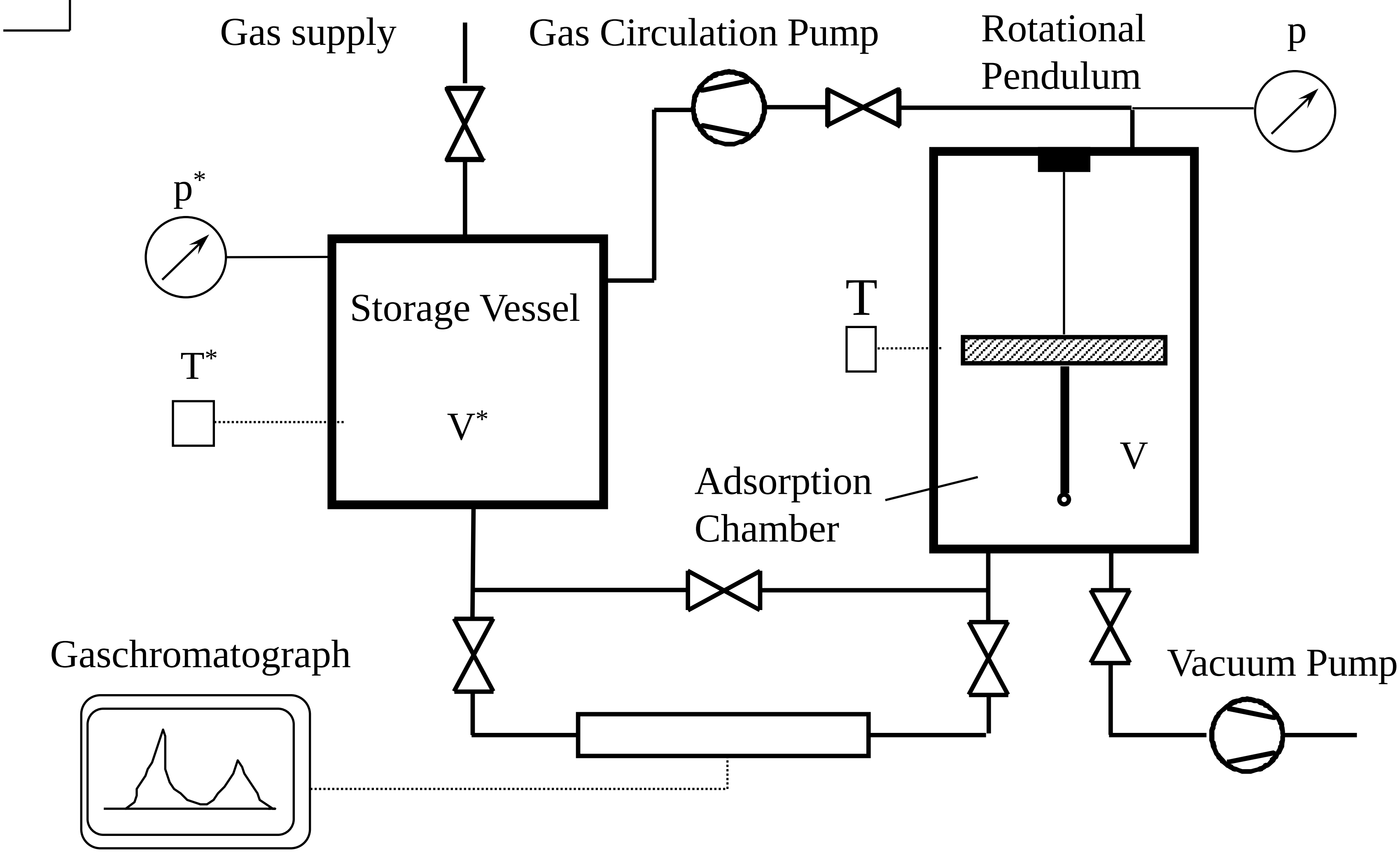
Oscillometric Measurements of Gas Adsorption Equilibria. Theory



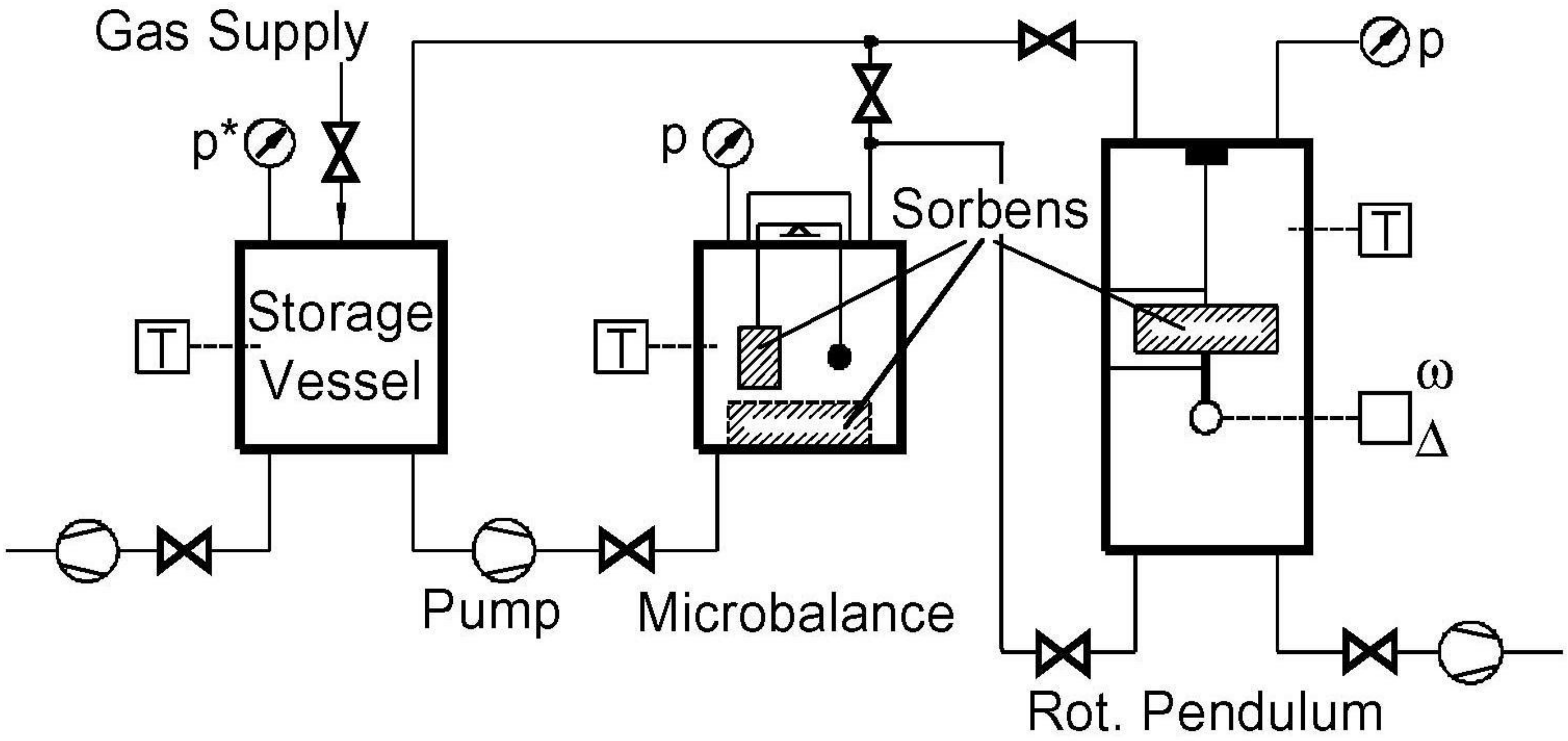
Experimental Setup for oscillometric-gravimetric measurements



Ring slit of rotational pendulum filled with polycarbonate pellets

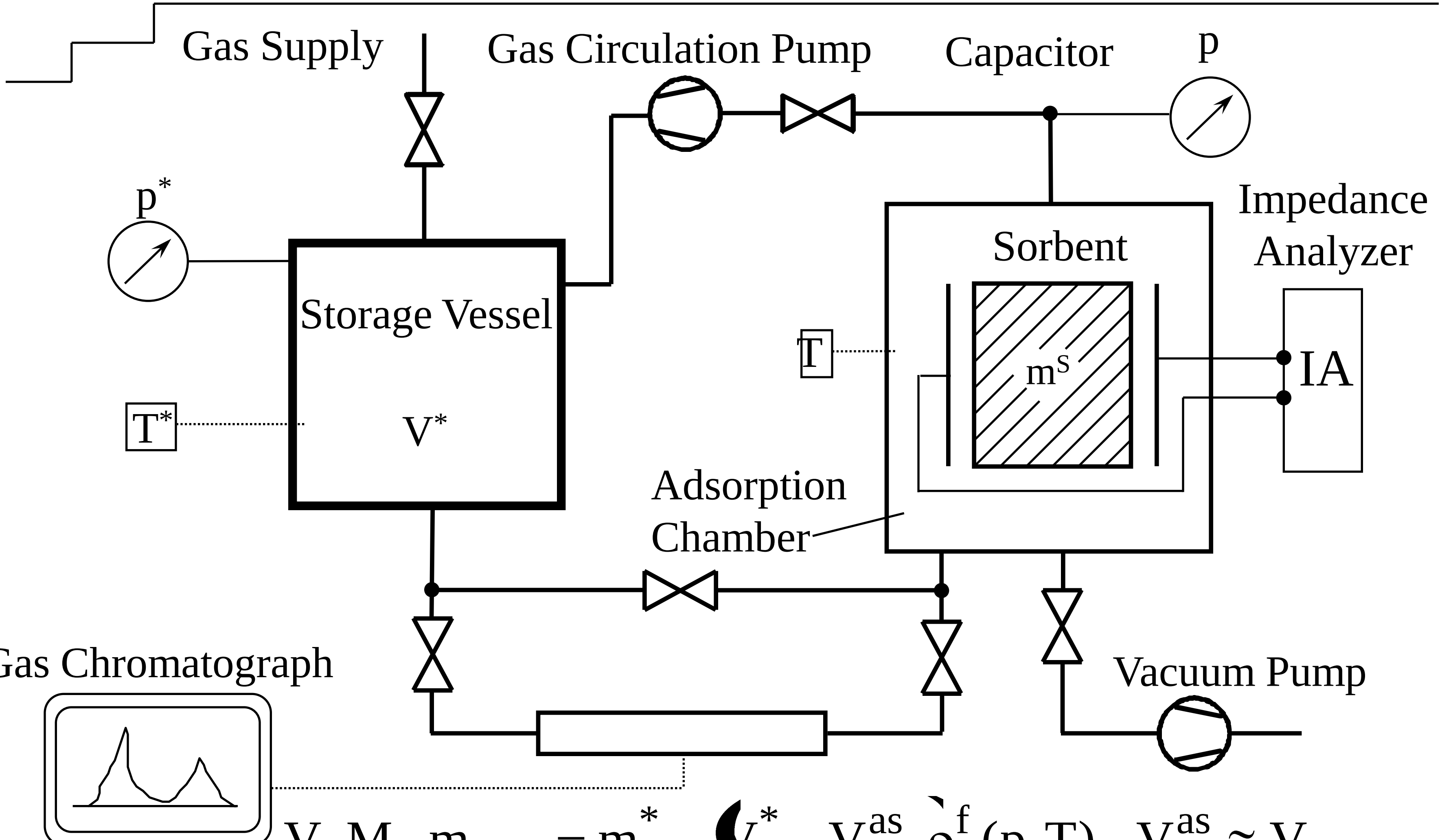


Experimental Setup for oscillometric-volumetric measurements



Volumetric-gravimetric-oscillometric method (N=2). Co(ad)sorption measurements in swelling sorbents (polymers) without using a GC

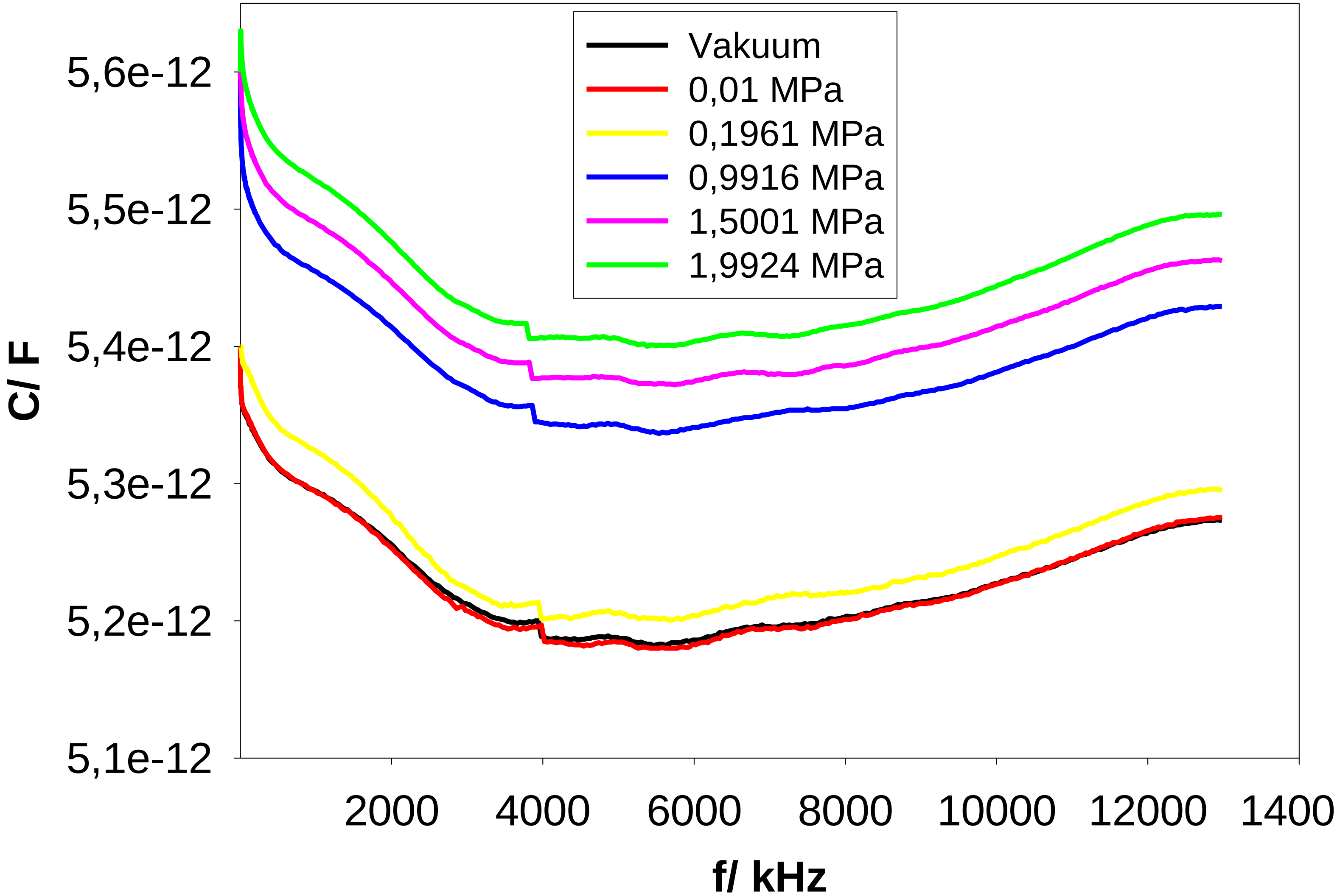
Institute of Fluid- & Thermodynamics
Prof. Dr. sc. techn. Jürgen U. KELLER



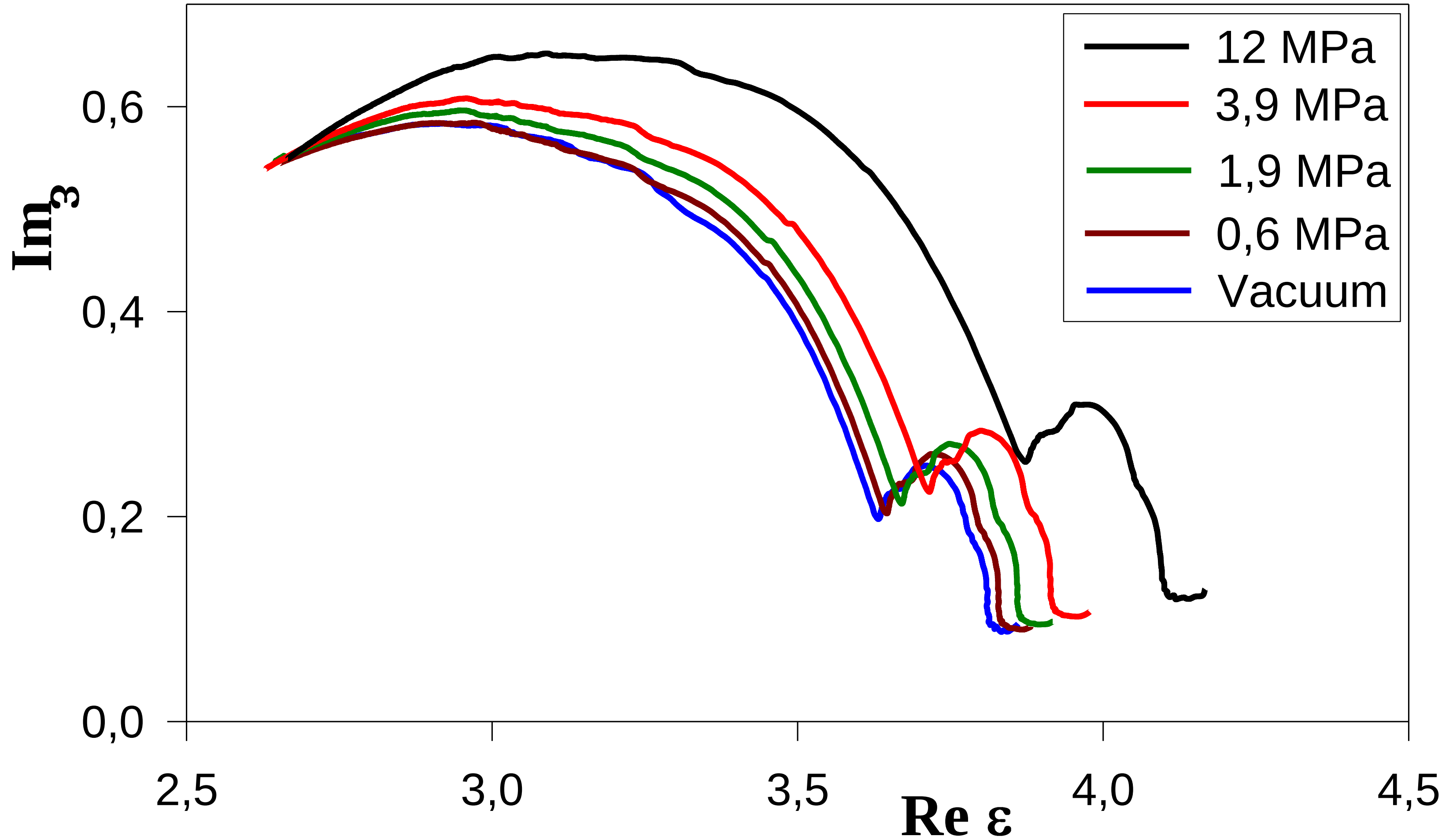
V, M $\quad m_{MG} = m^* - \left(V^* - V^{as}\right)\rho^f(p,T), \quad V^{as} \cong V_{He}$

DE $\quad \Omega_{DE} = \alpha(p,T)\, m_{MG}$

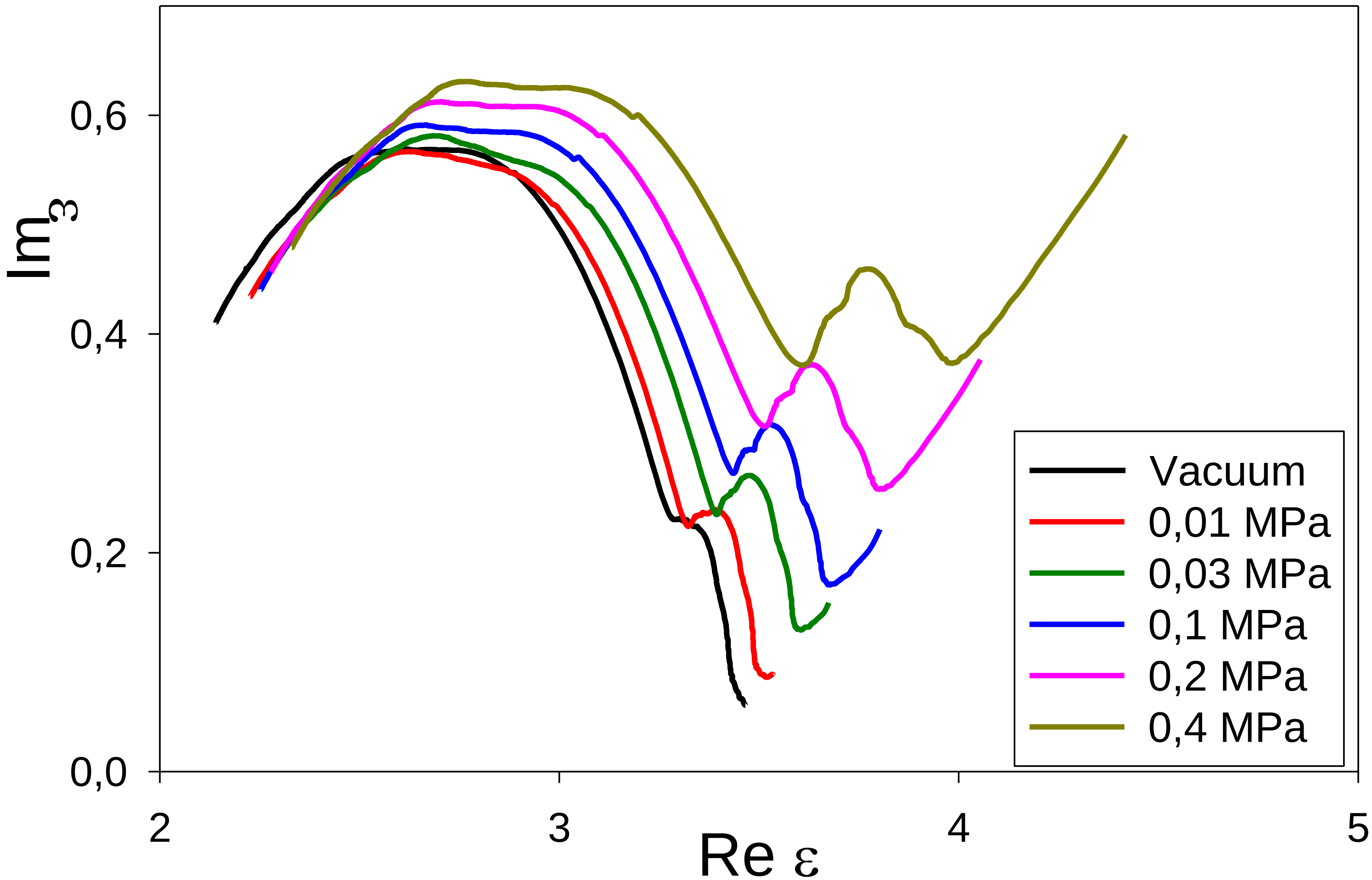
Experimental setup for volumetric-dielectric measurements



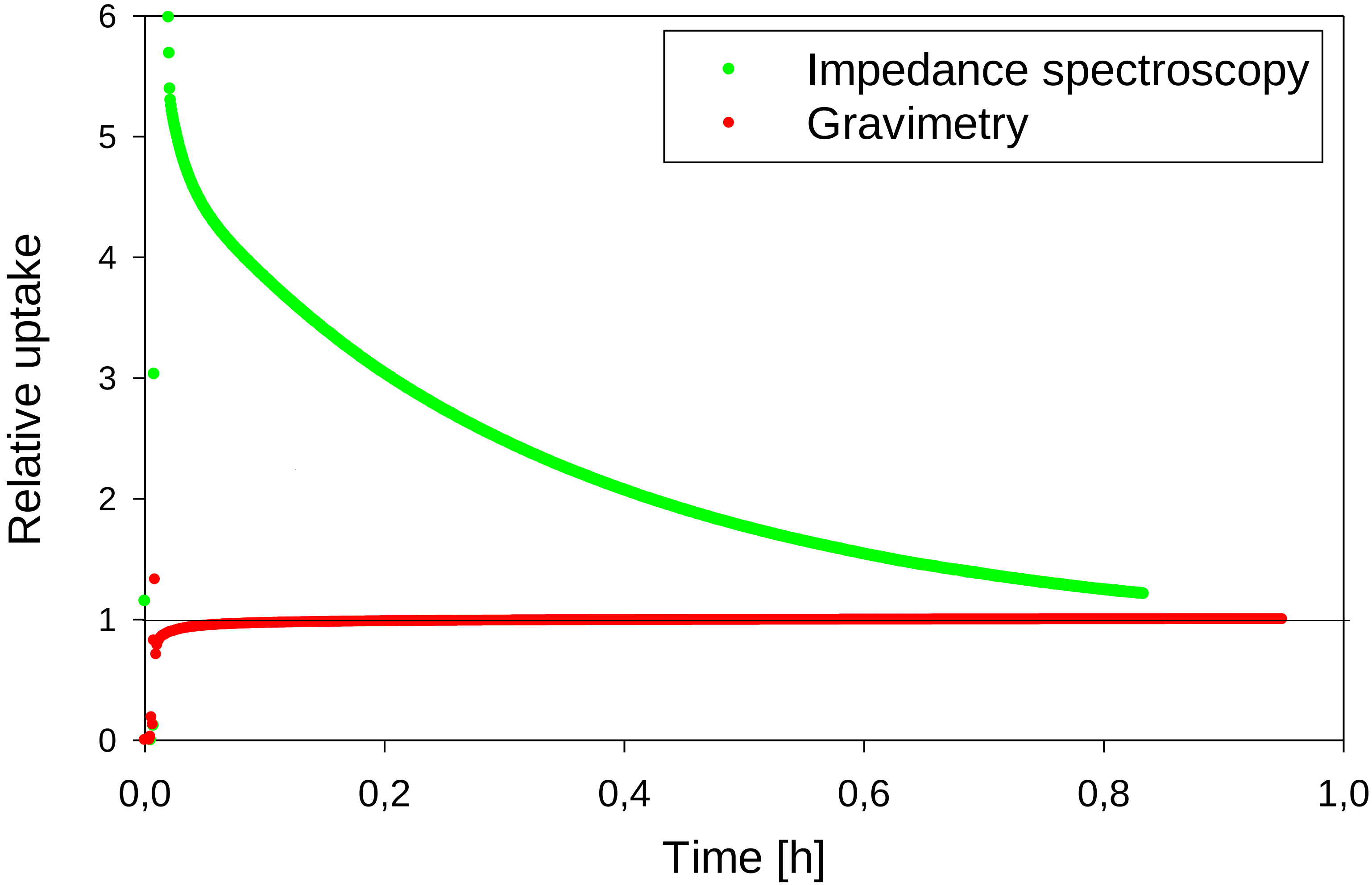
Impedance spectra of CO_2 on zeolite (DAY), T=298K



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

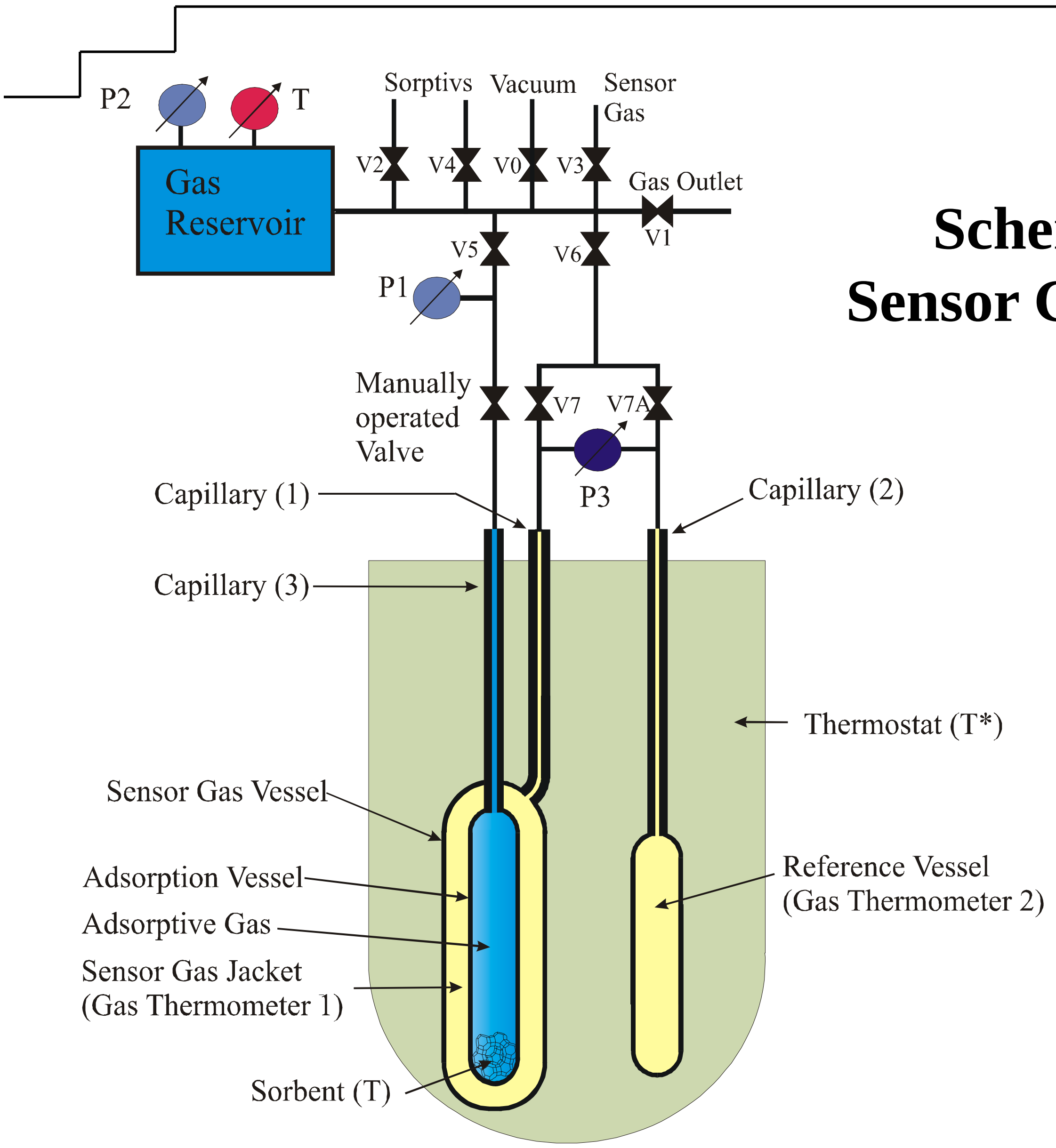


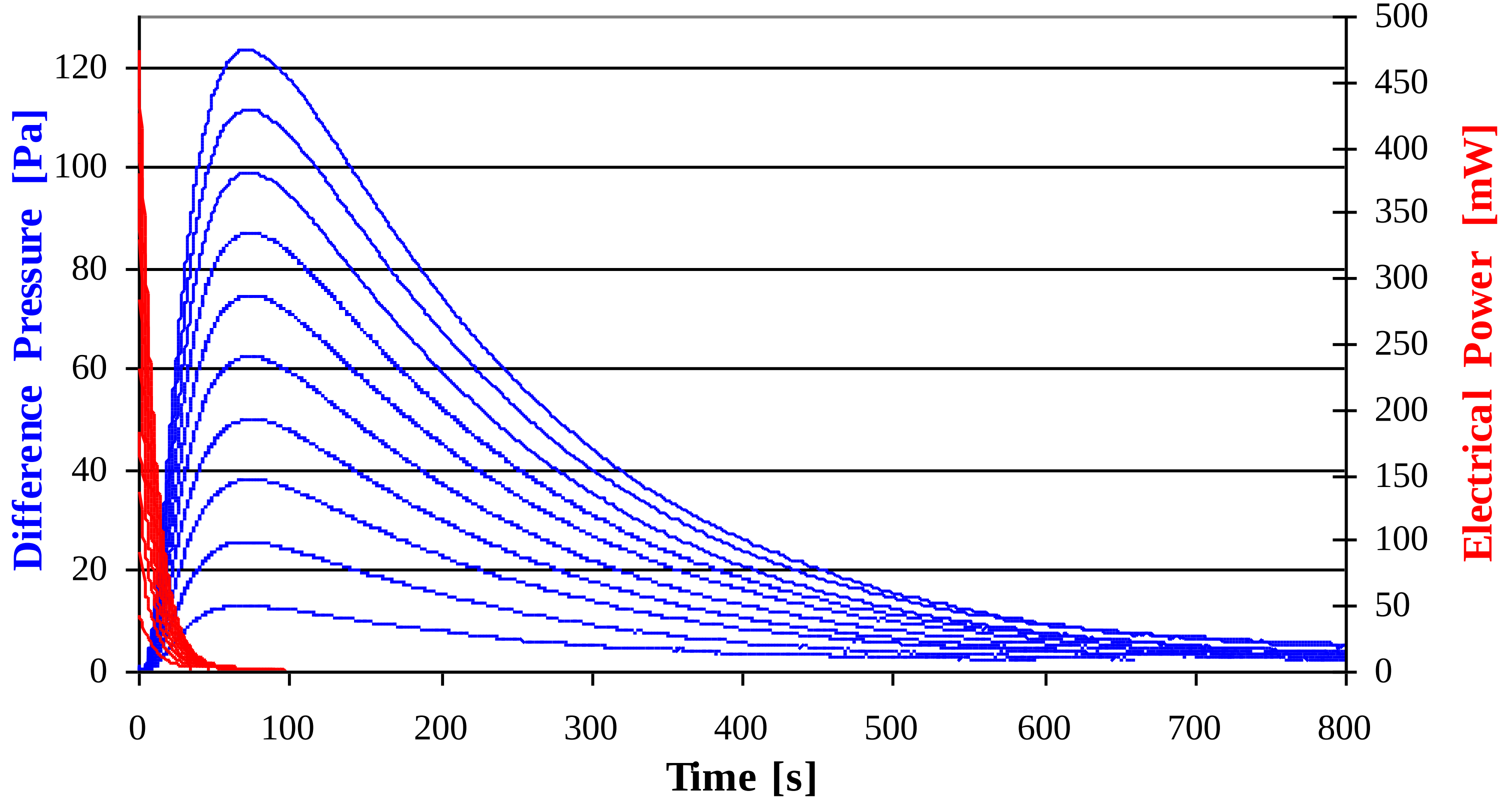
Cole-Cole-Plot for system H_2S / MS 13X, T=298K



Uptake curves of H_2S on MS 13X, T=298K

Schematic diagram of a Sensor Gas Calorimeter (SGC)

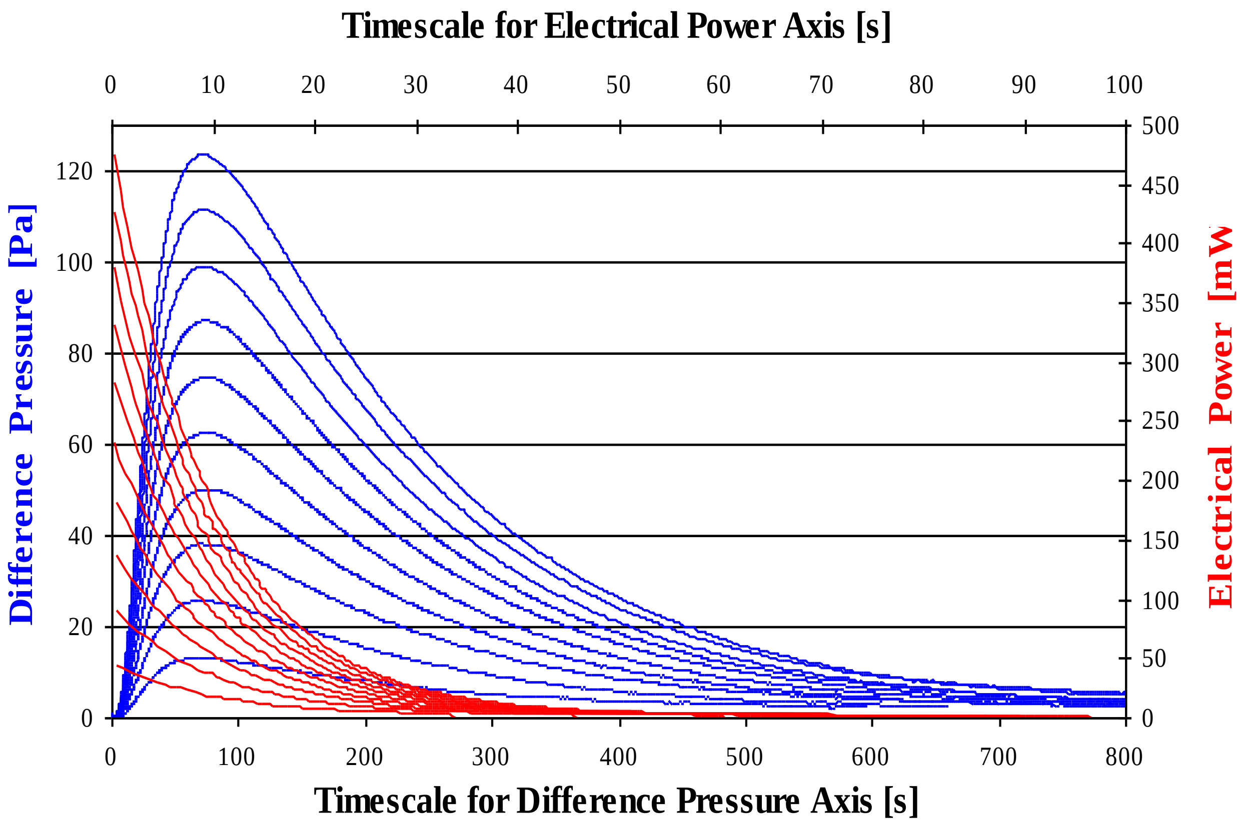




Calibration experiments in the SGC 0.5J to 5J

Sensor gas N_2 (1.6bar), T=298K, τ=10s

Ohmian heat release (red lines) → Pressure signal (blue lines)



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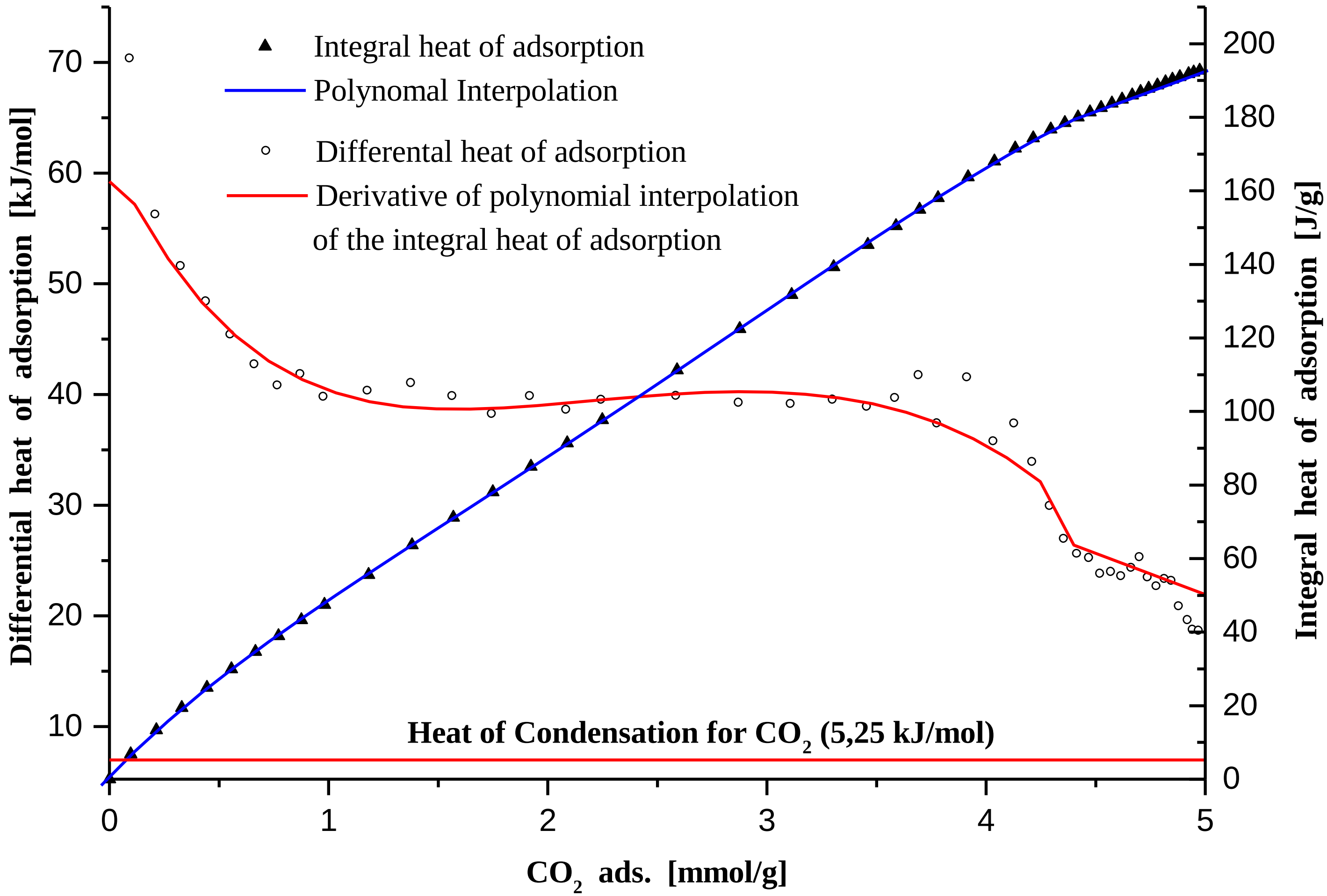

Heat of adsorption for CO_2 / Na13X, T=298K