Experimental Methods for Single- and Multi-Component Gas Adsorption Equilibria

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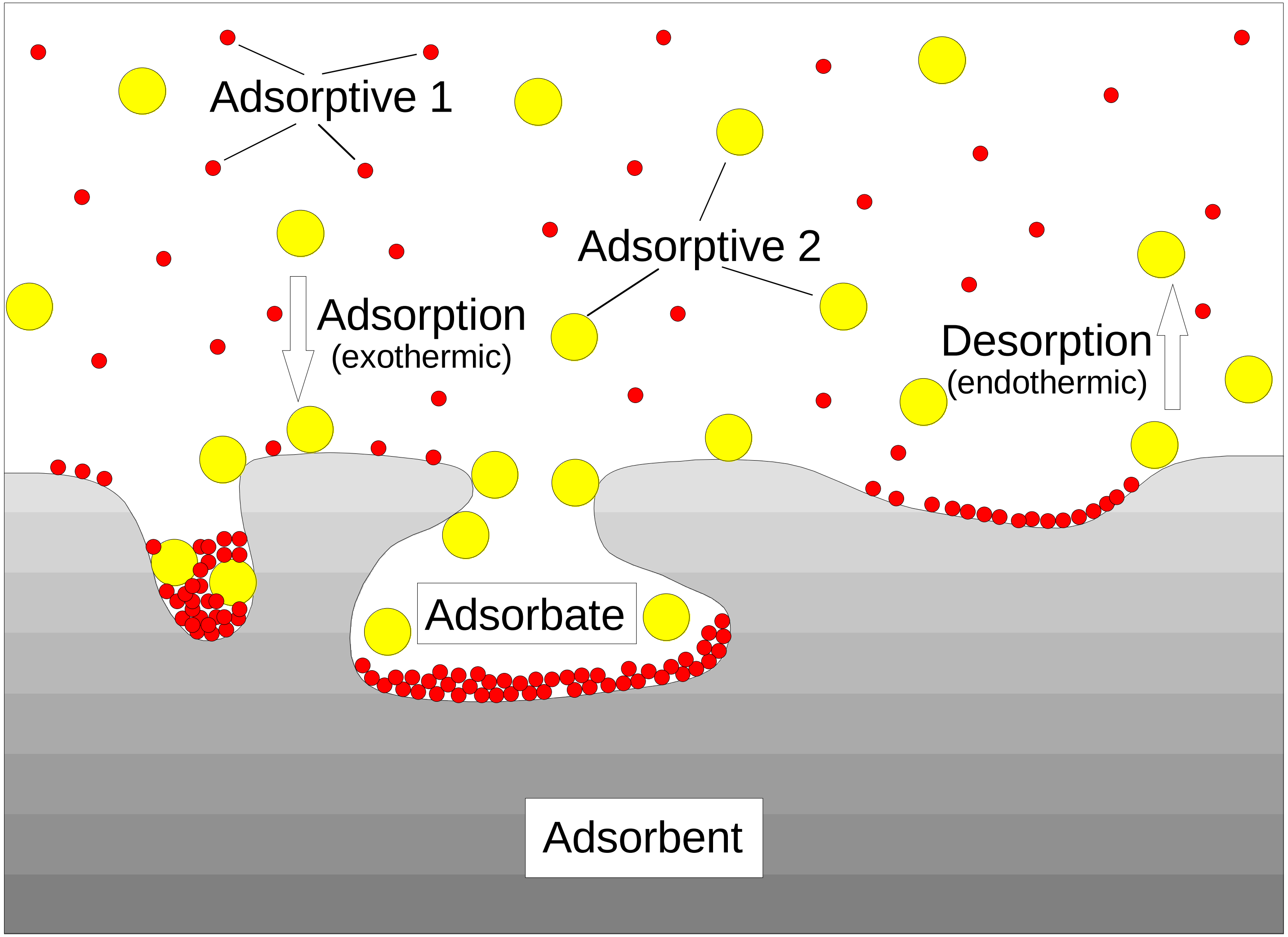
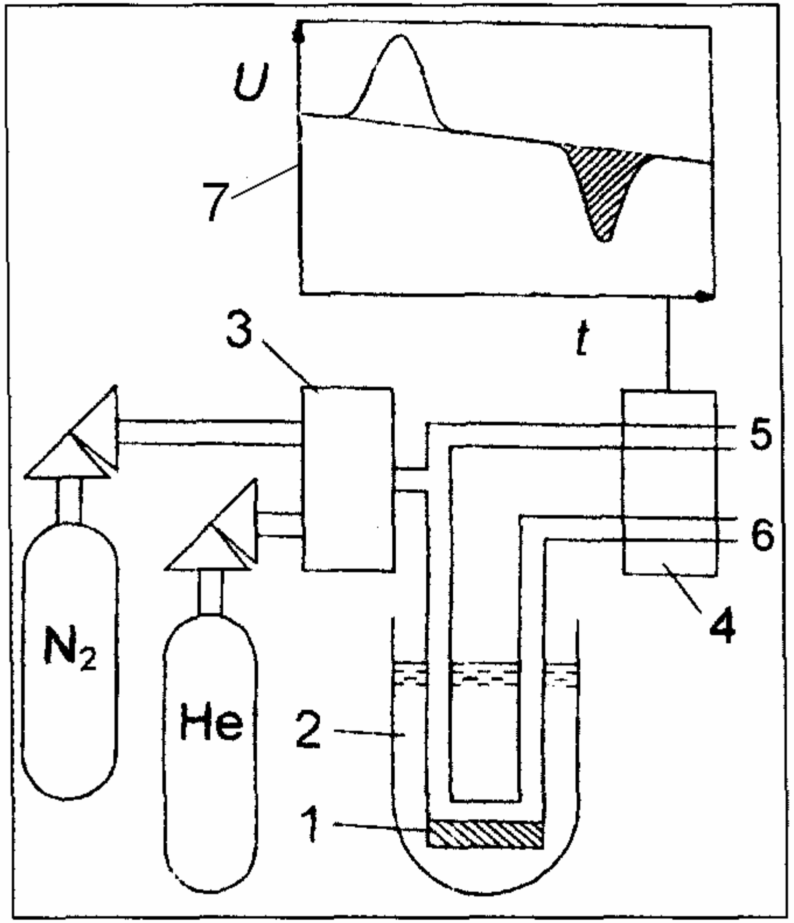

Adsorptive 1
Adsorptive 2
Adsorption
(exothermic)
Desorption
(endothermic)
Adsorbate
Adsorbent

Adsorption



1 Sample / Sorbent

2 Dewar vessel (N_2, 77 K)

3 Mixing chamber

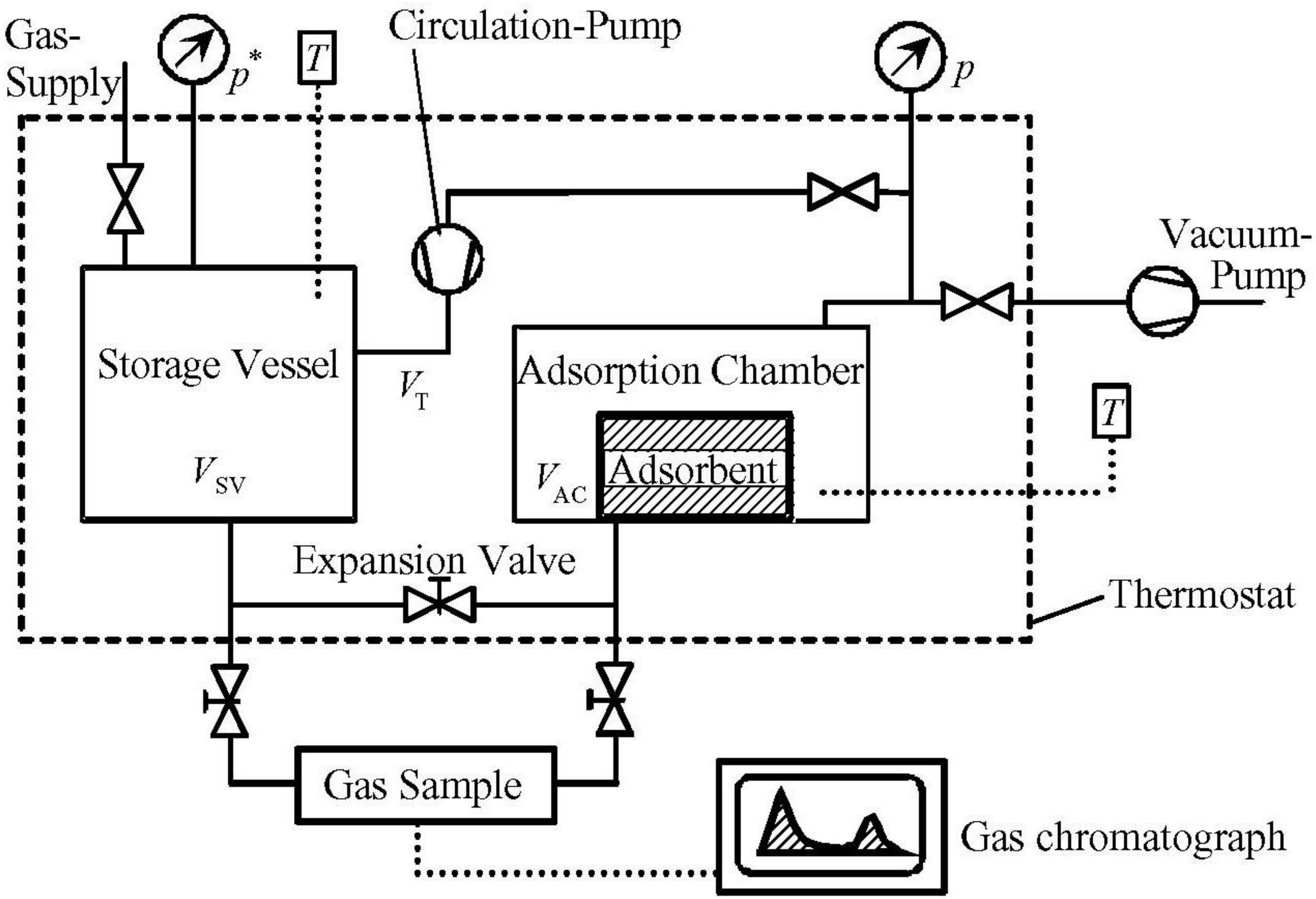
4 Thermal diffusivity detector (Δa)

5 Sorptive gas flow (original)

6 Reduced gas flow (changed)

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

Gas Flow Porosimeter (He, N_2, BET, 77 K)



Experimental setup for volumetric-chromatographic measurements of multi-component gas adsorption equilibria

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

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

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

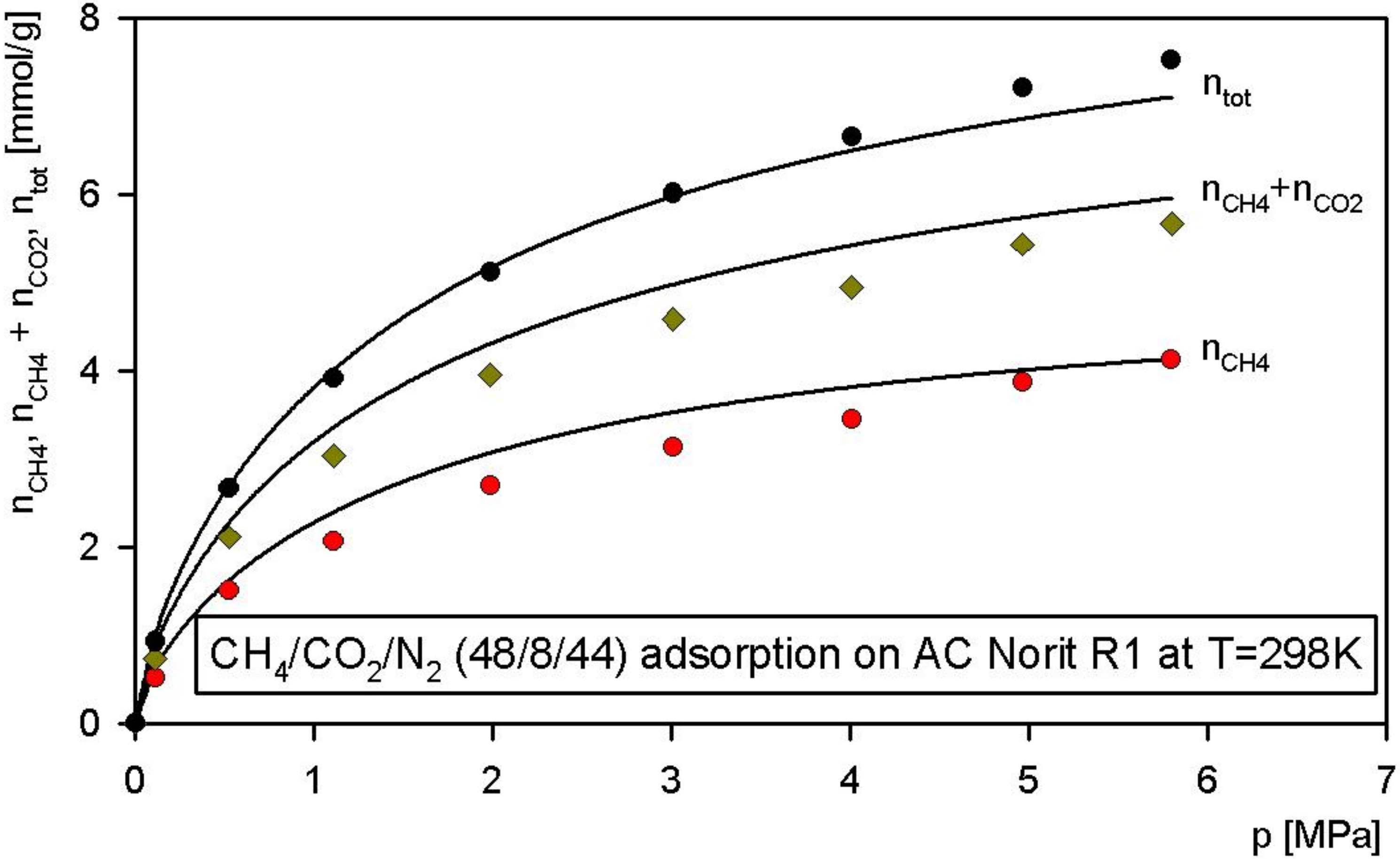
$(1-3): \underline{\Omega_i = m_i - \rho_i^f V^S}$ (4)

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

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

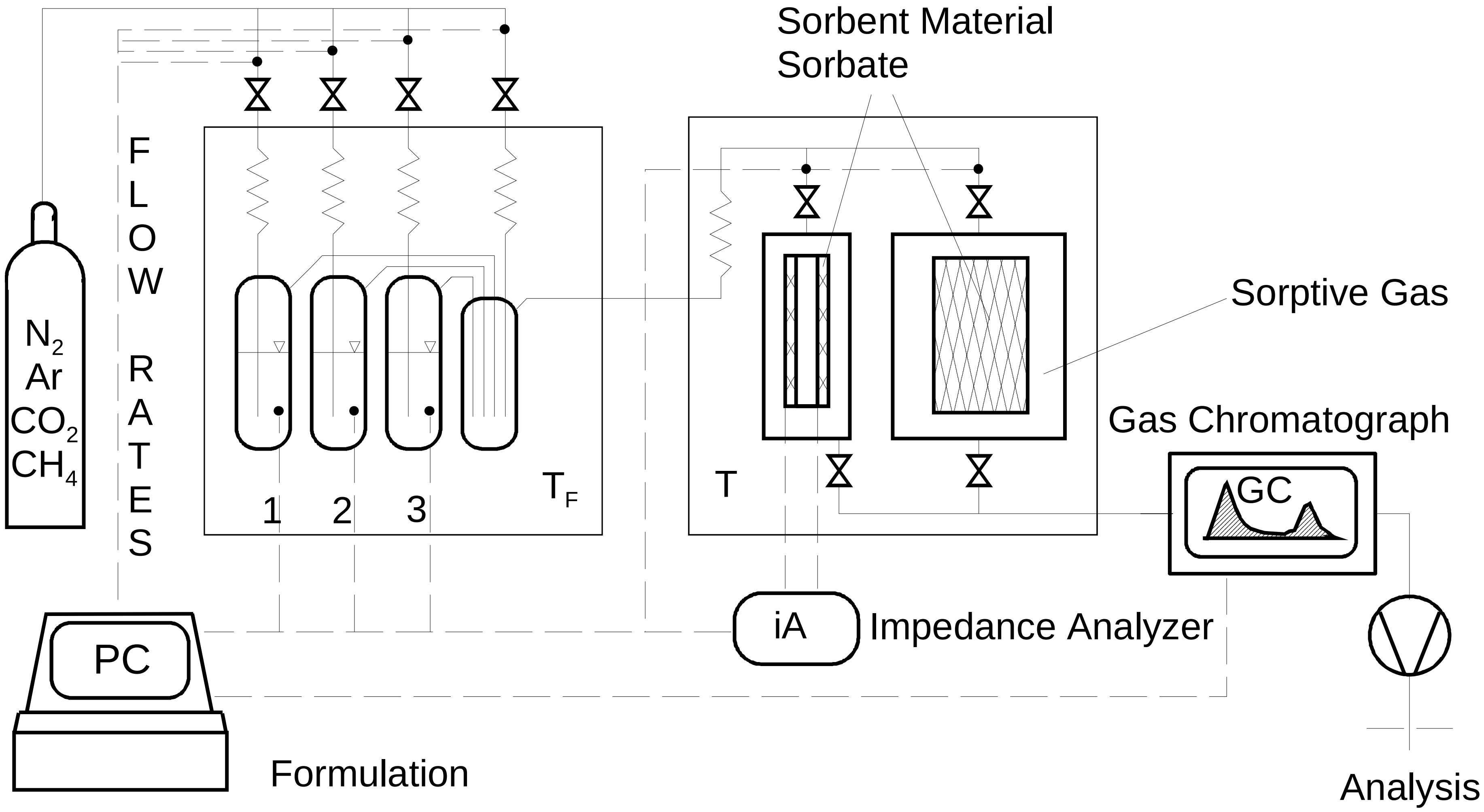
$V^S \cong V_{He}^S \quad m_i ...$ Gibbs excess mass

Volumetry / Chromatography (Closed Systems)



Adsorption equilibria of a CH4-CO2-N2 gas mixture on activated carbon ACR1. Data correlation:2-sites LAI

Gas – Solid – Adsorption Equilibria :
Volumetric – Chromatographic Analysis (N≥1)



Molar Balances $$n_i^* = n_i^f - n_i \quad , \quad i = 1 \ldots N$$

Total Amount (i) $$n_i^* = \int_0^\infty \left(\dot{n}_{i\,in} - \dot{n}_{i\,out} \right) dt$$

$$= \int_0^\infty \left(y_{i\,in} \dot{n}_{i\,in} - y_{i\,out} \dot{n}_{i\,out} \right) dt$$

Adsorptive's Amount (i) $$n_i^f = y_{i\,in} n^f$$

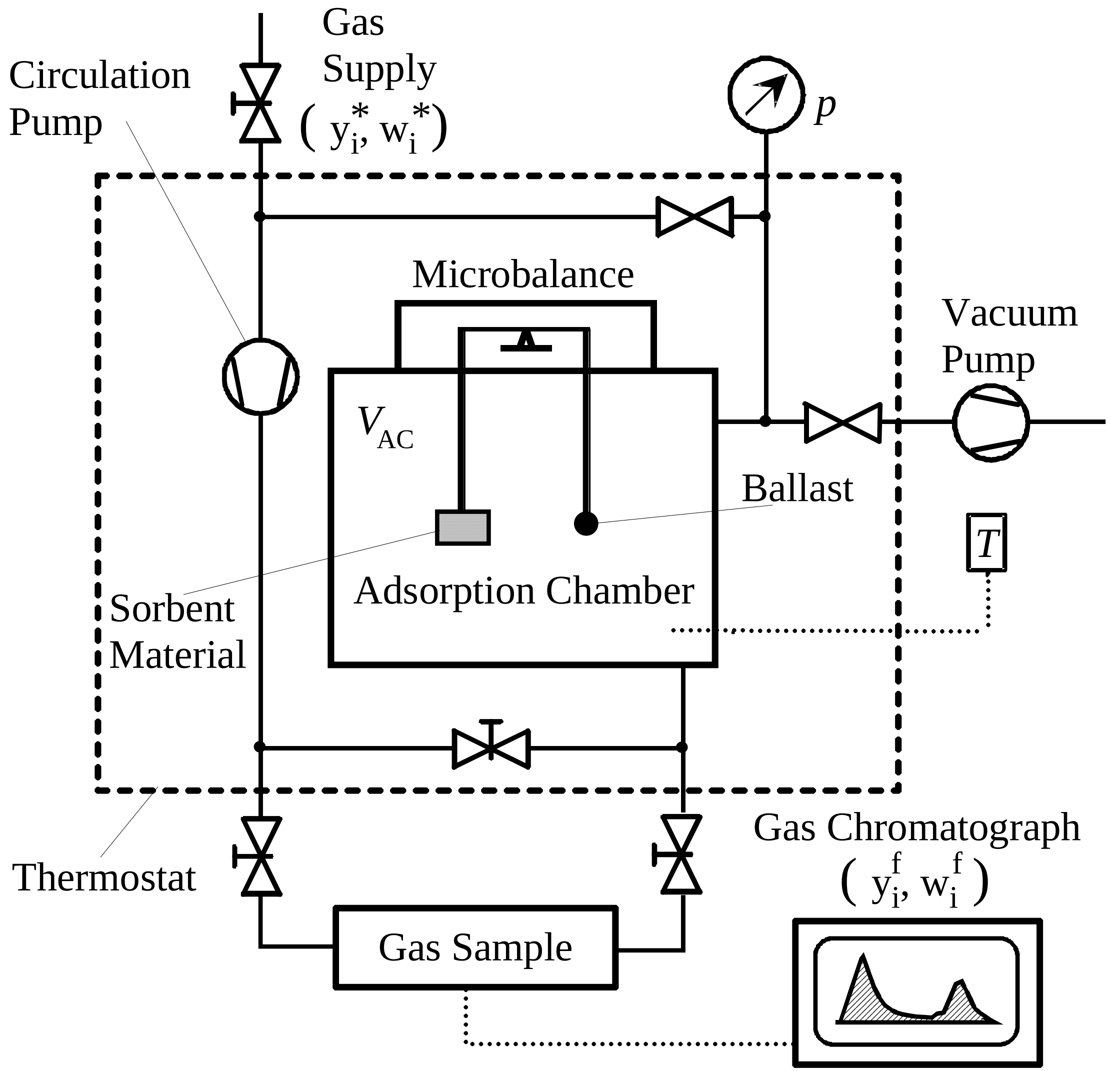
$$pV^f = n^f \mathbb{R} T$$

Geometry, He-Volume $$V^f = V^* - \left(V^s \right)_{He}$$

$$\dot{n}_{in} = \dot{n}_{CG} + \sum_k^N \dot{n}_{k\,in} \quad , \quad y_{k\,in} = \dot{n}_{k\,in} / \dot{n}_{in}$$

$$\dot{n}_{out} = \dot{n}_{CG} + \sum_k^N \dot{n}_{k\,out} \quad , \quad y_{k\,out} = \dot{n}_{k\,out} / \dot{n}_{out}$$

Volumetry / Chromatography (Open Systems)



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

Total mass of gas supplied to system:

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

Sorptive mass / mole number:

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

$$n^f = \frac{p\left(V_{AC} - V_{He}^s\right)}{R\,T\,Z\left(p, T, y_1^f \ldots y_N^f\right)} \qquad (3)$$

Microbalance:

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

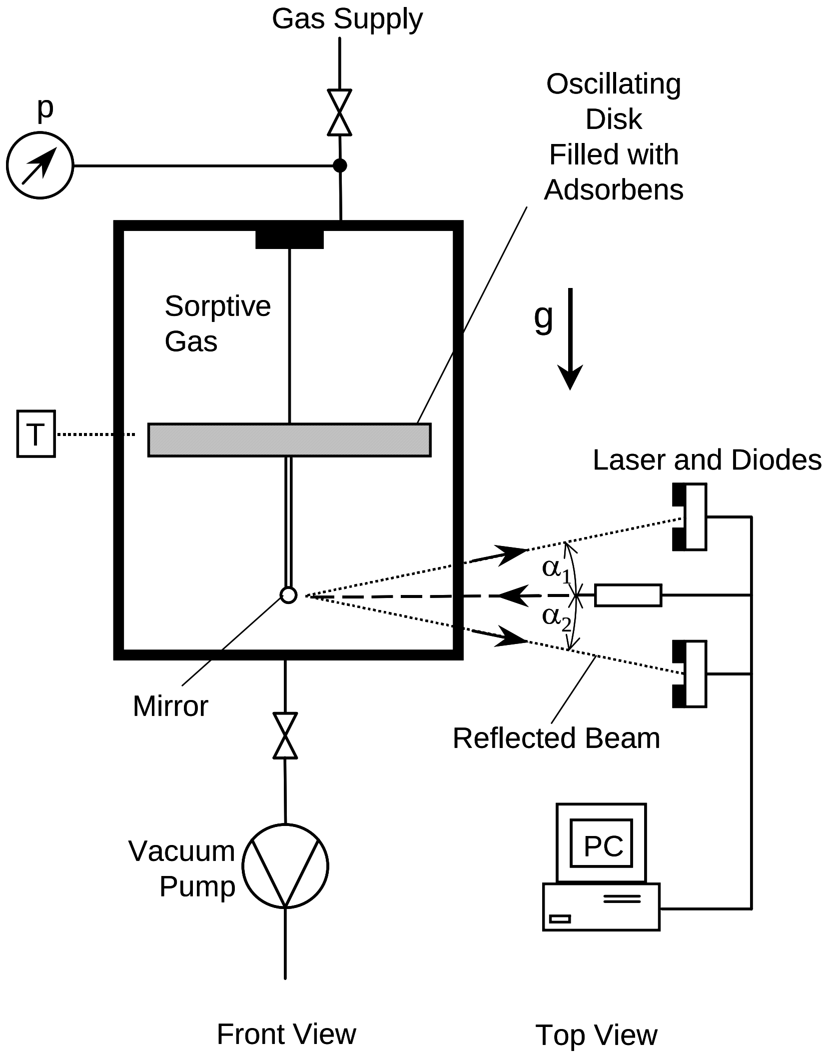
$$m^a = \Omega + \frac{m^f}{\left(V_{AC} - V_{He}^s\right)} V_{He}^s \qquad (4A)$$

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

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

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

Gravimetry / Chromatography (N ≥ 1)



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.

Ideal Pendulum $\left(m^s, m\right)$

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

Physical Pendulum $\left(m^*, m^s, m\right)$

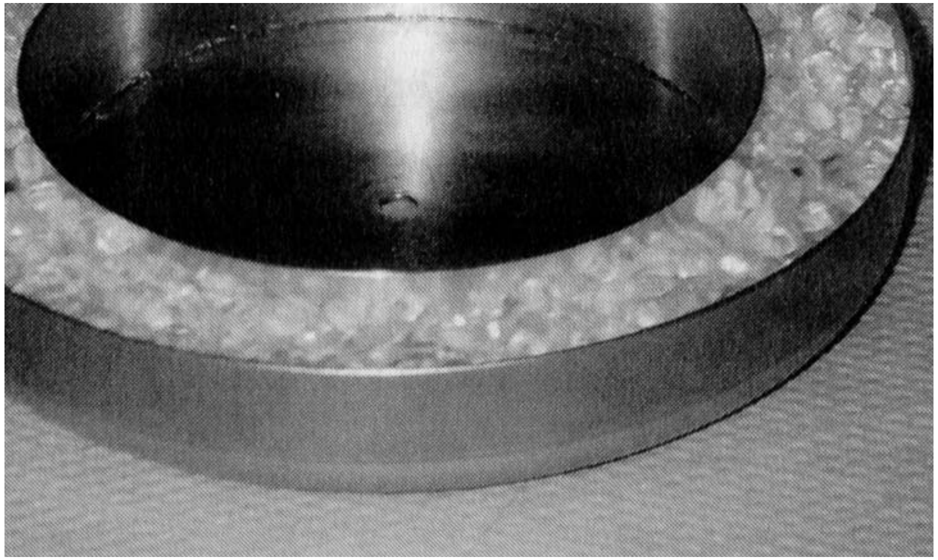
$$\frac{m}{m^s} = \frac{\frac{1+\Delta_0^2}{1+\Delta_E^2}\left(\frac{\omega_0}{\omega_E}\right)^2 - 1}{1-\frac{\Delta_0\omega_0}{\Delta^*\omega^*}}$$

ω^*, Δ^*... empty pendulum $\left(m^*\right)$, vacuum

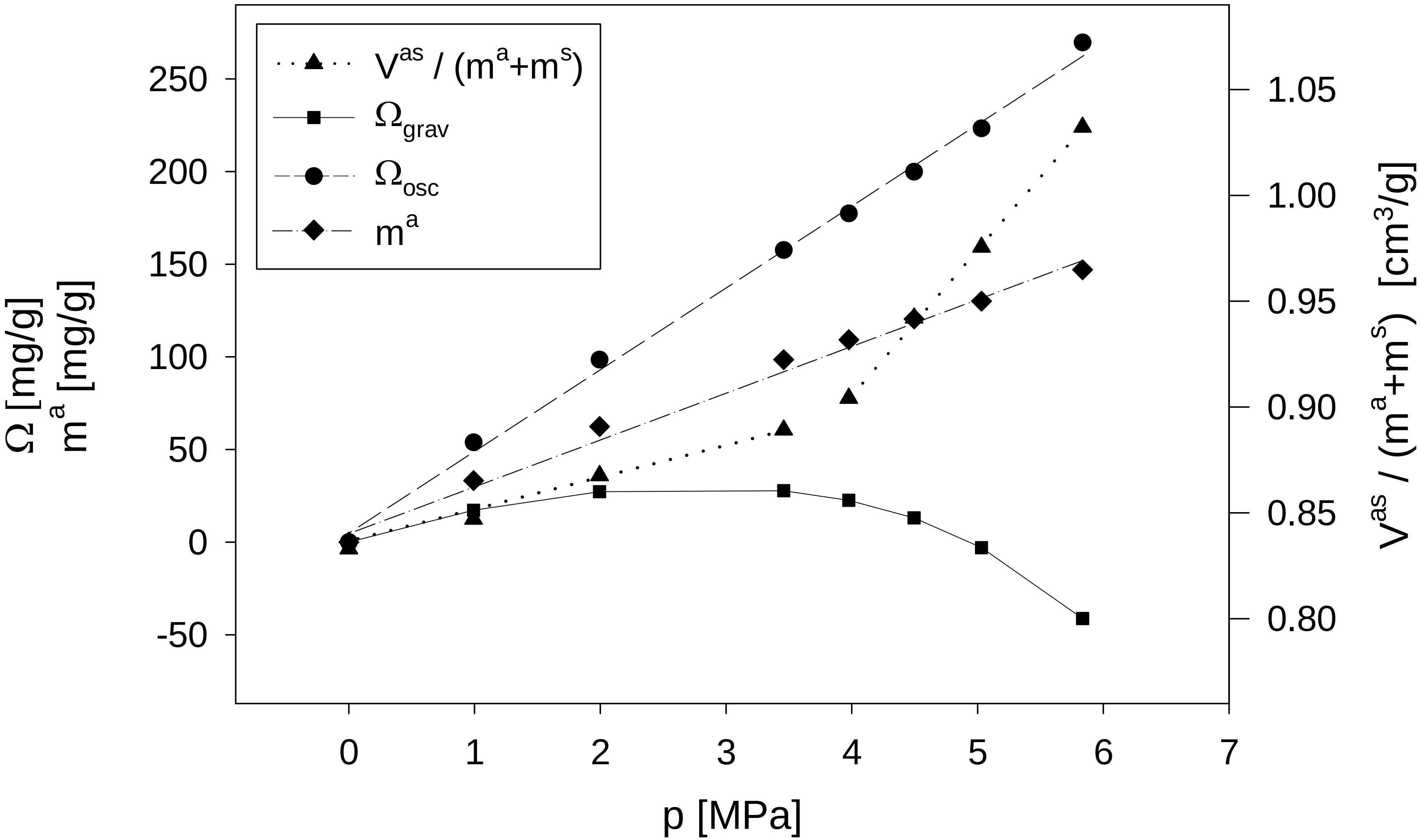
ω_0, Δ_0... pendulum and adsorbent $\left(m^*, m^s\right)$, vacuum

ω_E, Δ_E... pendulum, adsorbent, adsorbate $\left(m^*, m^s, m\right)$, gas

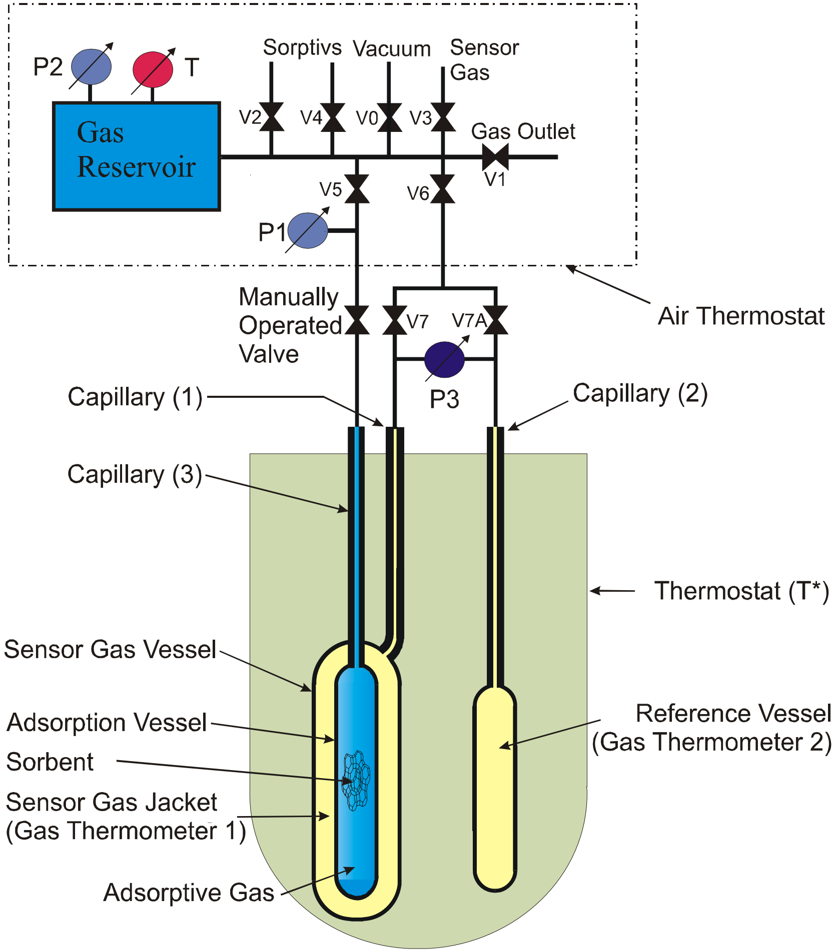
Oscillometric Measurements of Gas Adsorption Equilibria. Theory



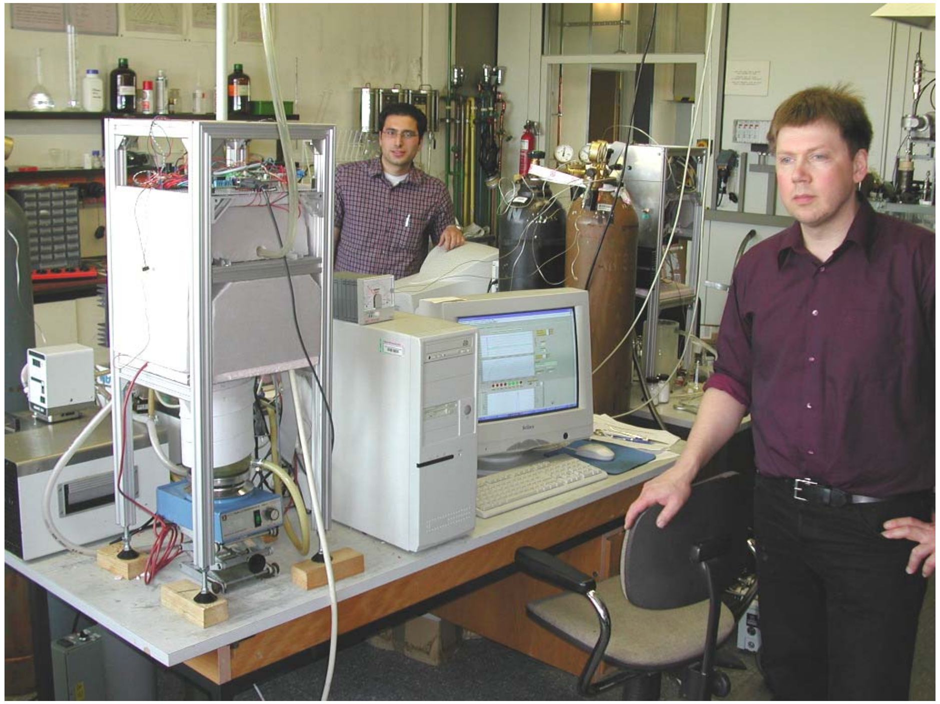
Rotational pendulum and ring slit filled with polycarbonate pellets



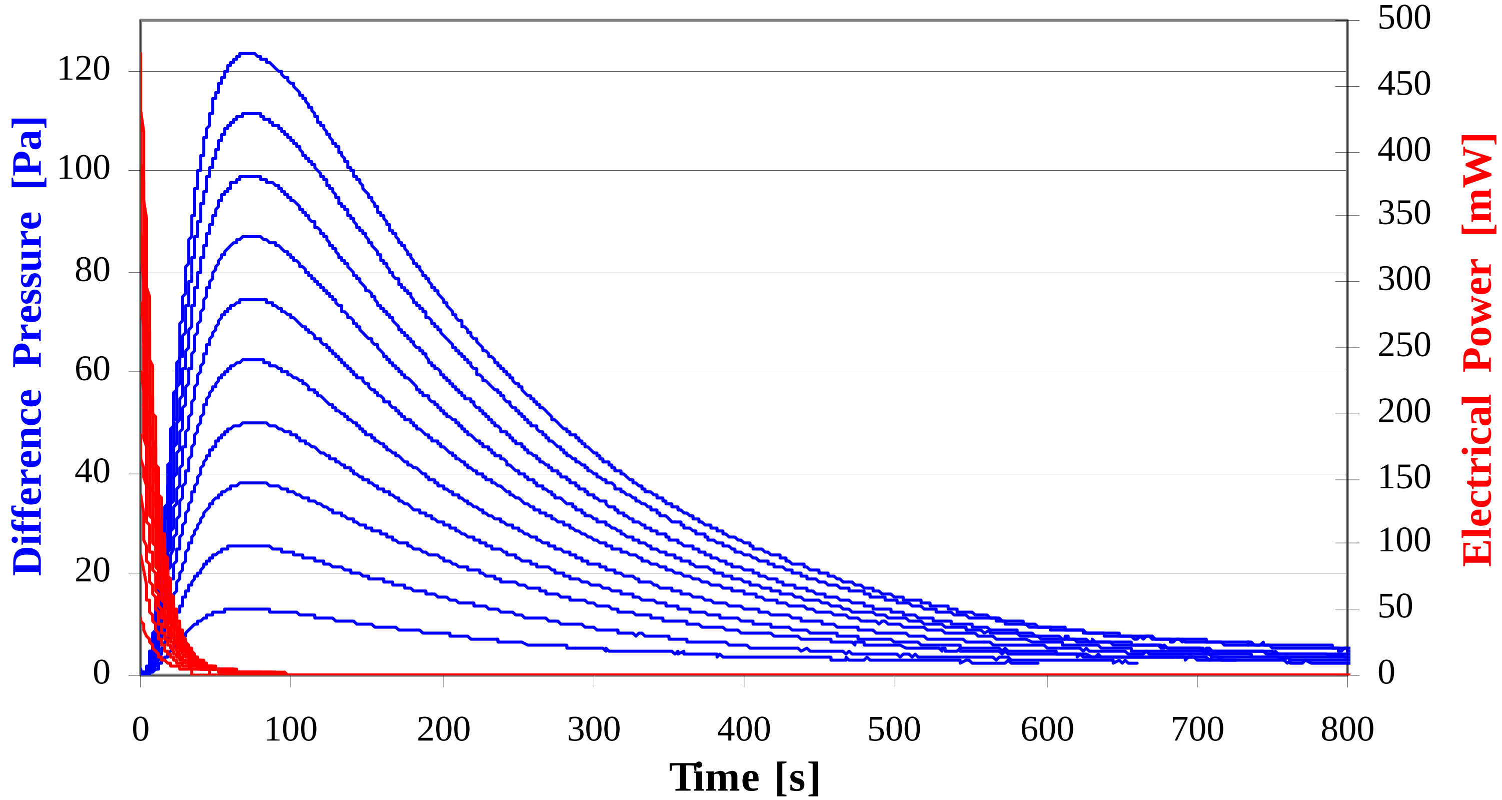
Swelling and sorption isotherm of polycarbonate / CO_2 at 293 K



Schematic diagram of a sensor gas calorimeter (SGC)



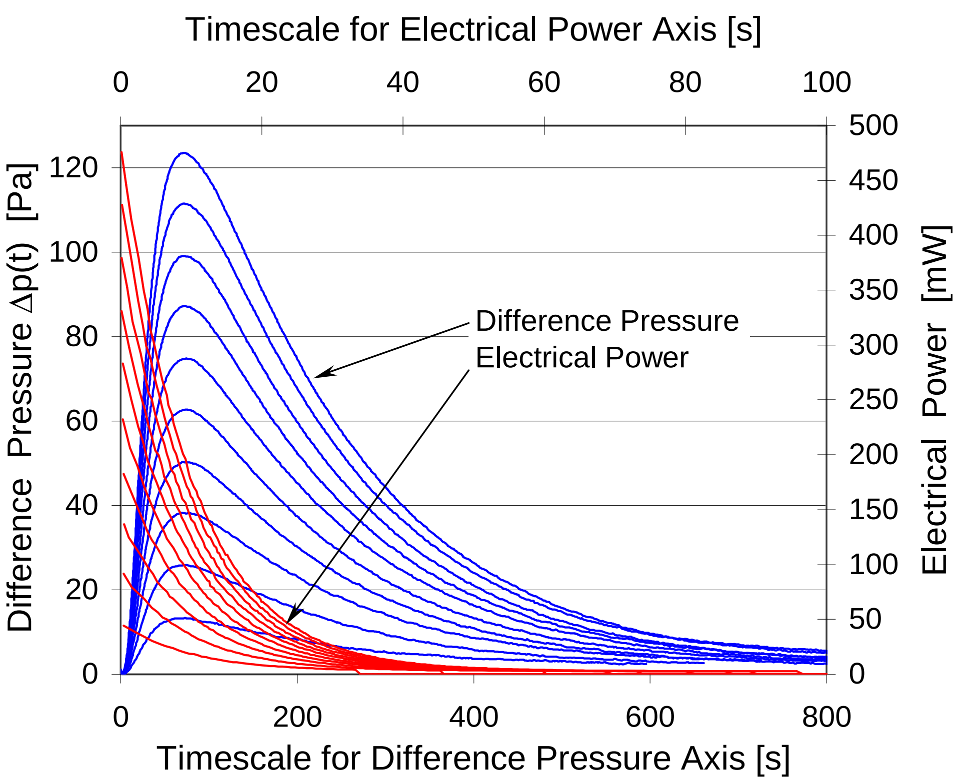
Sensor gas calorimeter (SGC) for simultaneous measurements of adsorption isotherms and enthalpies.



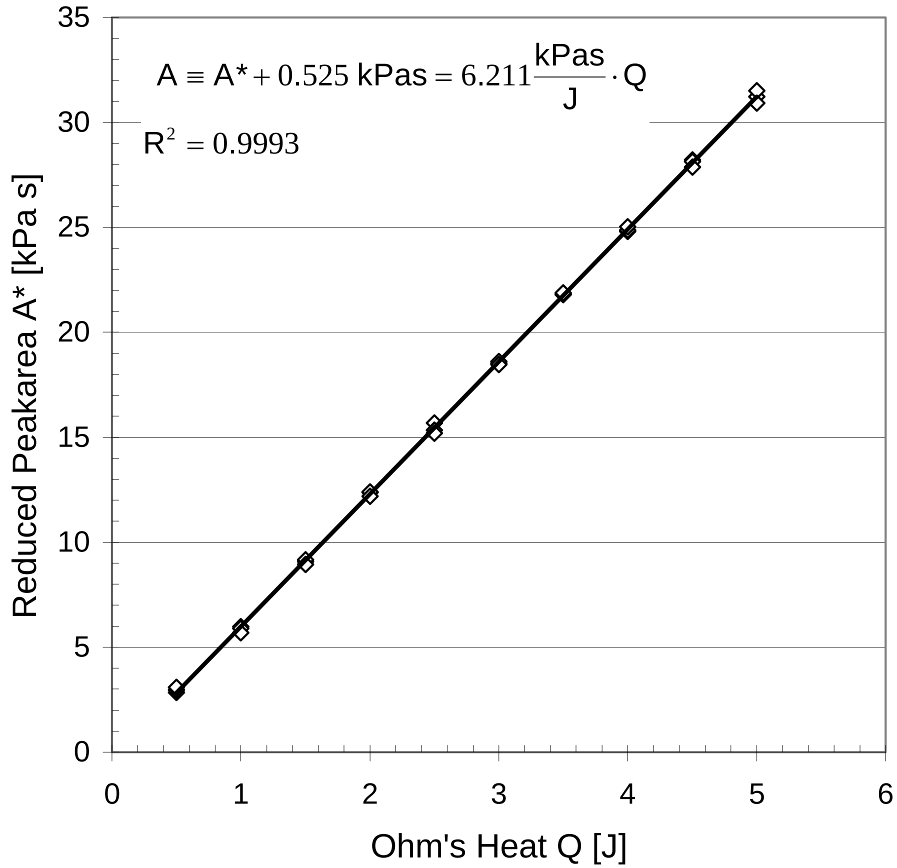
Calibration experiments in the SGC 0.5J to 5J

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

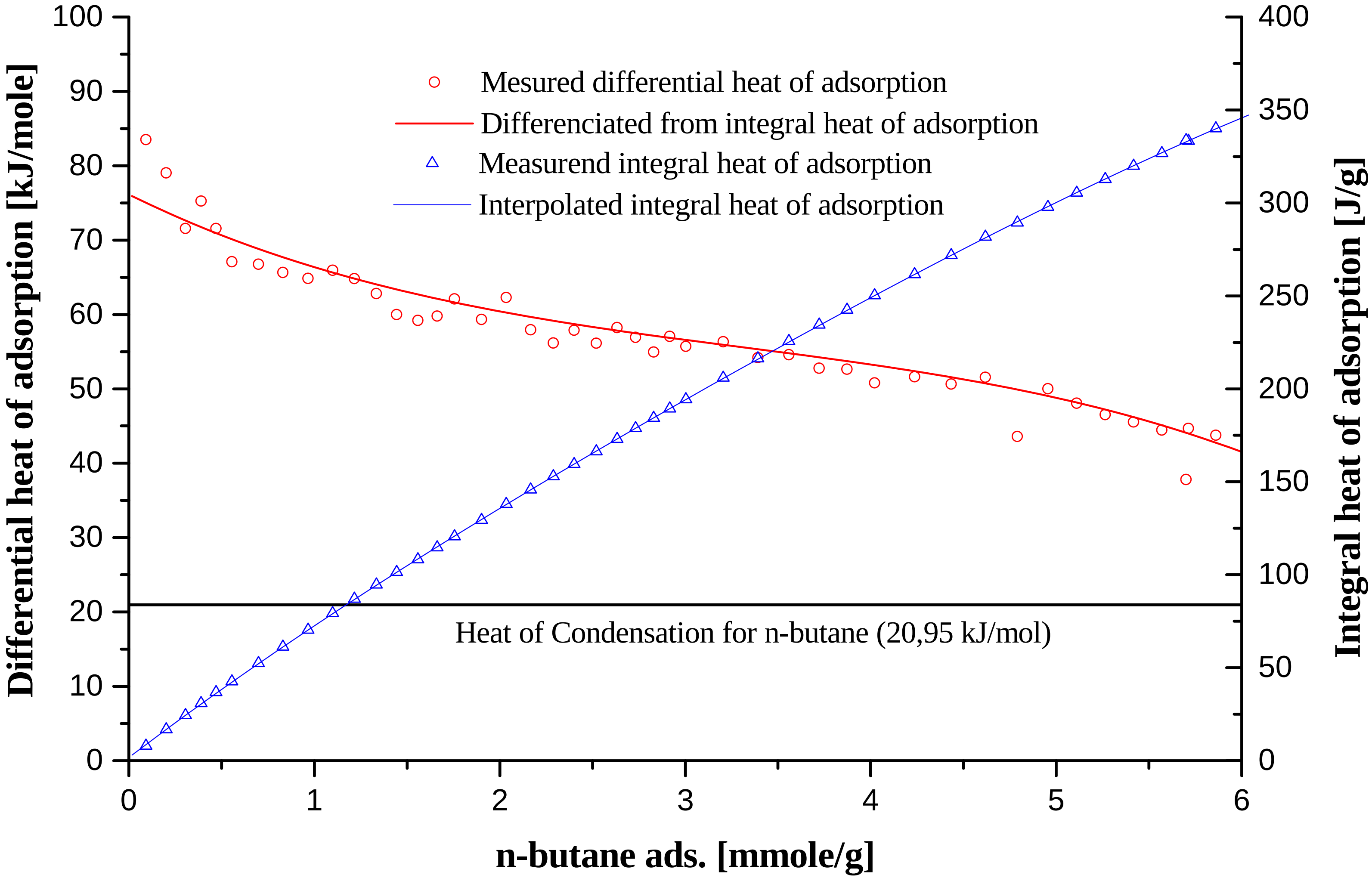
Ohm's heat release (red lines) $\rightarrow$ Pressure signal (blue lines)



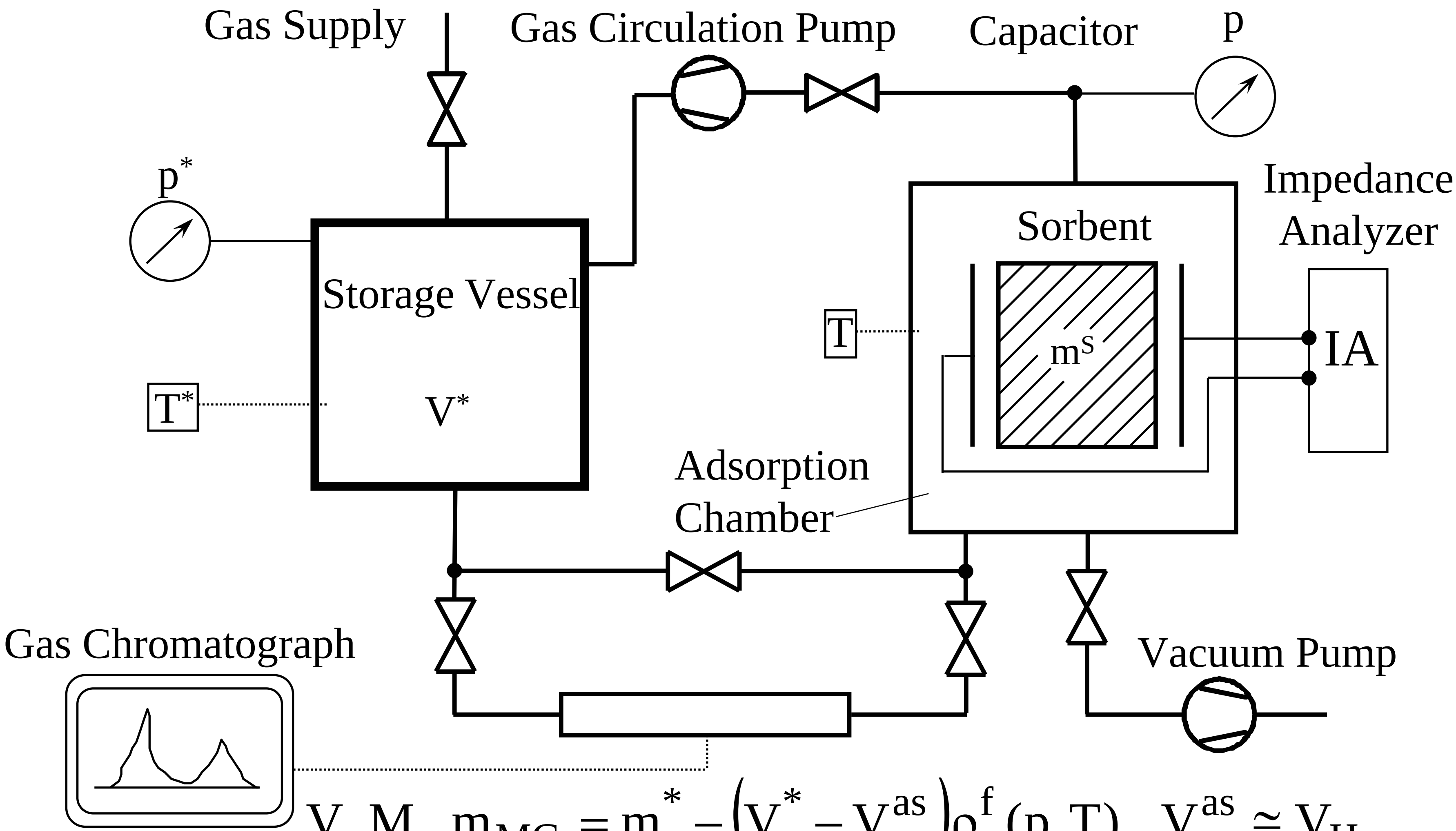
Correlation
Peak Area (A / Pas)
Qhm's heat (Q / J)



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



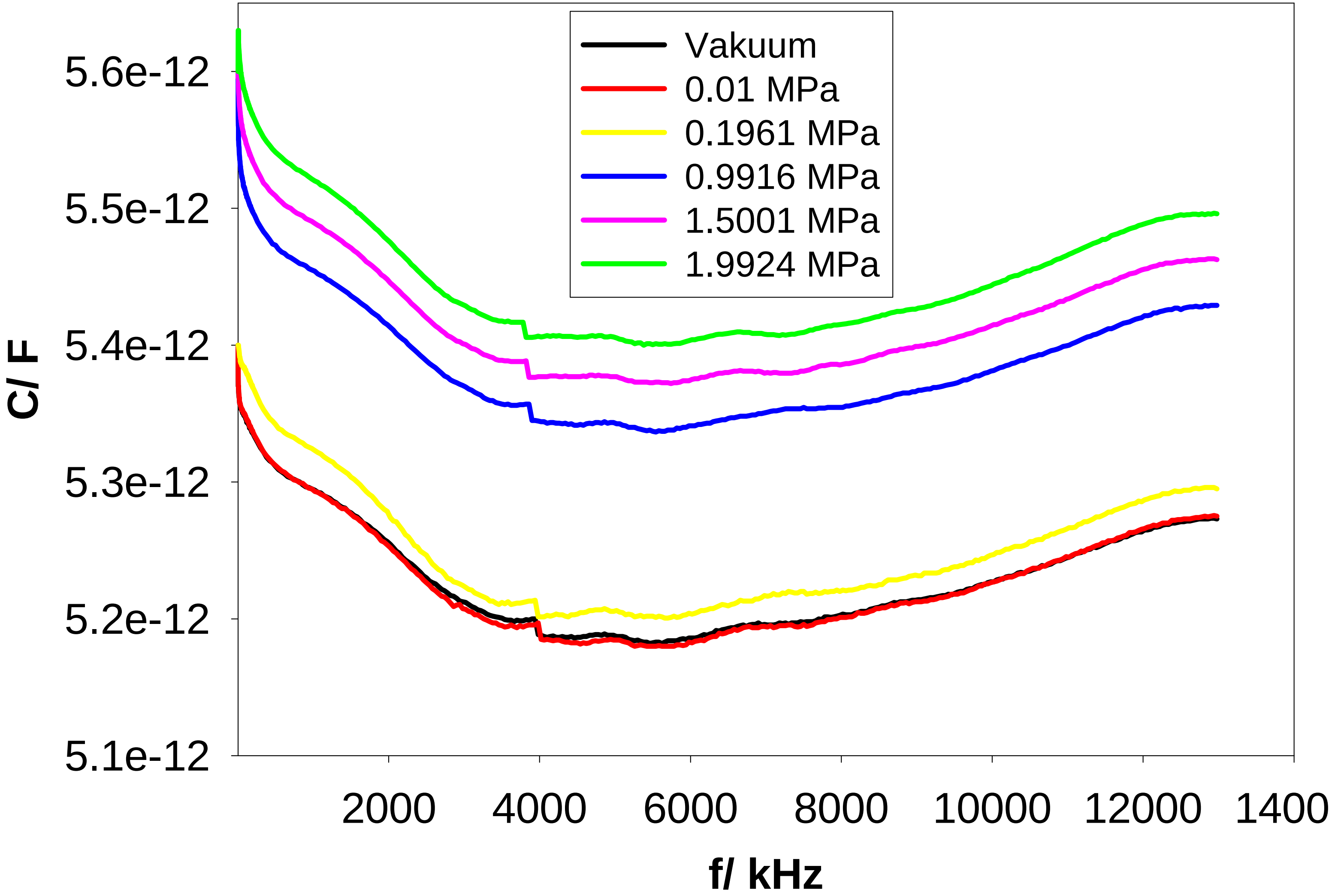
Differential and integral heat of adsorption for activated carbon AC BAX 1500 / n-butane (C_4H_{10}) at 298K



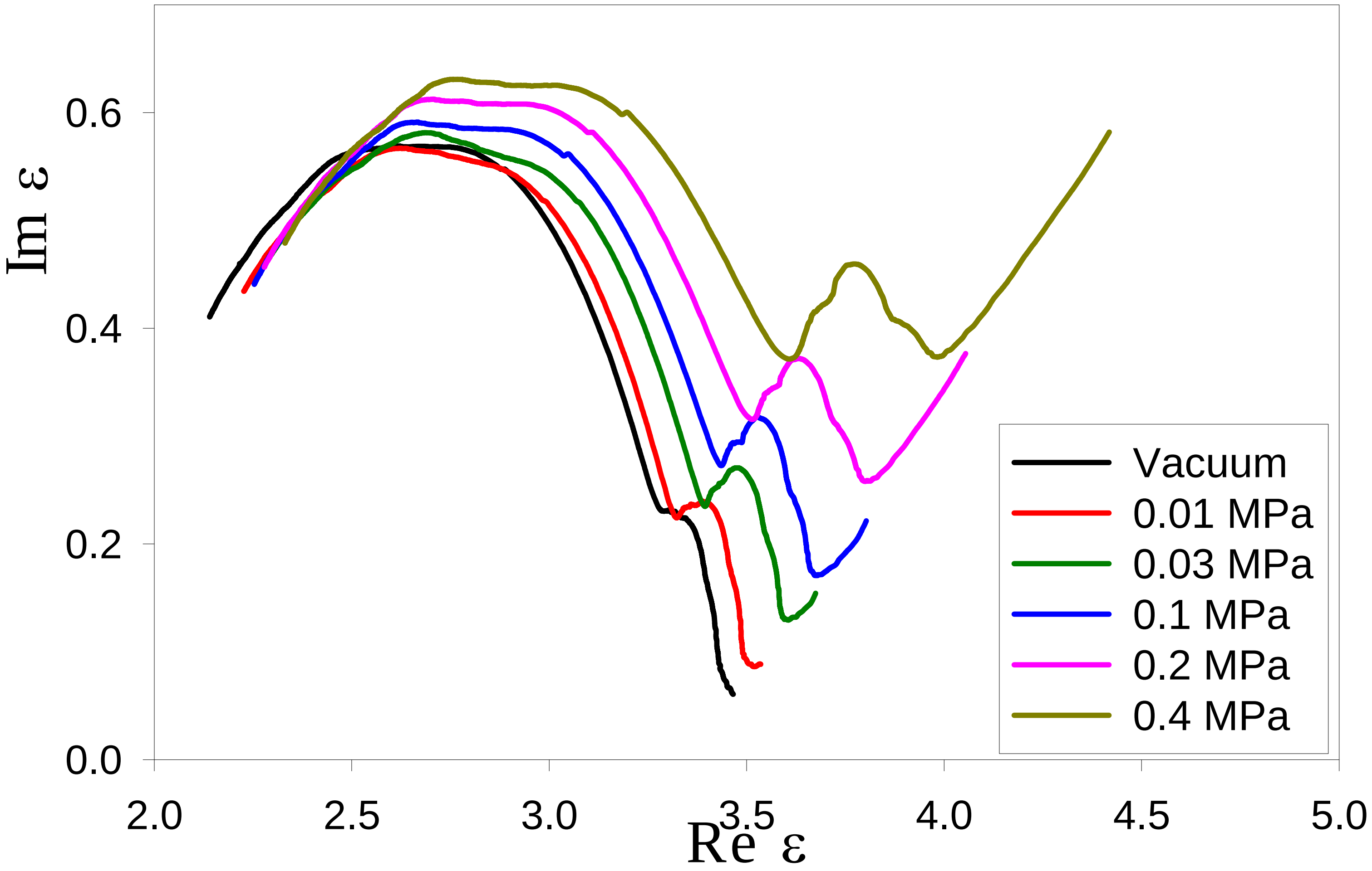
V, M $m_{MG} = m^* - \left(V^* - V^{as}\right)\rho^f(p,T)\,,\ V^{as} \cong V_{He}$

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

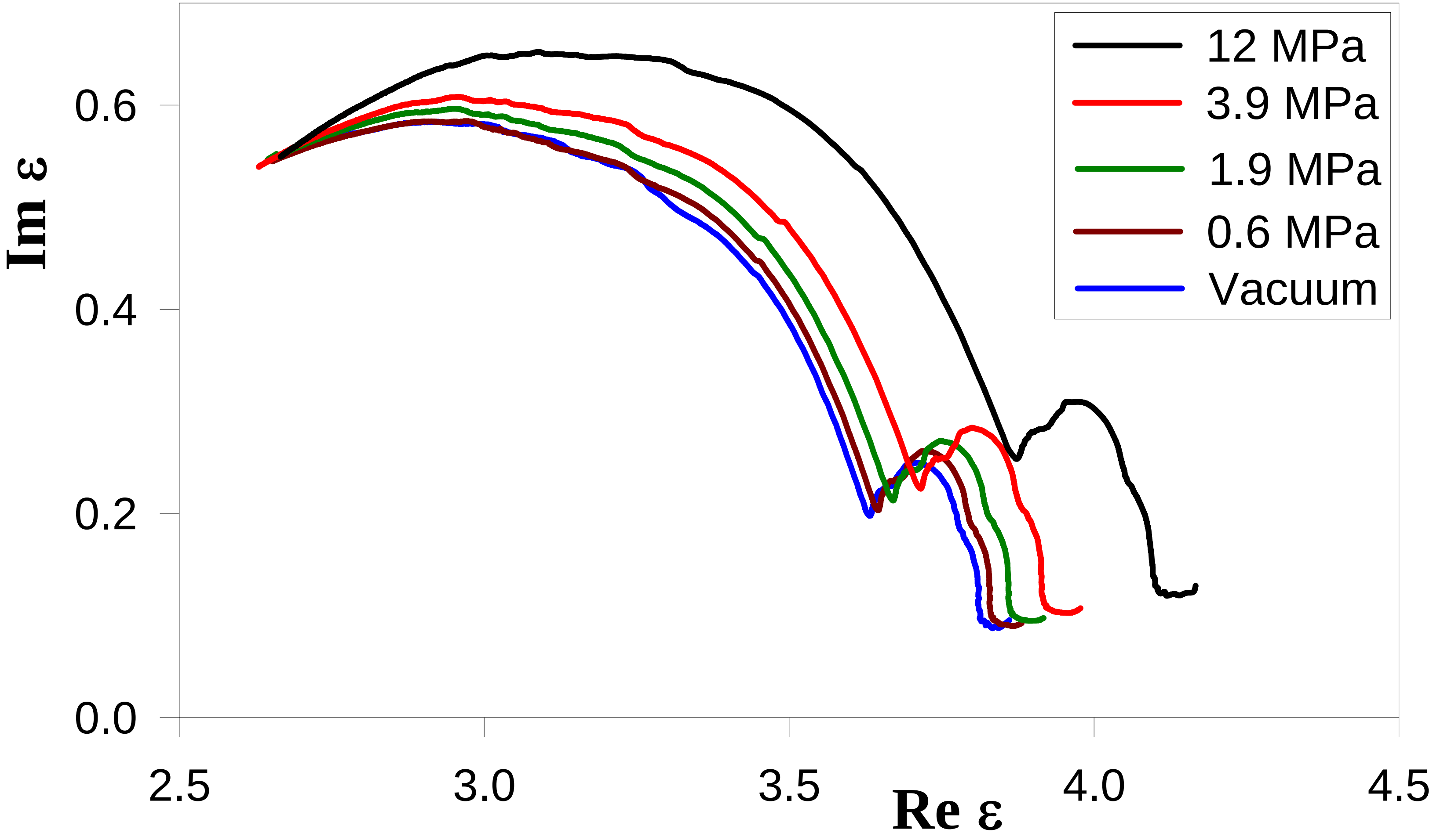
Experimental setup for volumetric-dielectric measurements



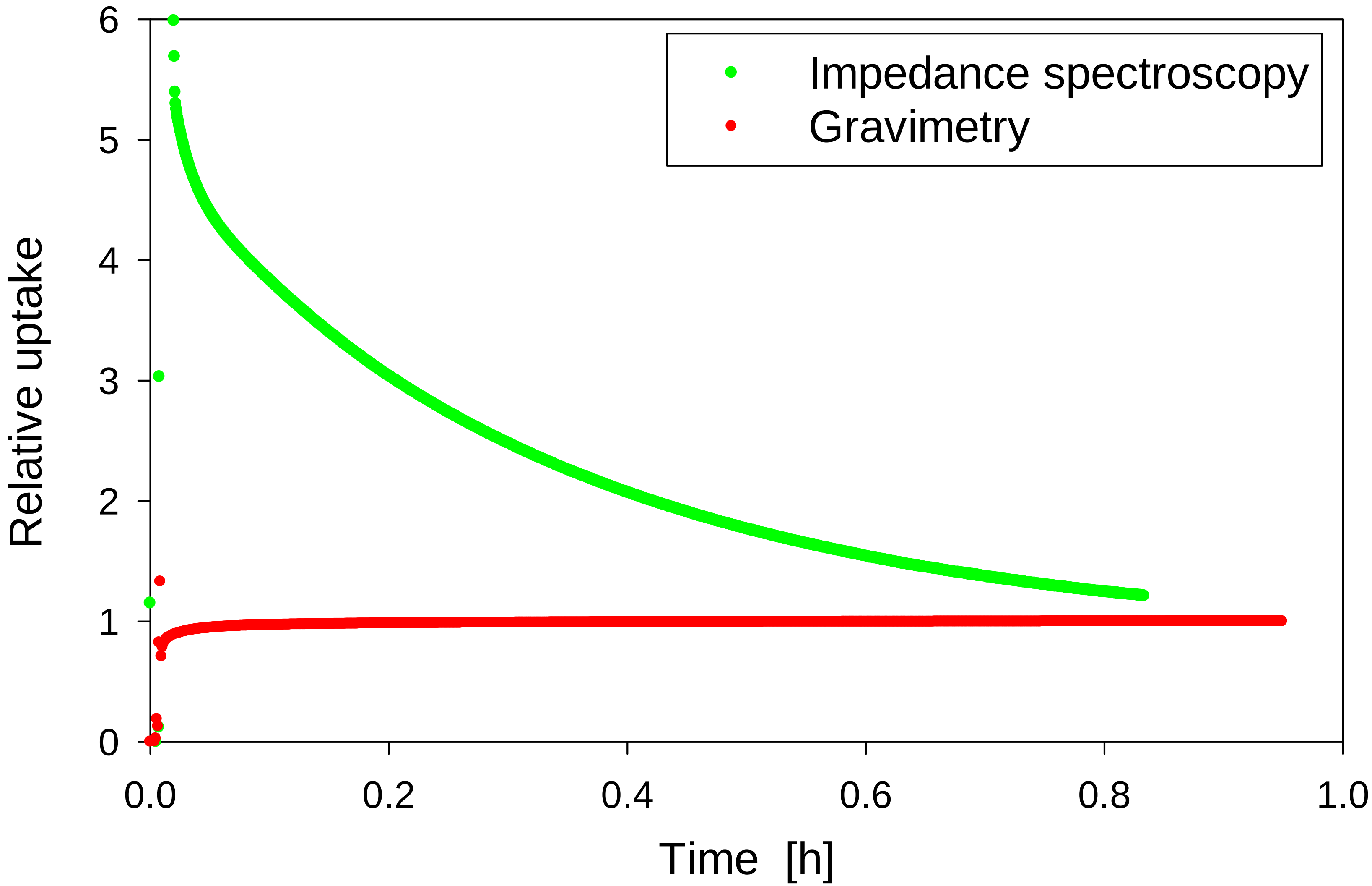
Impedance spectra of CO_2 on zeolite (DAY), T=298K



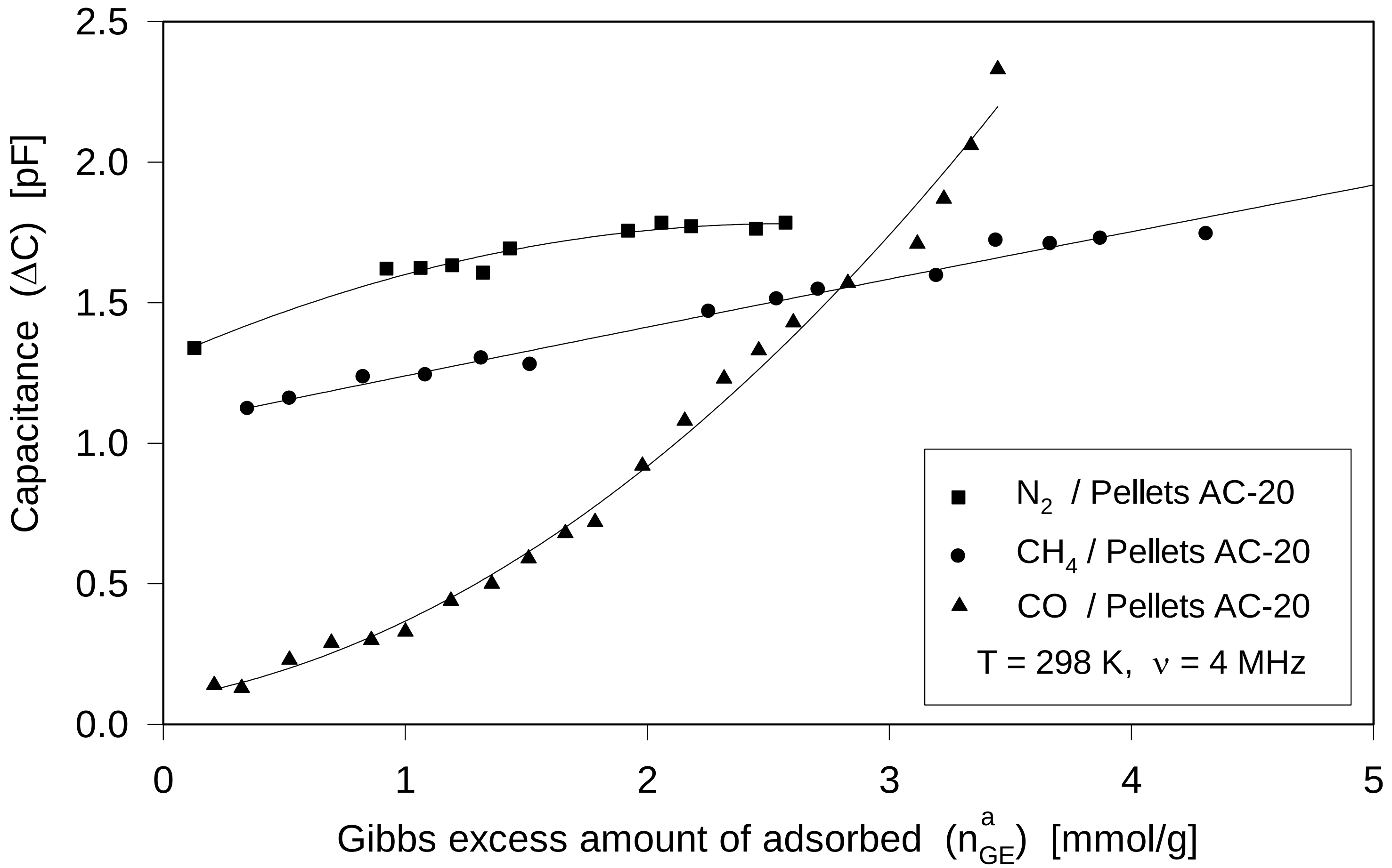
Cole-Cole-Plot for system H_2S / MS 13X, T=298K



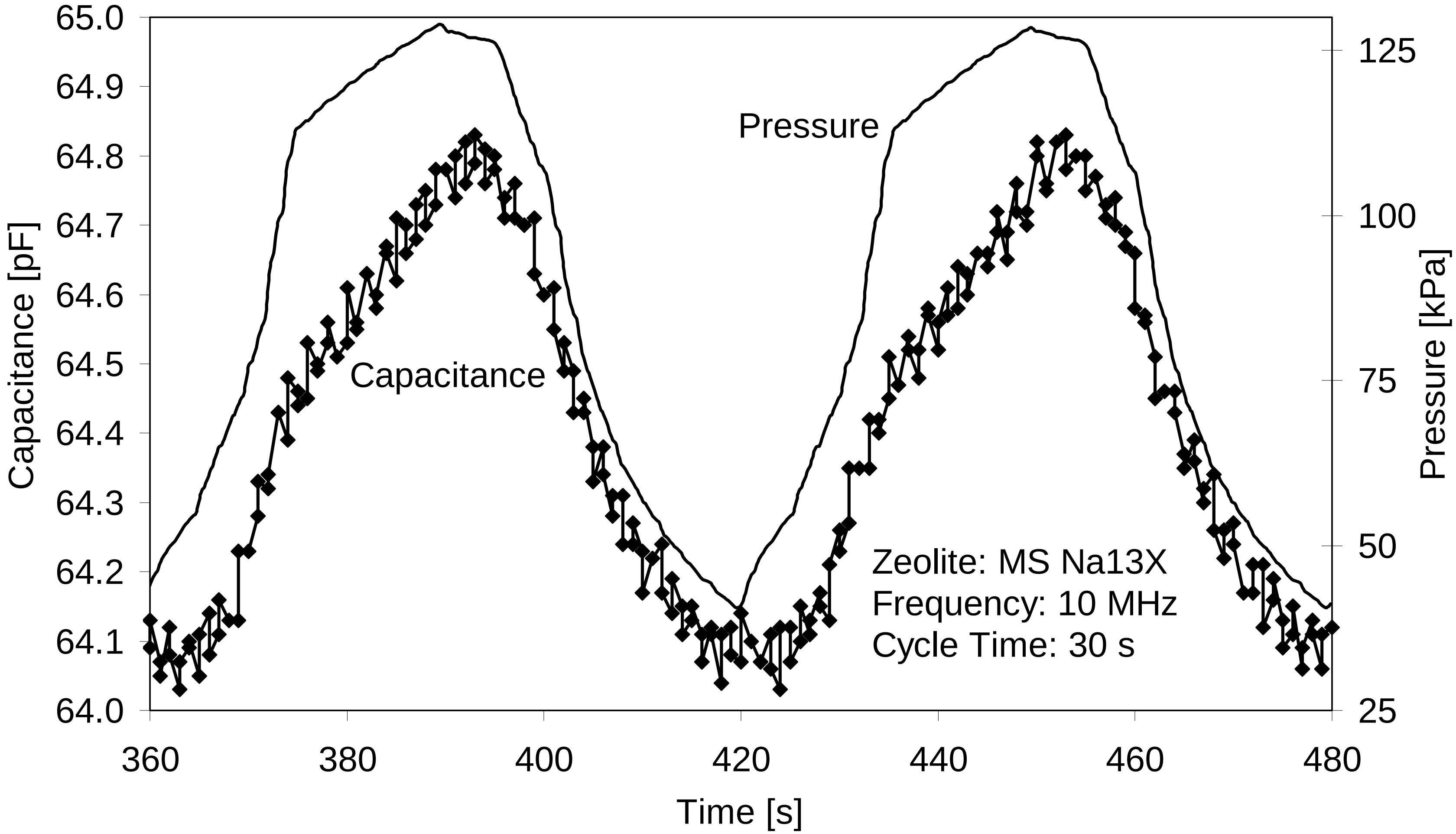
Cole-Cole-Plot for system CO / MS 13X, T=298K



Uptake curves of H_2S on 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 ≤ 4MPa).

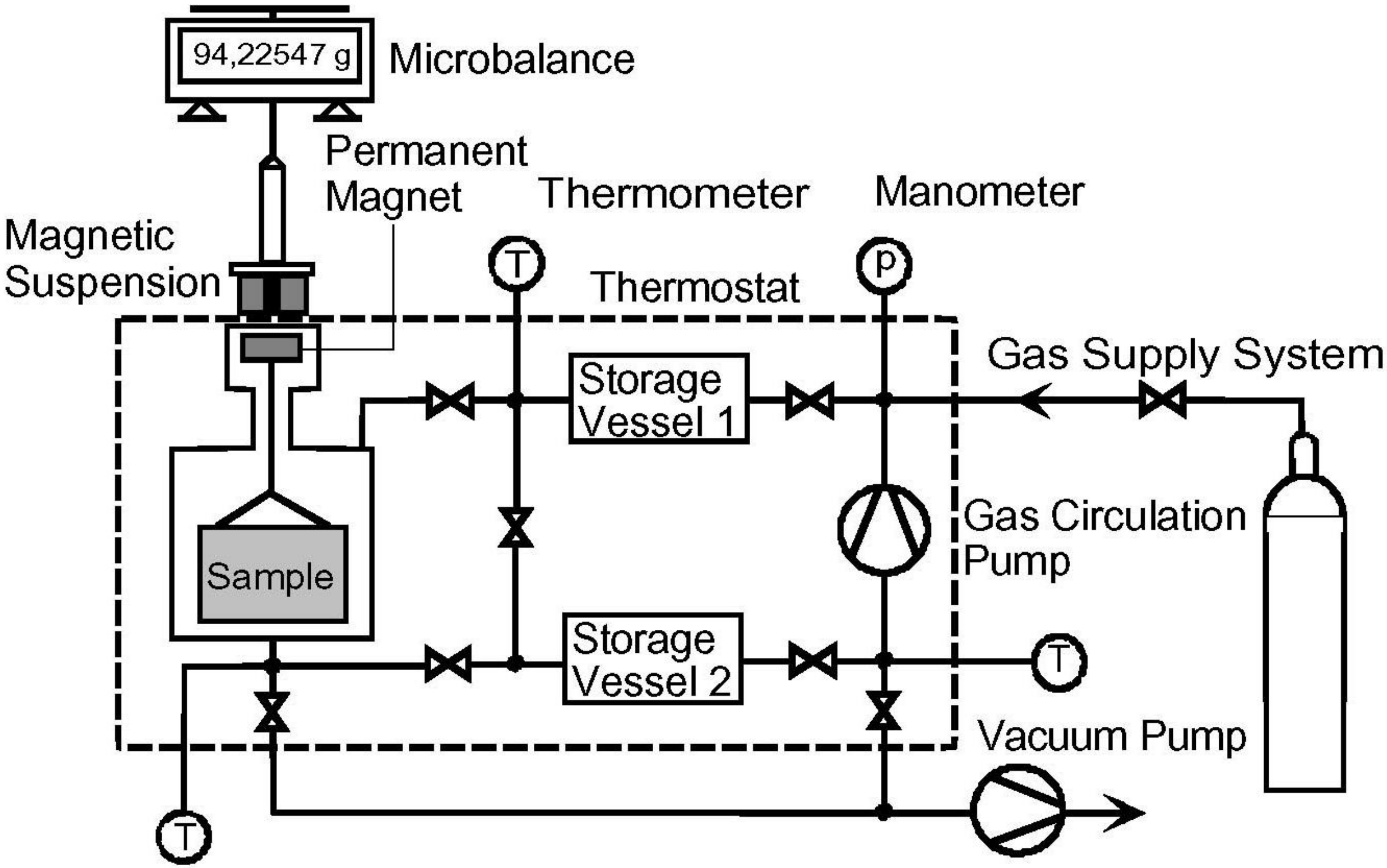


Combined manometric (p) and dielectric (ε_r) measurements of ad- and desorption of N_2 on MSNa13X (UOP) at 293K.

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				



Experimental Setup for volumetric-gravimetric measurements of binary coadsorption equilibria ($M_1 \neq M_2$)

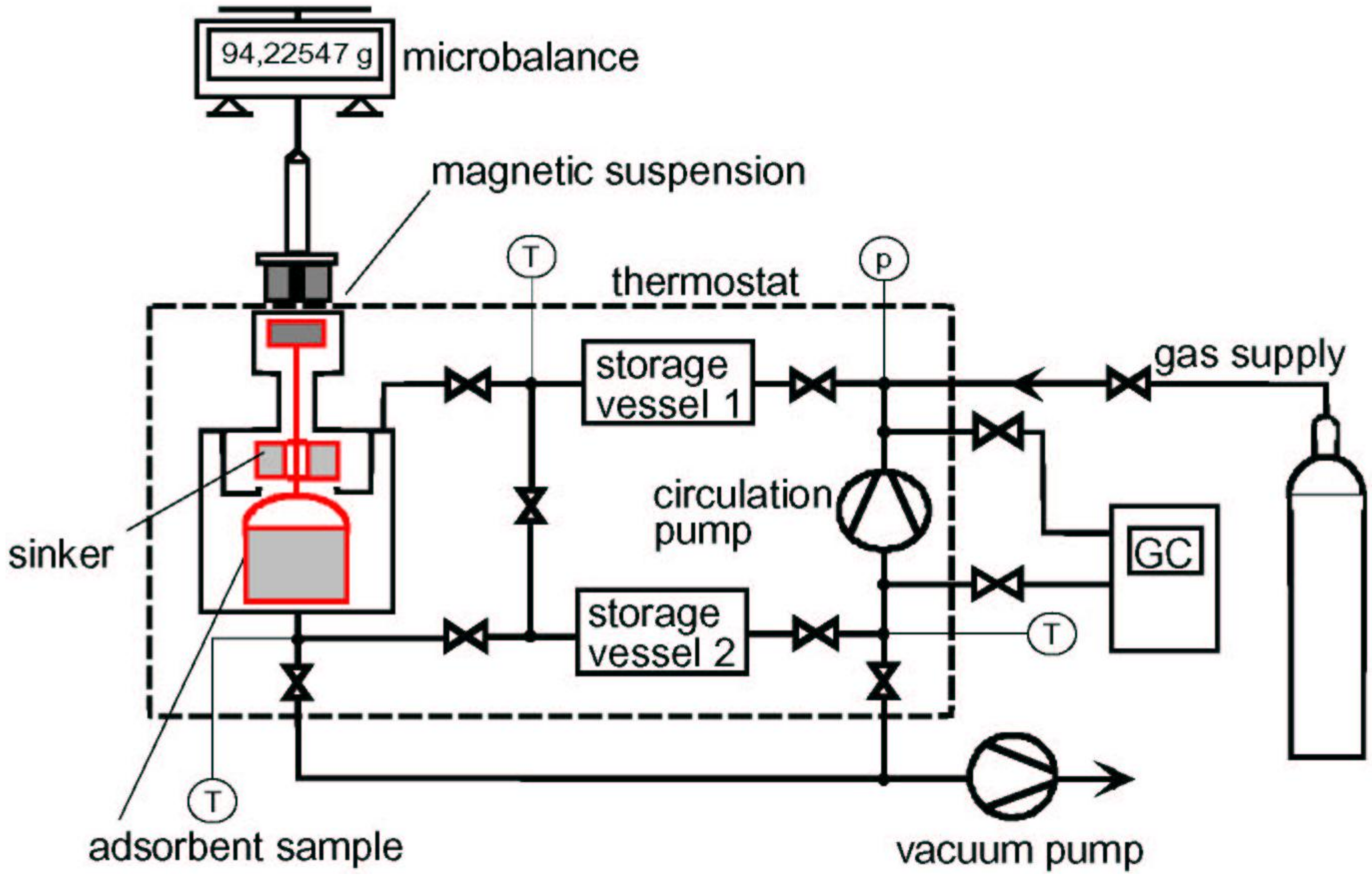
Mass balances $$m_i^* = m_i^f + \left(1 + \frac{m_0^s}{m^s}\right) m_i \qquad i = 1, 2$$

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

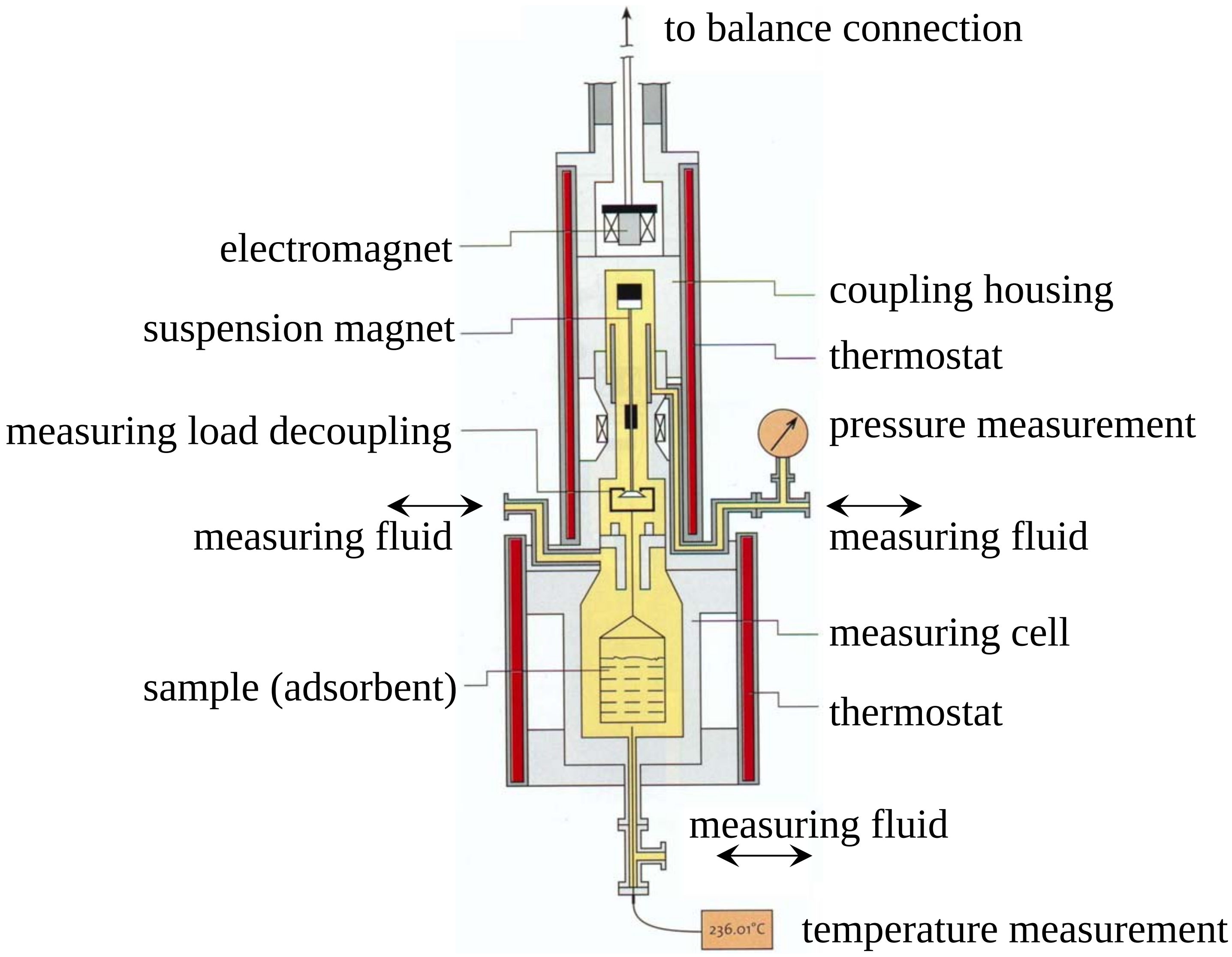
Adsorptive's equation of state $$\frac{m_1^f}{M_1} + \frac{m_2^f}{M_2} = \frac{p\left(V^* + V^f\right)}{Z R T}$$

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

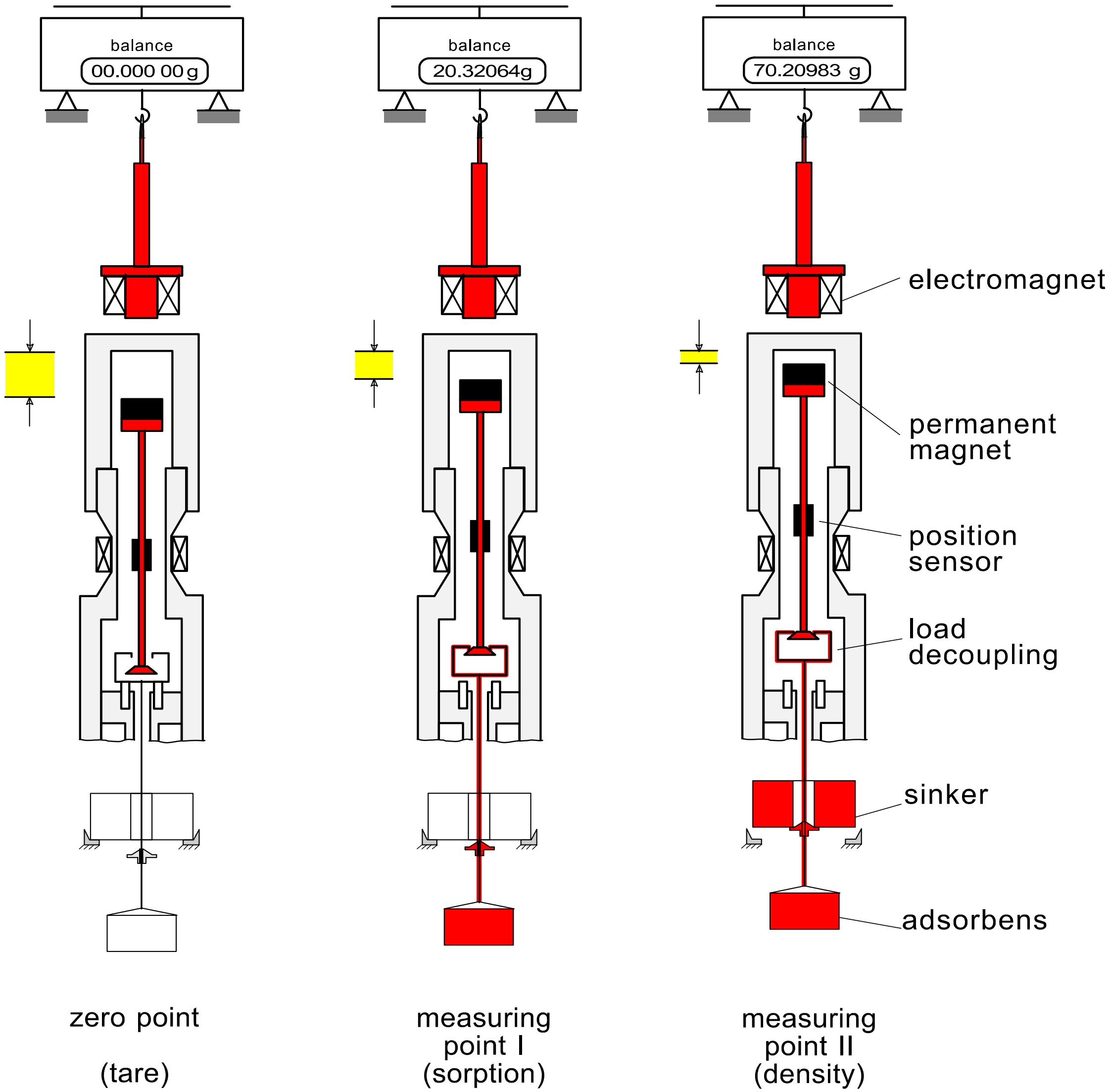
Volumetric-Gravimetric Measurements of Binary Coadsorption Equilibria (Theory)



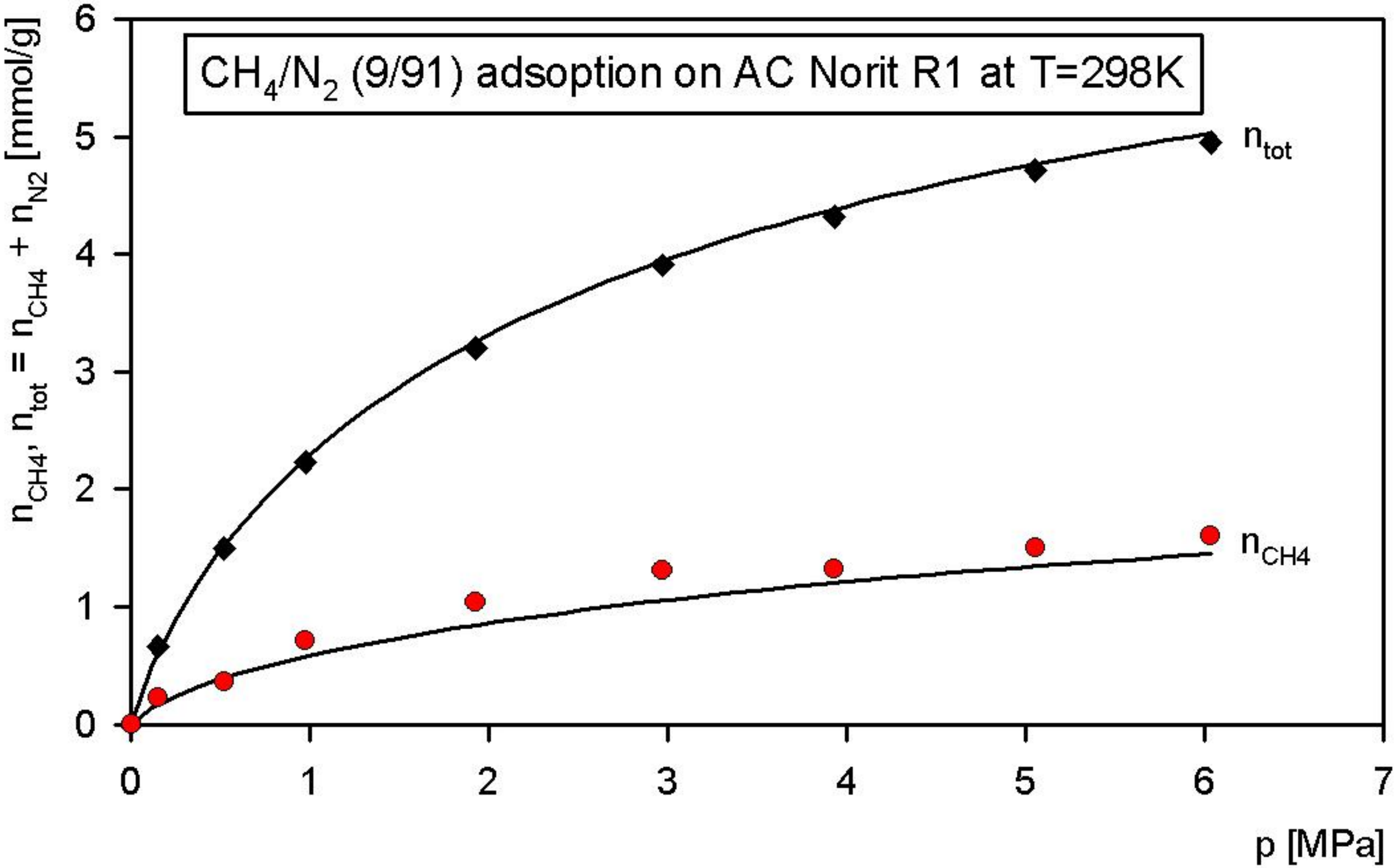
Schematic diagram of a volumetric-gravimetric-chromatographic installation with magnetic suspension balance for coadsorption measurements (N ≥ 1)



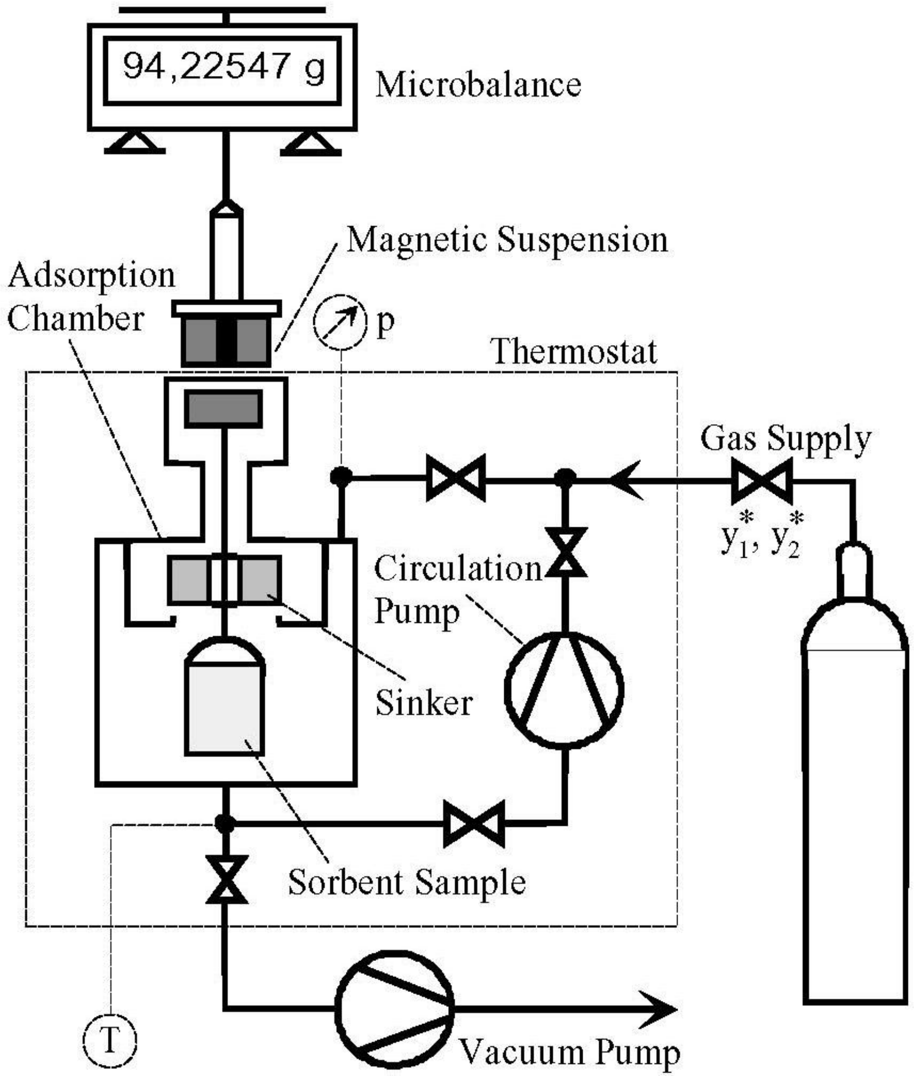
Magnet suspension balance for sorption measurements (Rubotherm, Bochum, Germany)



Magnetic Suspension Balance for Simultaneous Sorption and Density Measurements (Rubotherm, Bochum, Germany)



Coadsorption equilibria of methane/nitrogen gas mixtures on activated carbon (Norit R1). Data correlation: 2 sites LAI.



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

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

Total gas mass supplied $$m^* = m_1^* + m_2^* = m_1^a + m_2^a + m_1^f + m_2^f \tag{2}$$

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

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

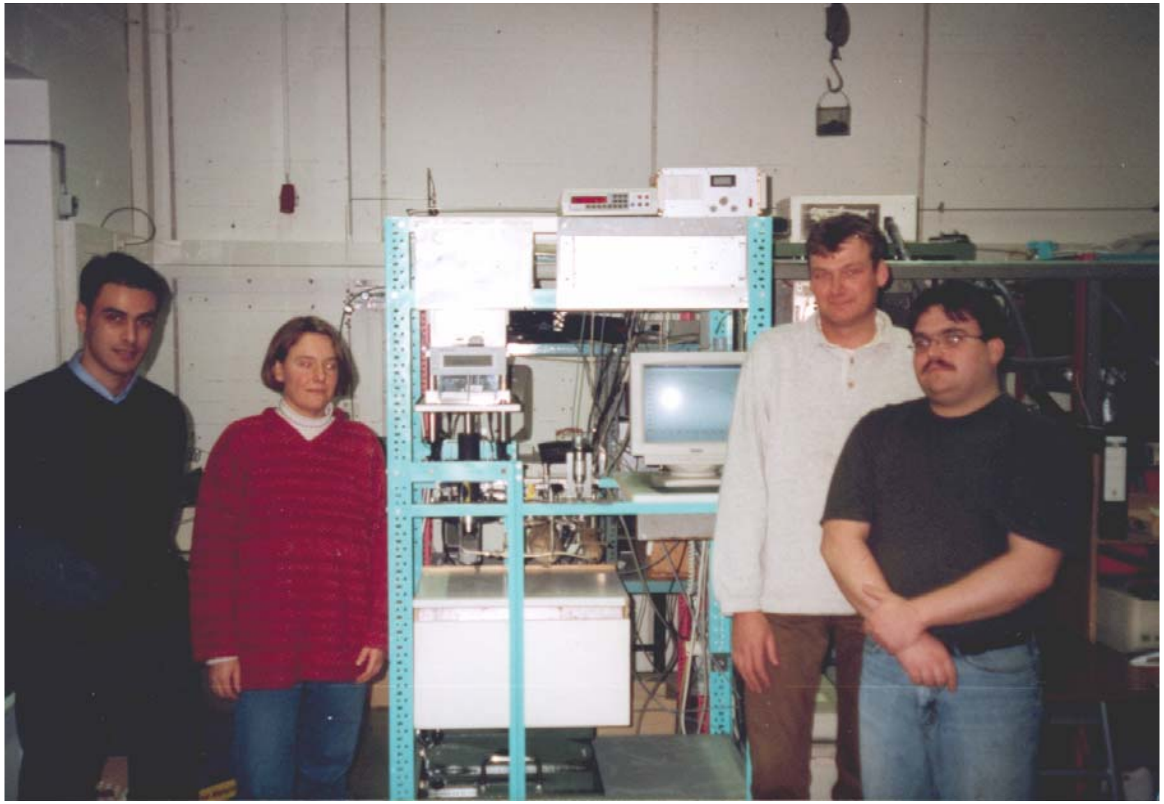
Sorptive gas masses $$m_1^f + m_2^f = \rho^f \left(V^* - V^{as}\right) \tag{3}$$

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

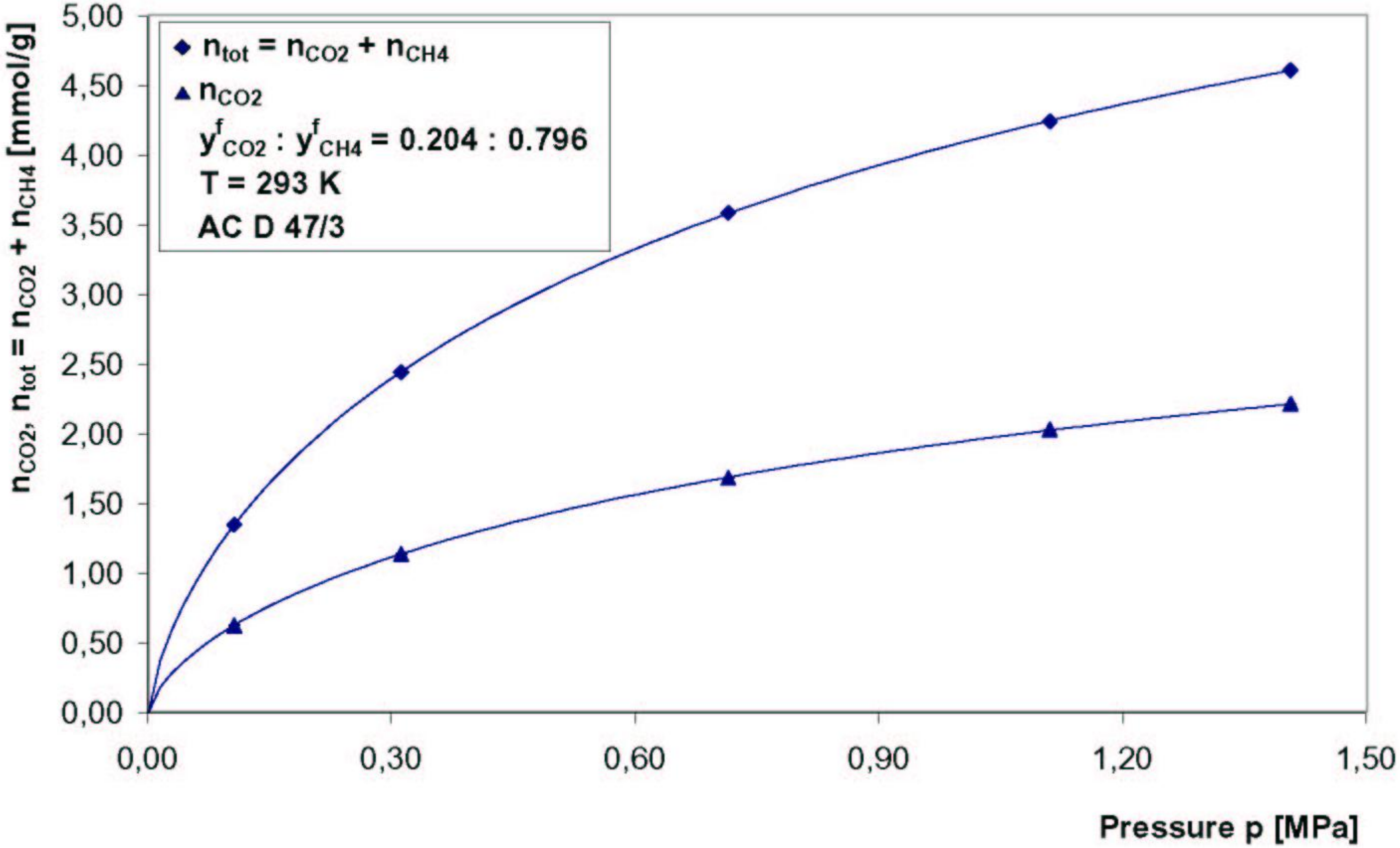
(1, 2A, 3, 4) $$V^{as} = V_{He}^s \tag{5}$$

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

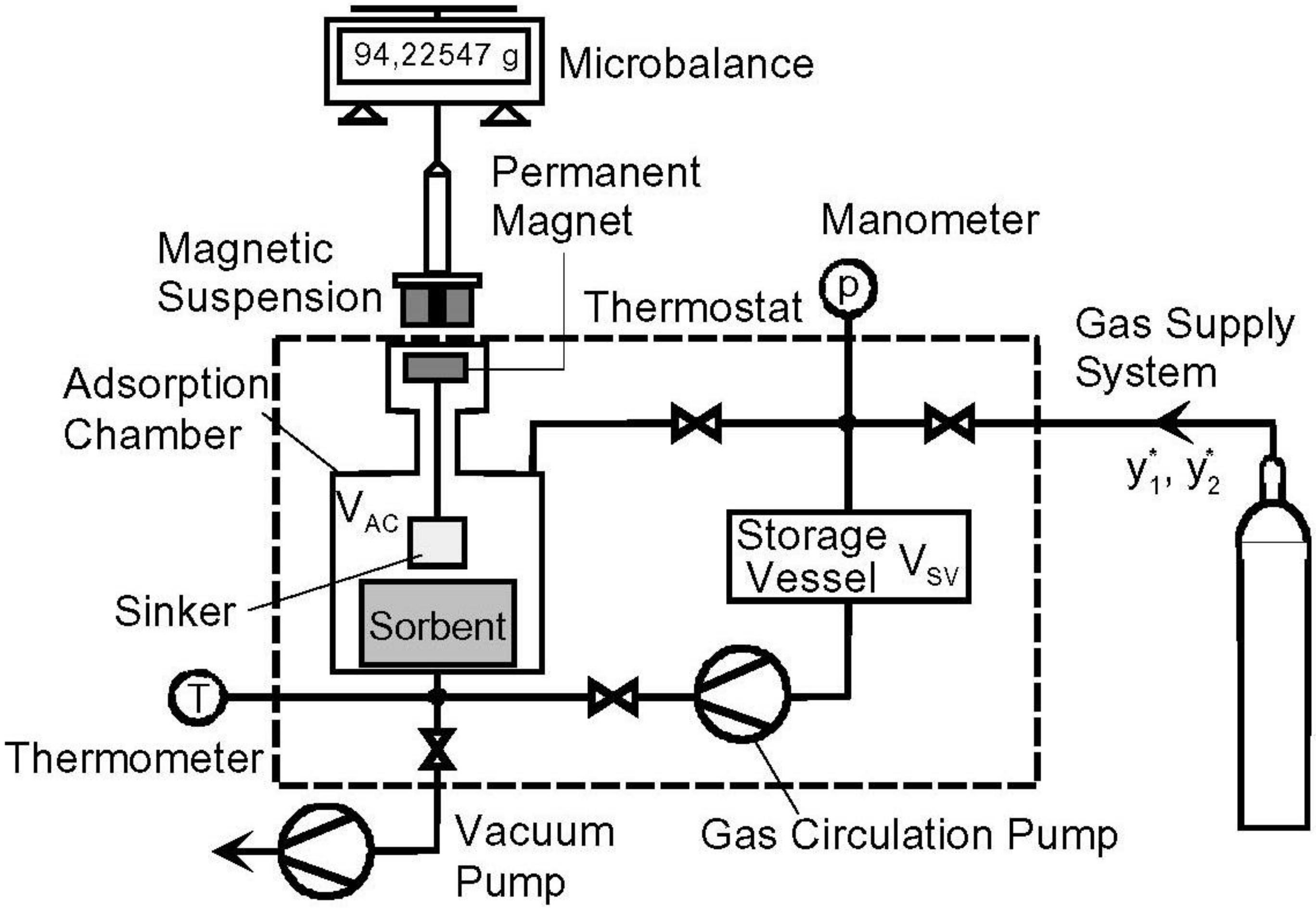
Densimetric-Gravimetric Measurements (DGMs) of Coadsorption Equilibria (Theory)



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



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



Installation for Densimetric-Volumetric Measurements (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)

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

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

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

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

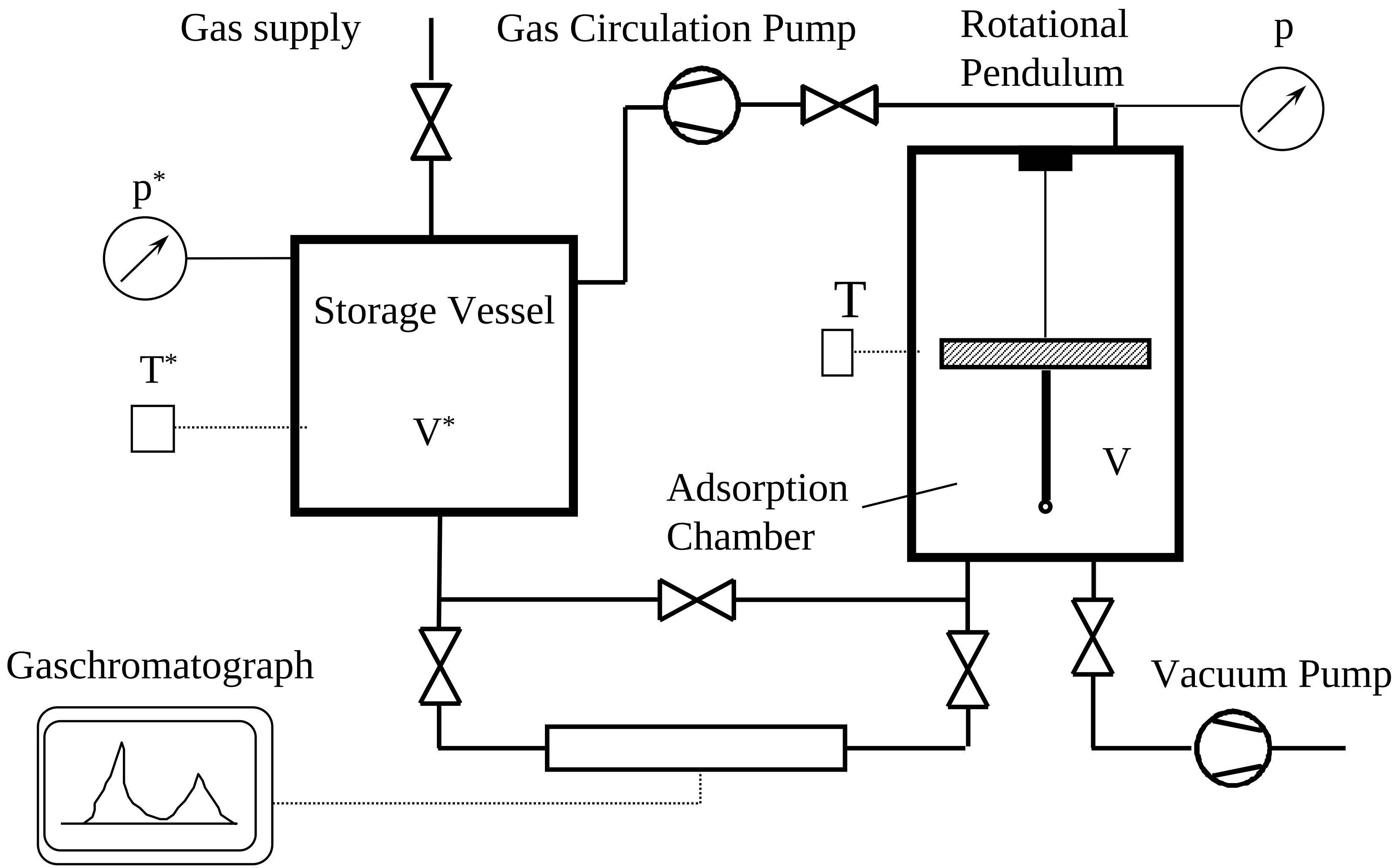
$$m_{iGE}^a = m_i^* - \frac{M_i}{M_i - M_{i+1}} \left(\rho^f - \frac{p\,M_{i+1}}{R\,T\,Z(p, T, w_i)} \right) \left(V^* - V_{He}^s\right) \qquad (6)$$

Densimetric-Volumetric Measurements (DGMs) of Coadsorption Equilibria (Theory).

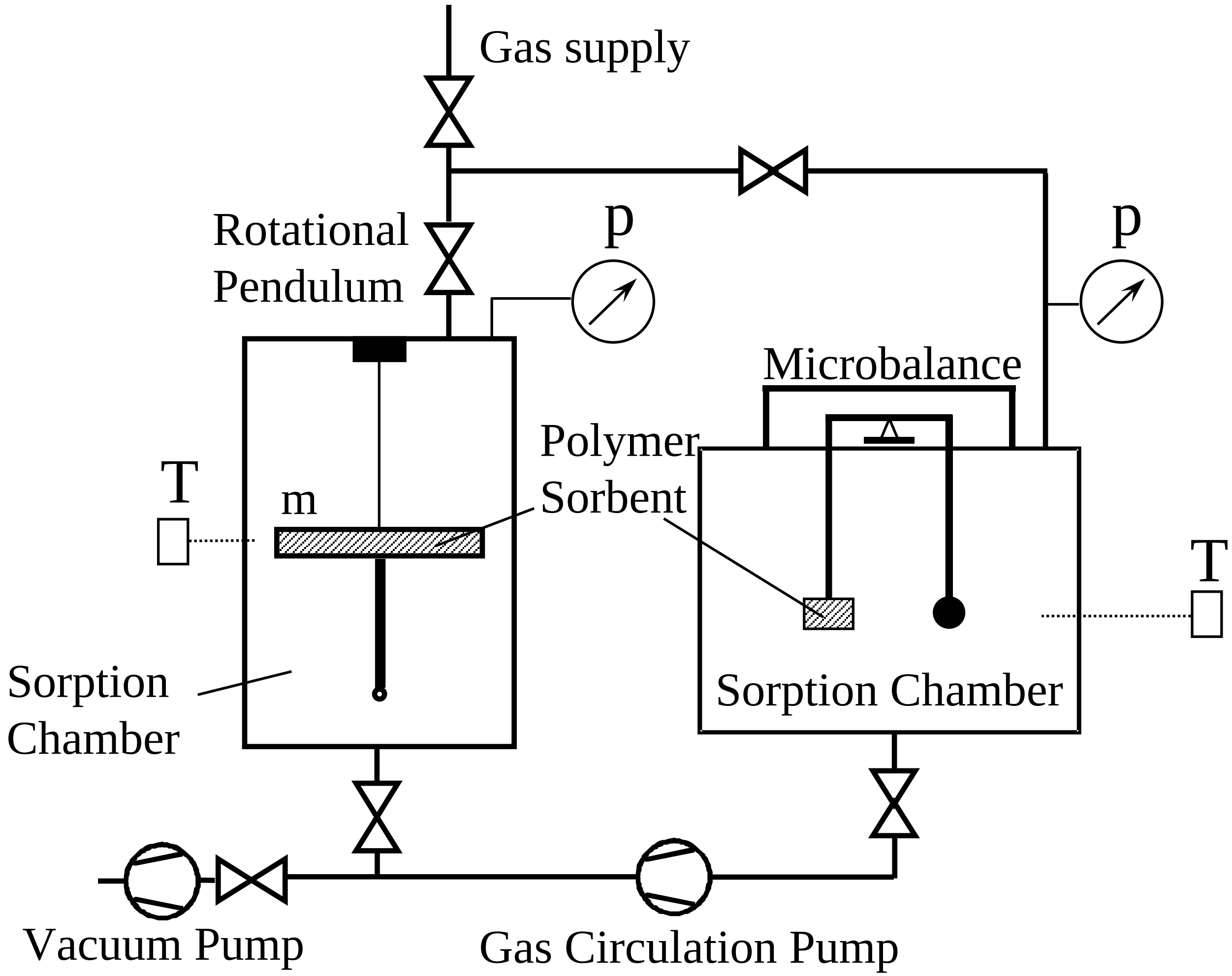
Automated MSB (2) (Rubotherm AG, Bochum) for Densimetric-Volumetric Measurements (DVMs) of binary coadsorption equilibria

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.

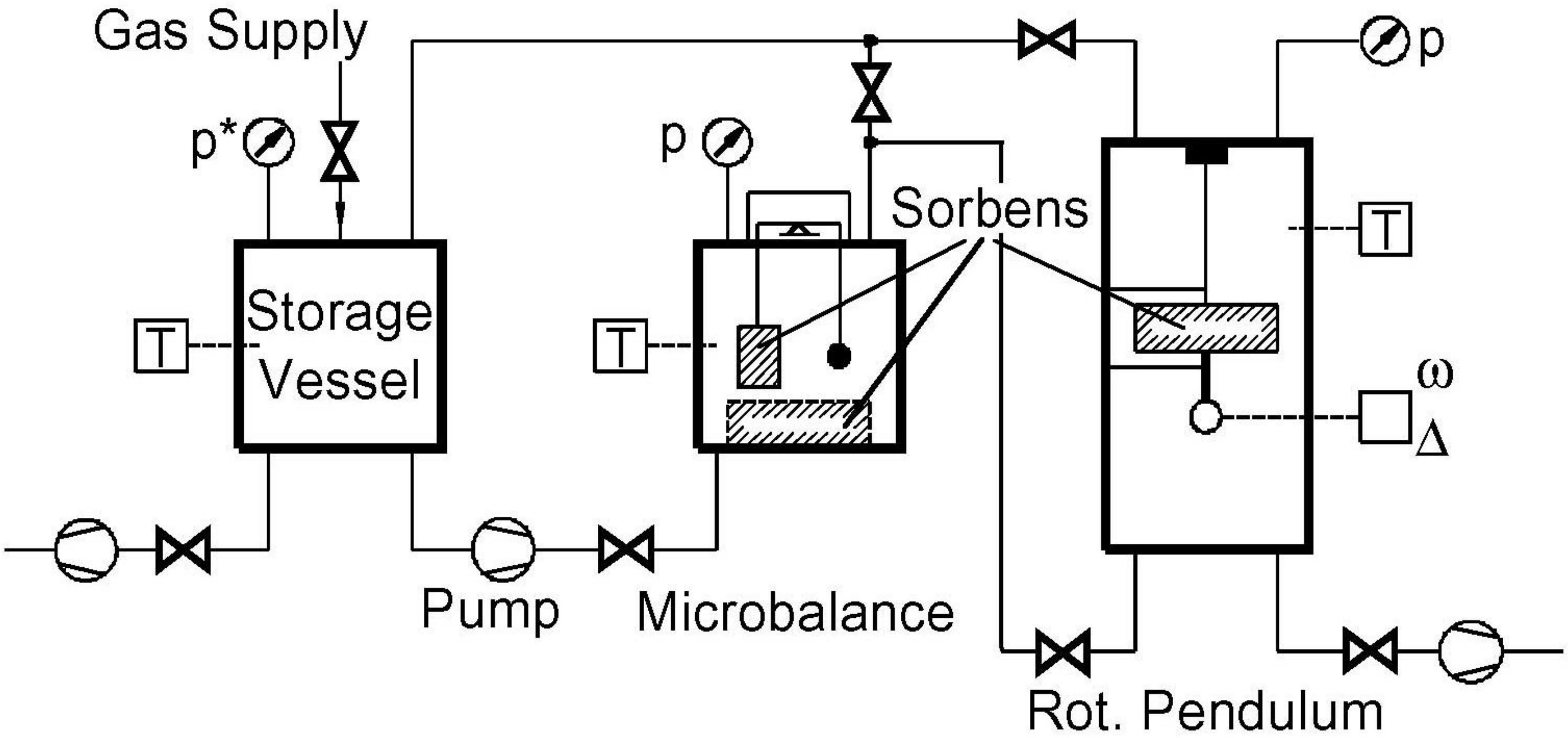
Criterion	DGMs	DVMs
1. Equipment needed	Magnetic suspension balance (3 positions)	Spring balance (quartz), microbalance, magnetic suspension balance (2 positions)
2. Operation	sophisticated	fairly simple
3. Automation	sophisticated	fairly simple
4. Kinetics	can be observed	hardly observable
5. Activation 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



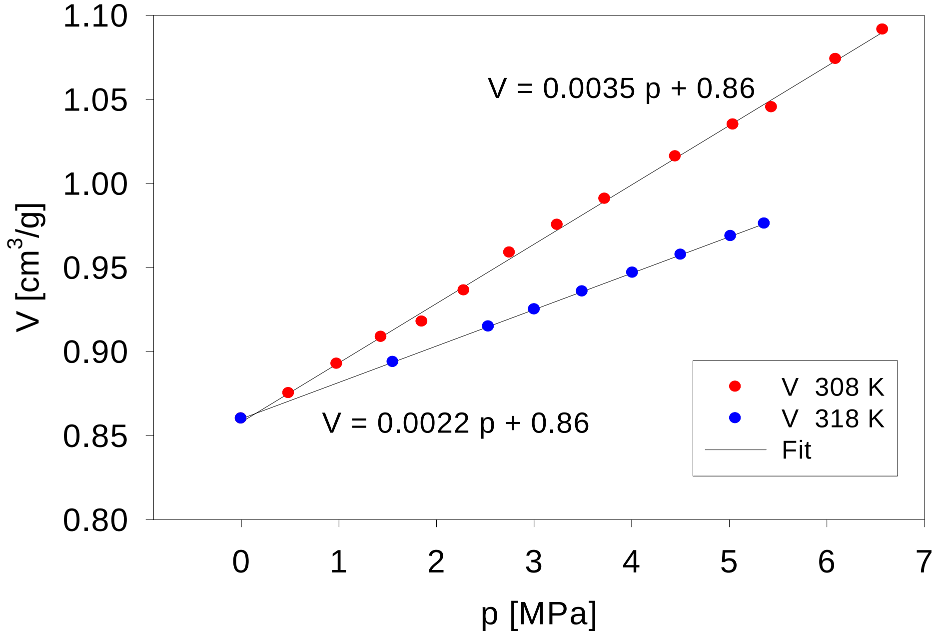
Experimental Setup for oscillometric-volumetric measurements of gas sorption equilibria in swelling materials.



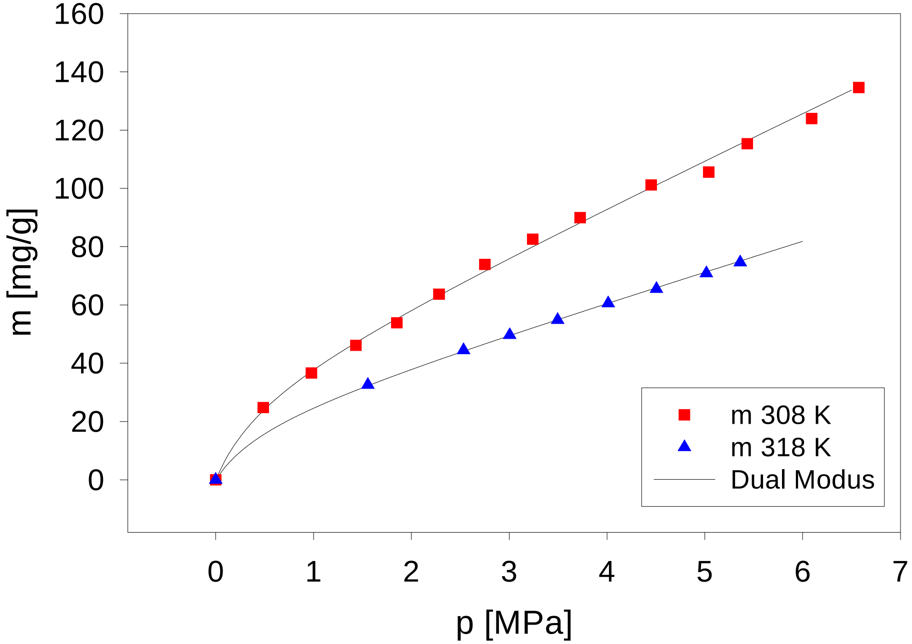
Experimental Setup for oscillometric-gravimetric measurements of gas sorption equilibria in swelling materials.



Volumetric-gravimetric-oscillometric method (N=2). Co(ad)sorption measurements in swelling sorbent materials (polymers) without using a gas chromatograph.



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



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

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.