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

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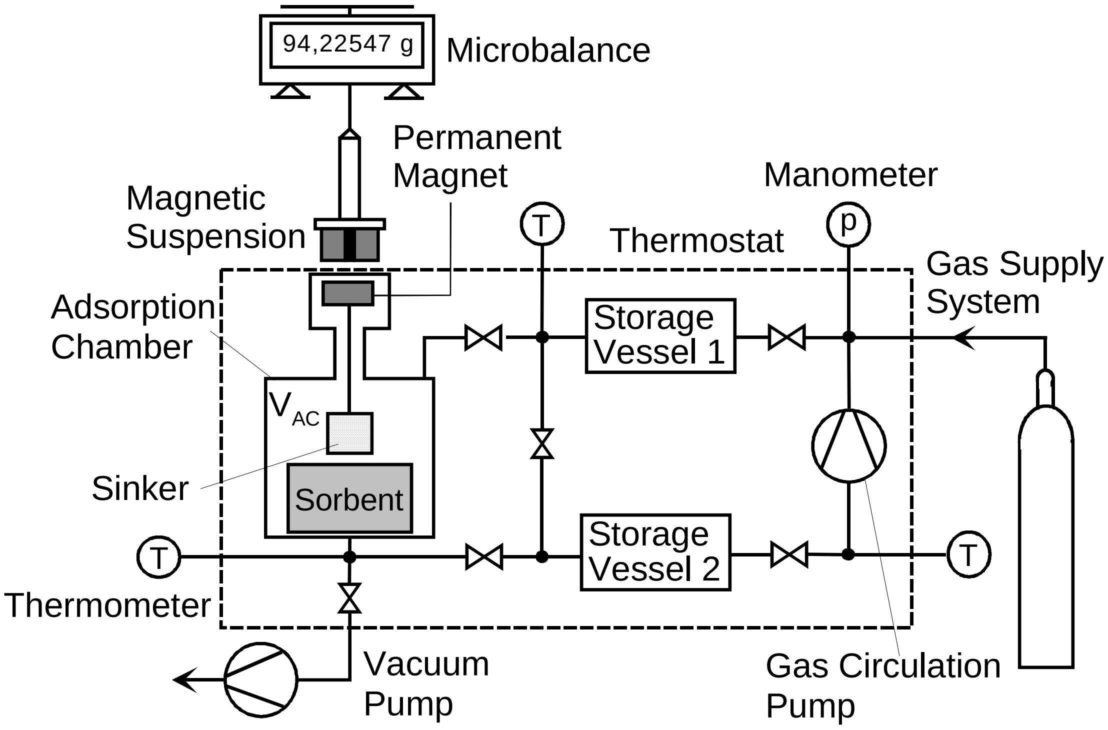
1. Volumetry / Manometry and Densimetry
2. Gravimetry and Densimetry
3. Oscillometry
4. Impedance Spectroscopy
5. Calorimetry and Volumetry
6. Calorimetry and Spectroscopy

Acknowledgements



Instrument for volumetric-densimetric measurements of binary coadsorption equilibria of gas mixtures on porous solids without using a gas chromatograph. The sorptive gas prepared in the system is assumed to be a binary mixture with known initial molar concentrations (y^*_1, y^*_2). © IFT University of Siegen, 2002.

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)

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

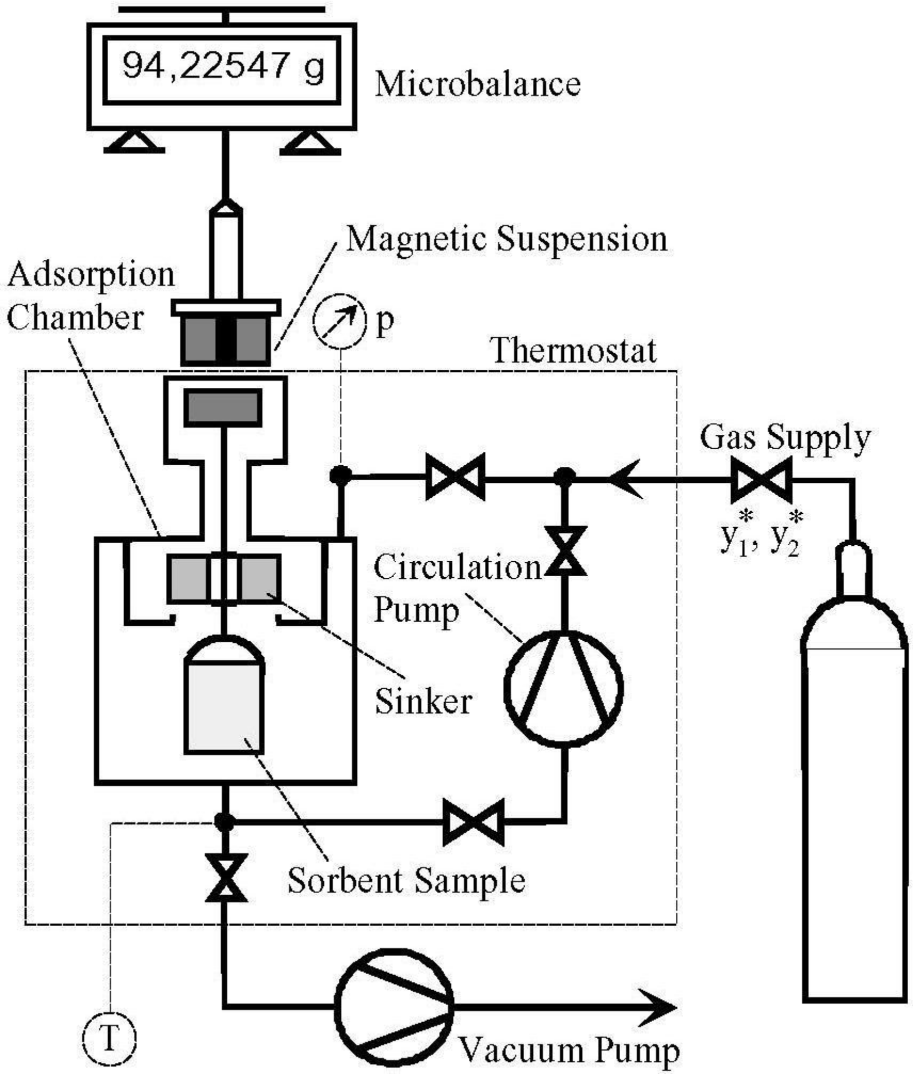
$$\frac{m_1^f}{M_1} + \frac{m_2^f}{M_2} = \frac{p \;\; V^* - V^{as}}{R\,T\,Z \;\; p, T, w_i} \qquad (4)$$

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

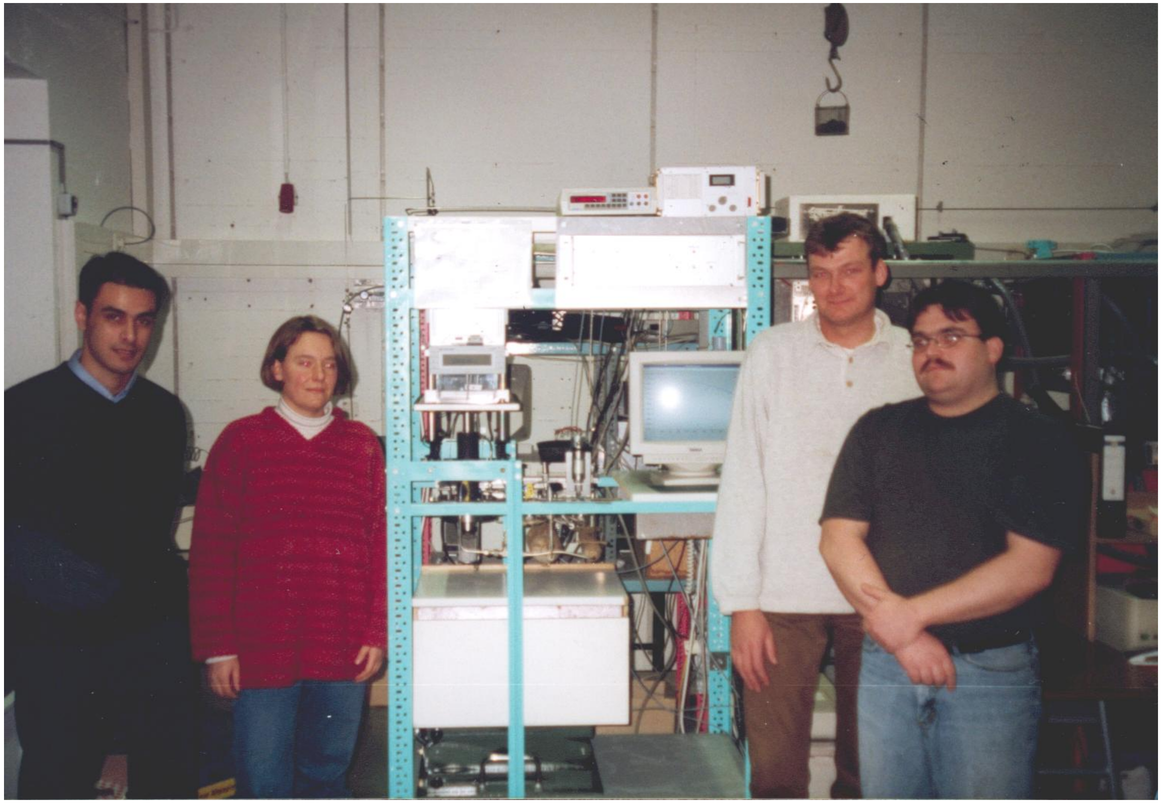
$$(1-4) \quad V^{as} = V_{He}^s \qquad (5)$$

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

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

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

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

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

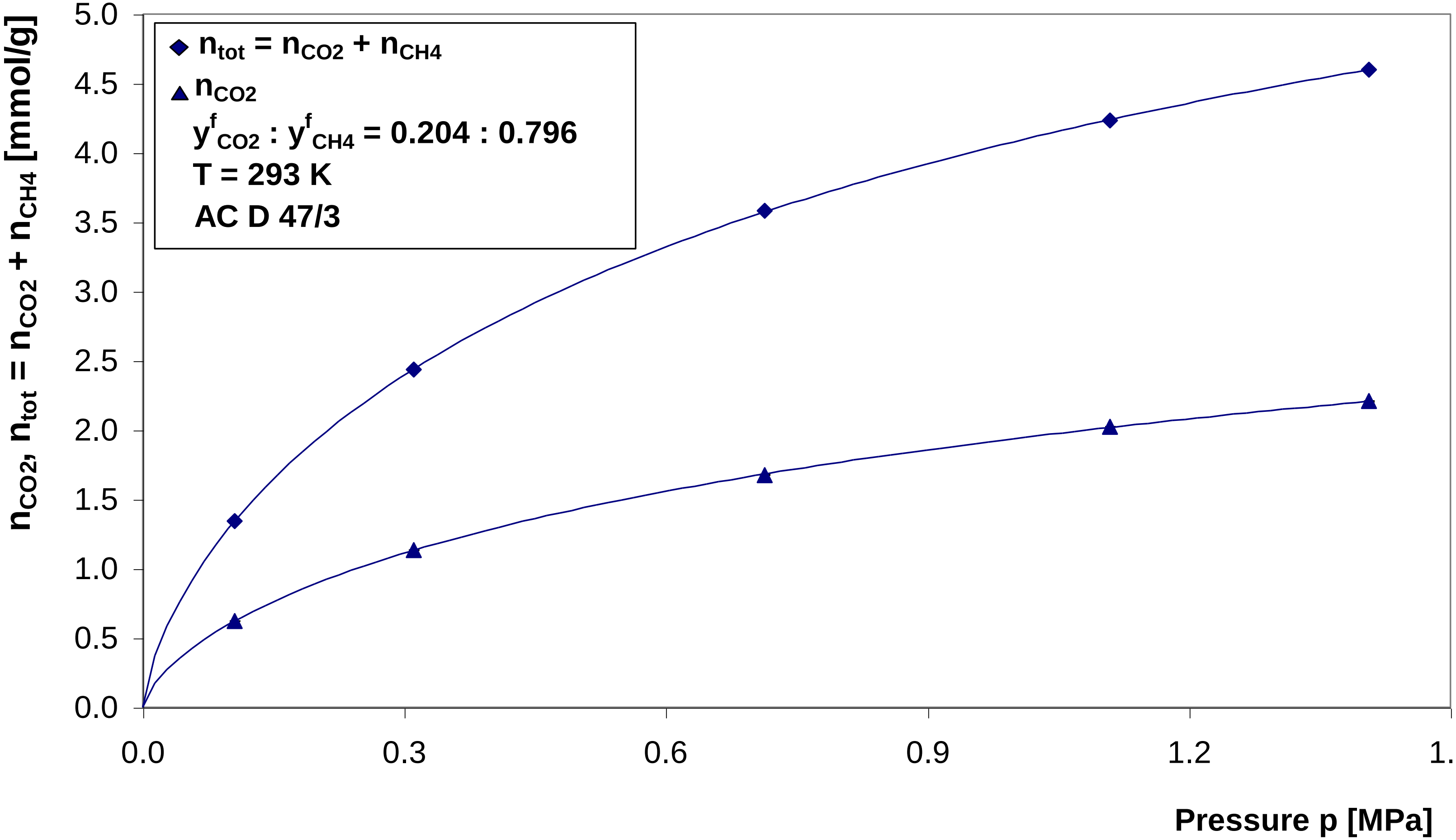
Sorptive gas masses $$m_1^f + m_2^f = \rho^f \; V^* - V^{as} \tag{3}$$

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

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

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

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

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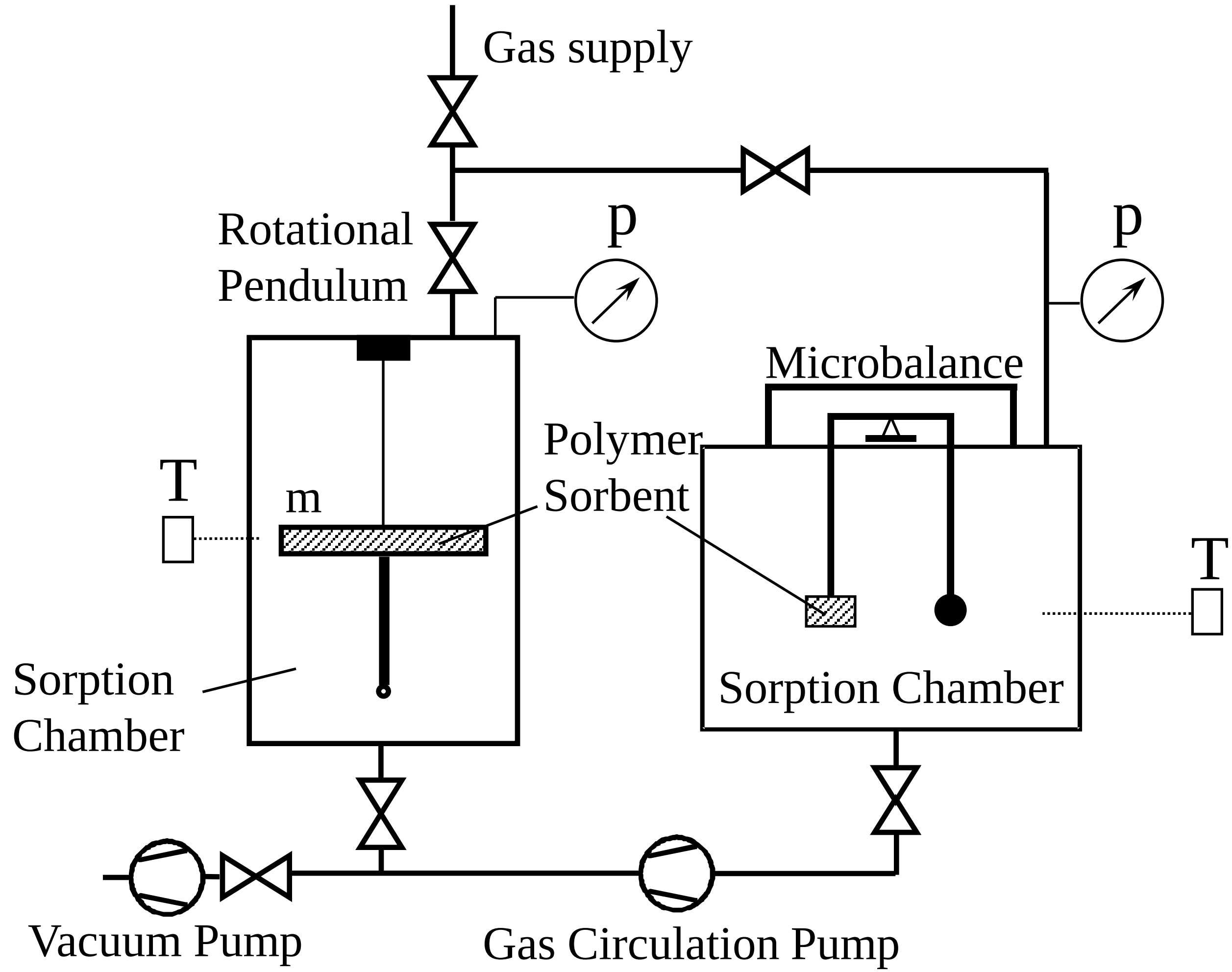


Experimental setup for oscillometric-gravimetric measurements

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

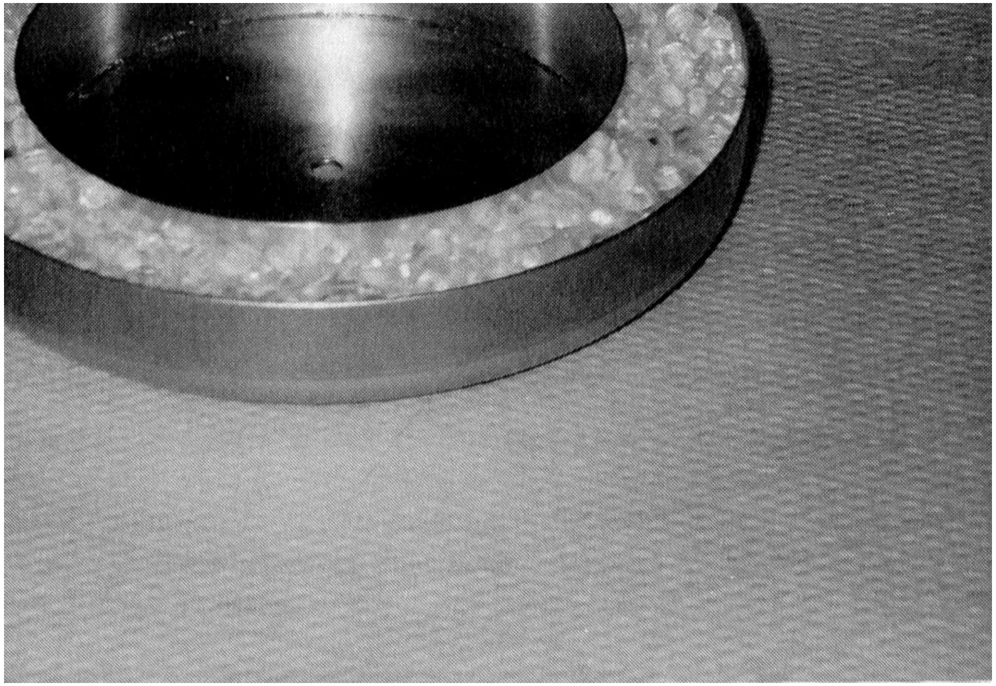
$$\frac{m}{m^s} = \frac{\dfrac{1+\Delta_0^2}{1+\Delta_E^2}\left(\dfrac{\omega_0}{\omega_E}\right)^2 - 1}{1 - \dfrac{\Delta_0\omega_0}{\Delta^*\omega^*}}$$

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

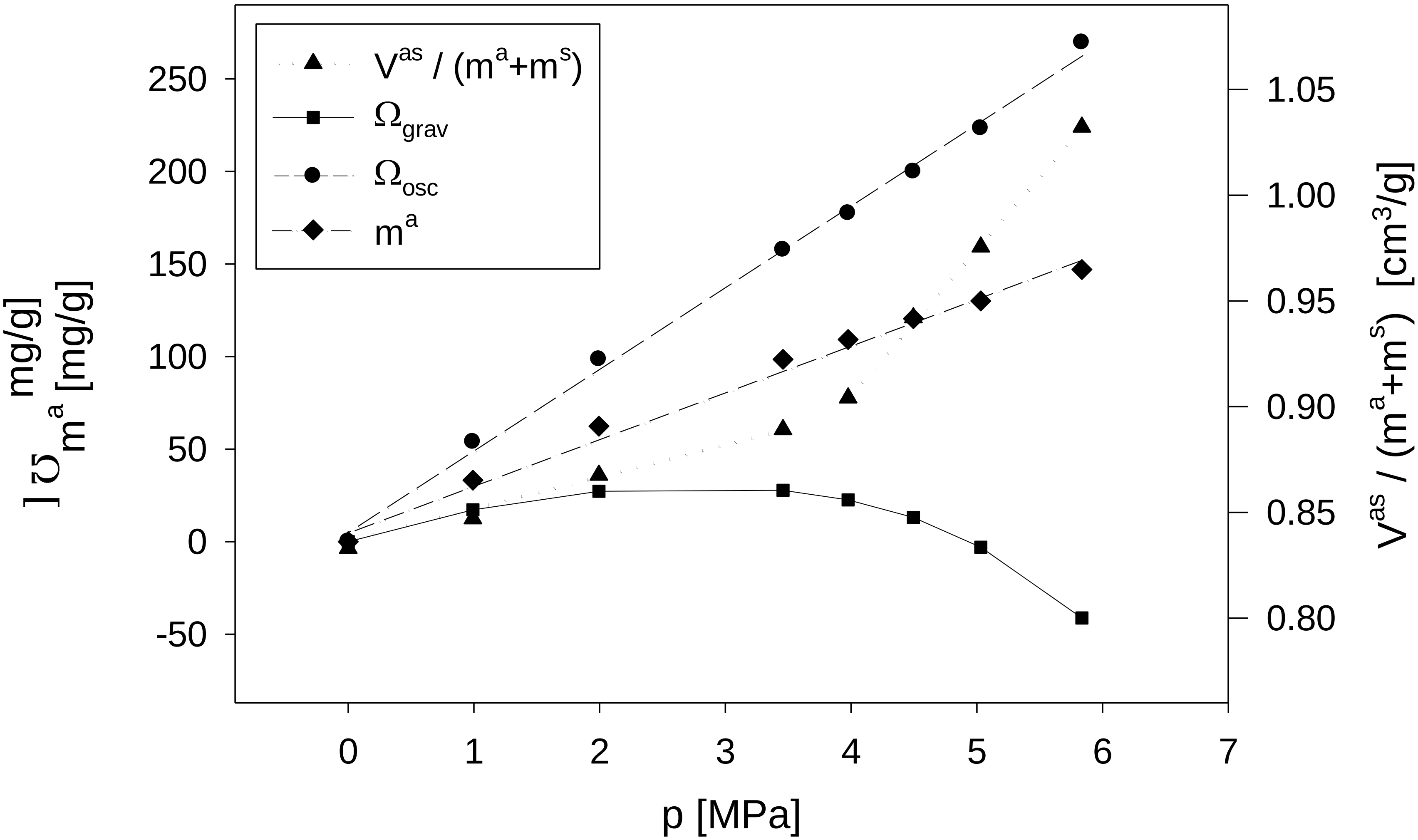
ω_0, Δ_0... pendulum and adsorbent m^*, m^s , vacuum

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

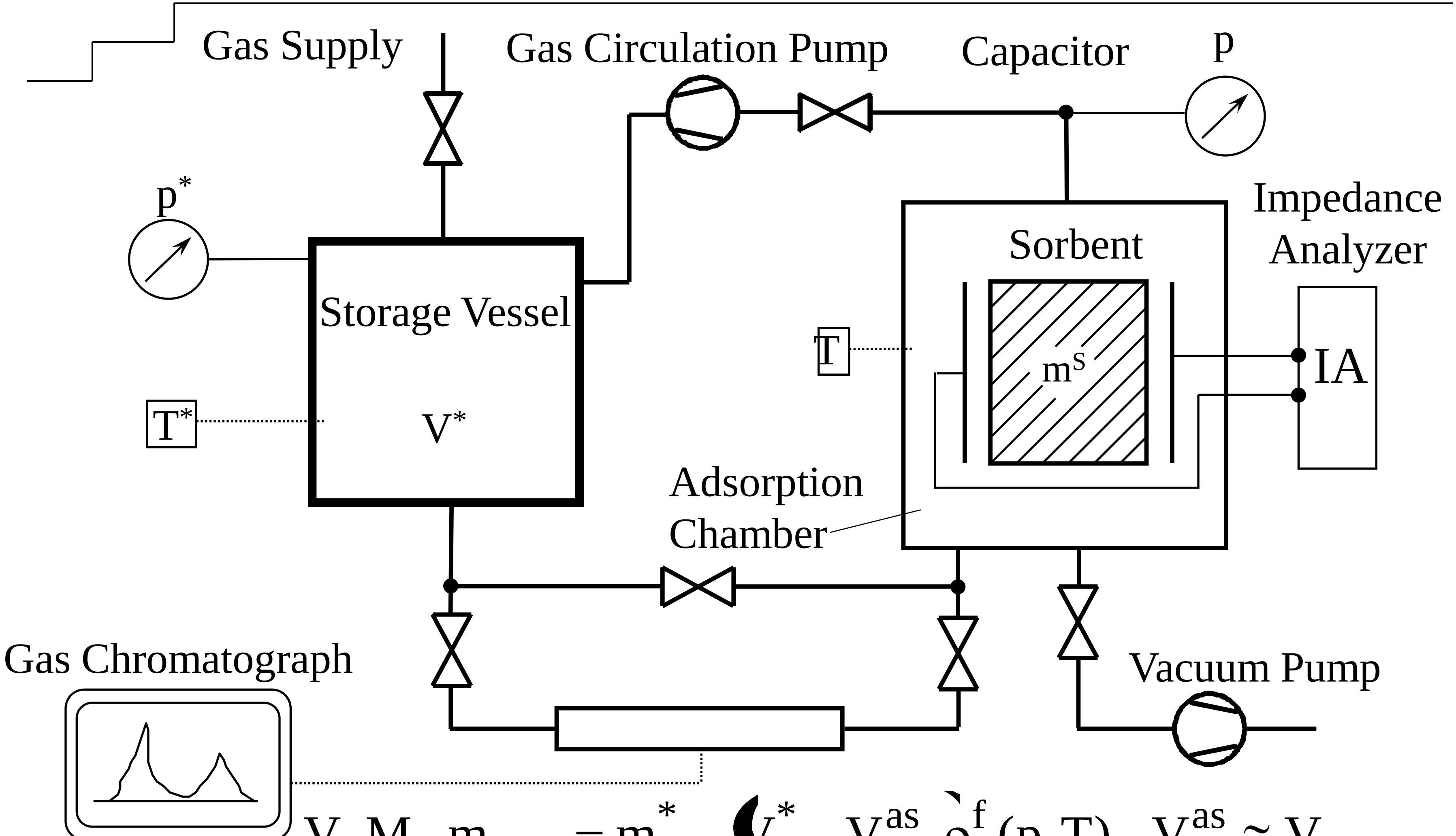
Oscillometric measurements of gas adsorption equilibria. Theory



Ring slit of rotational pendulum filled with polycarbonate pellets



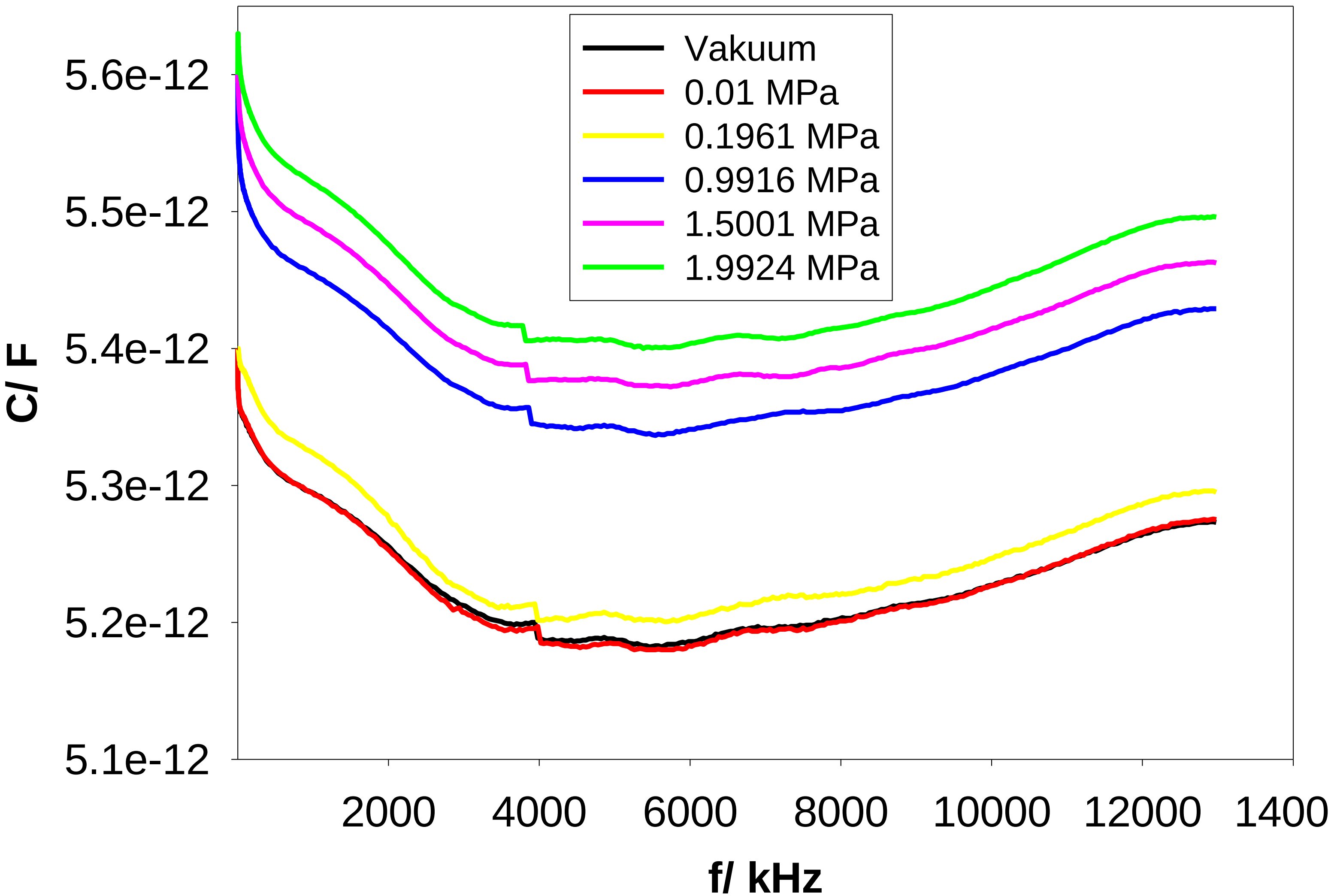
Swelling and sorption isotherm of polycarbonate / CO_2 at 293 K



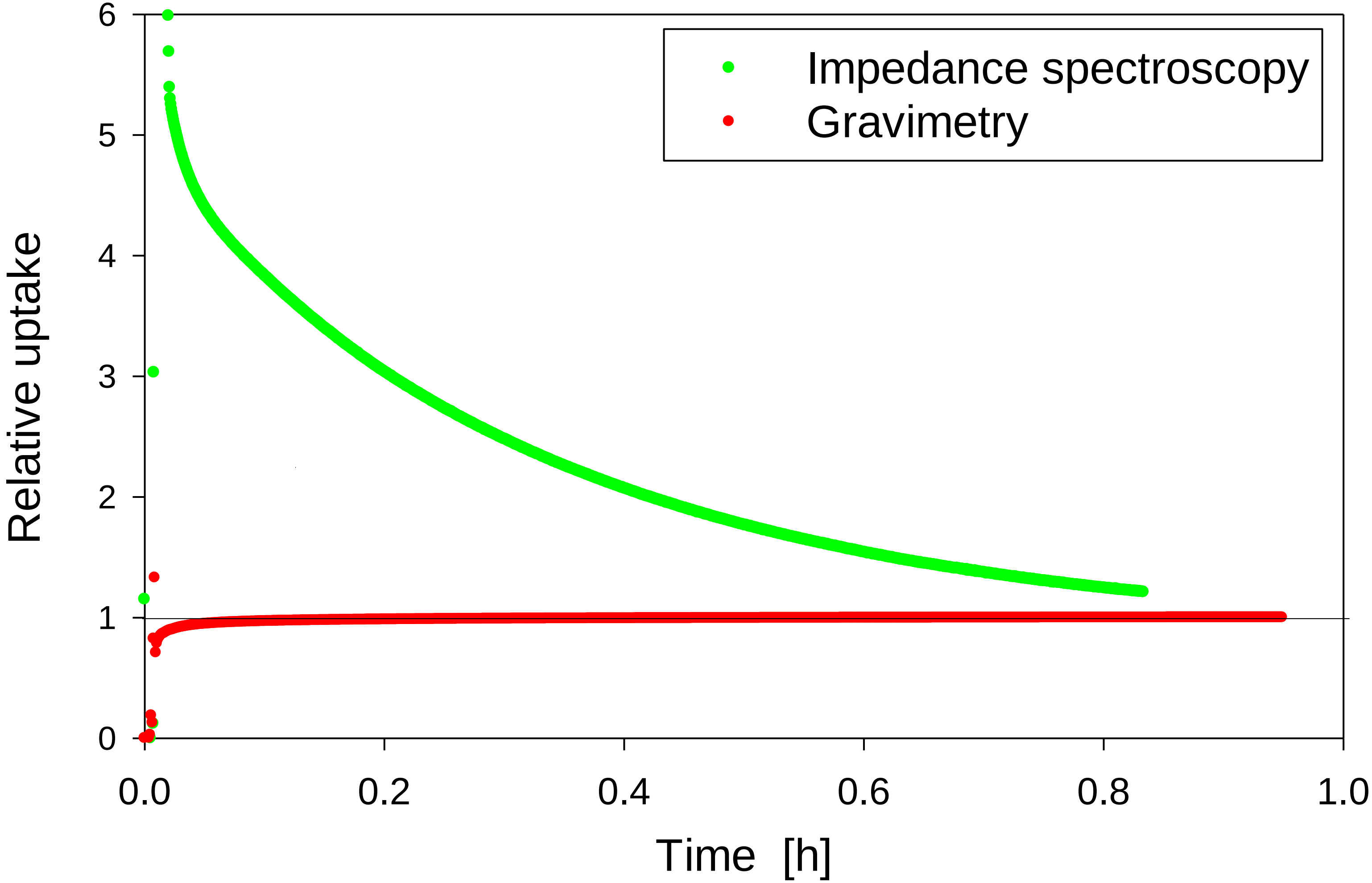
V, M $\quad m_{MG} = m^{*} - \left(V^{*} - V^{as}\right)\rho^{f}(p,T), \quad V^{as} \cong V_{He}$

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

Experimental setup for volumetric-dielectric measurements

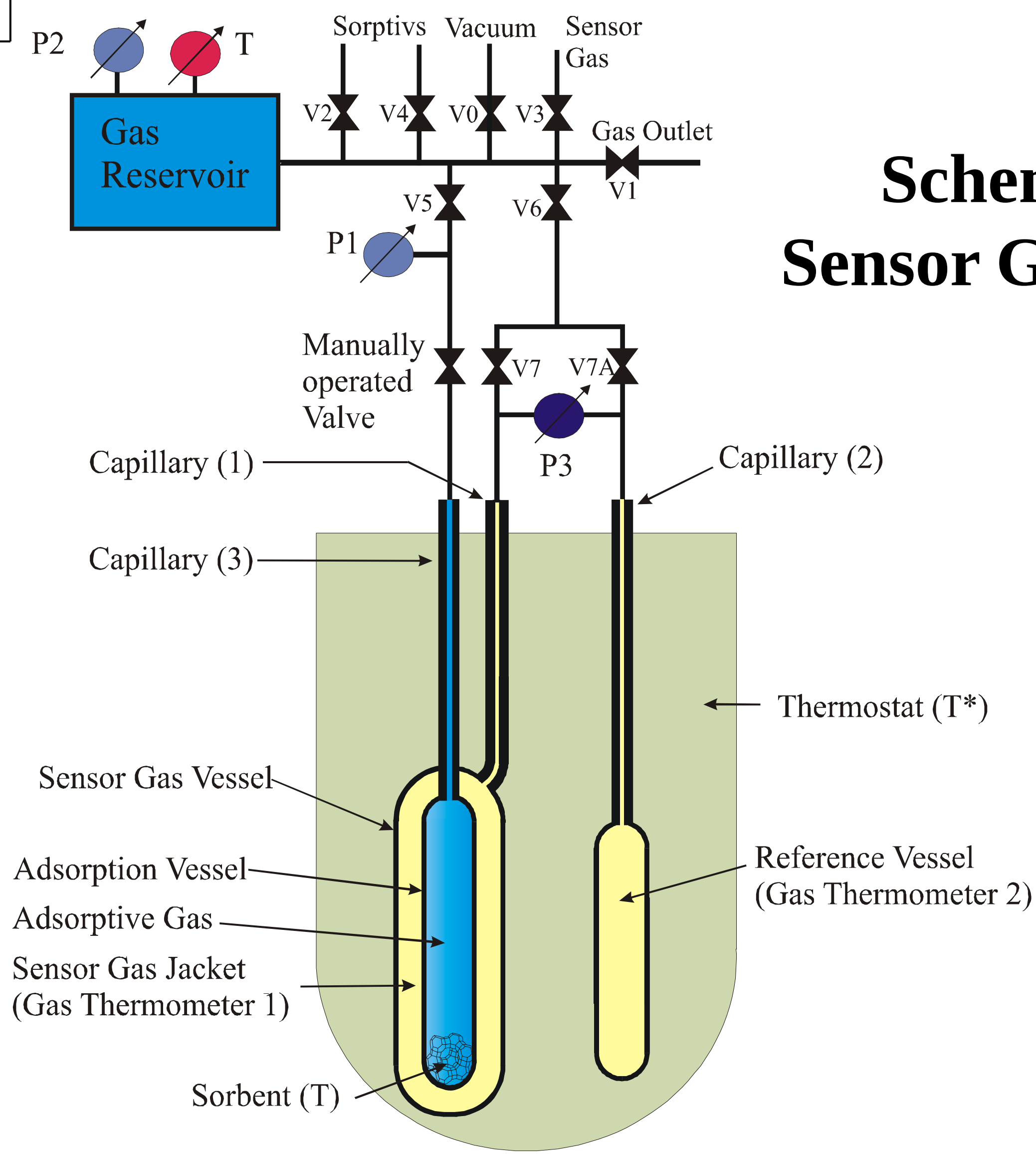


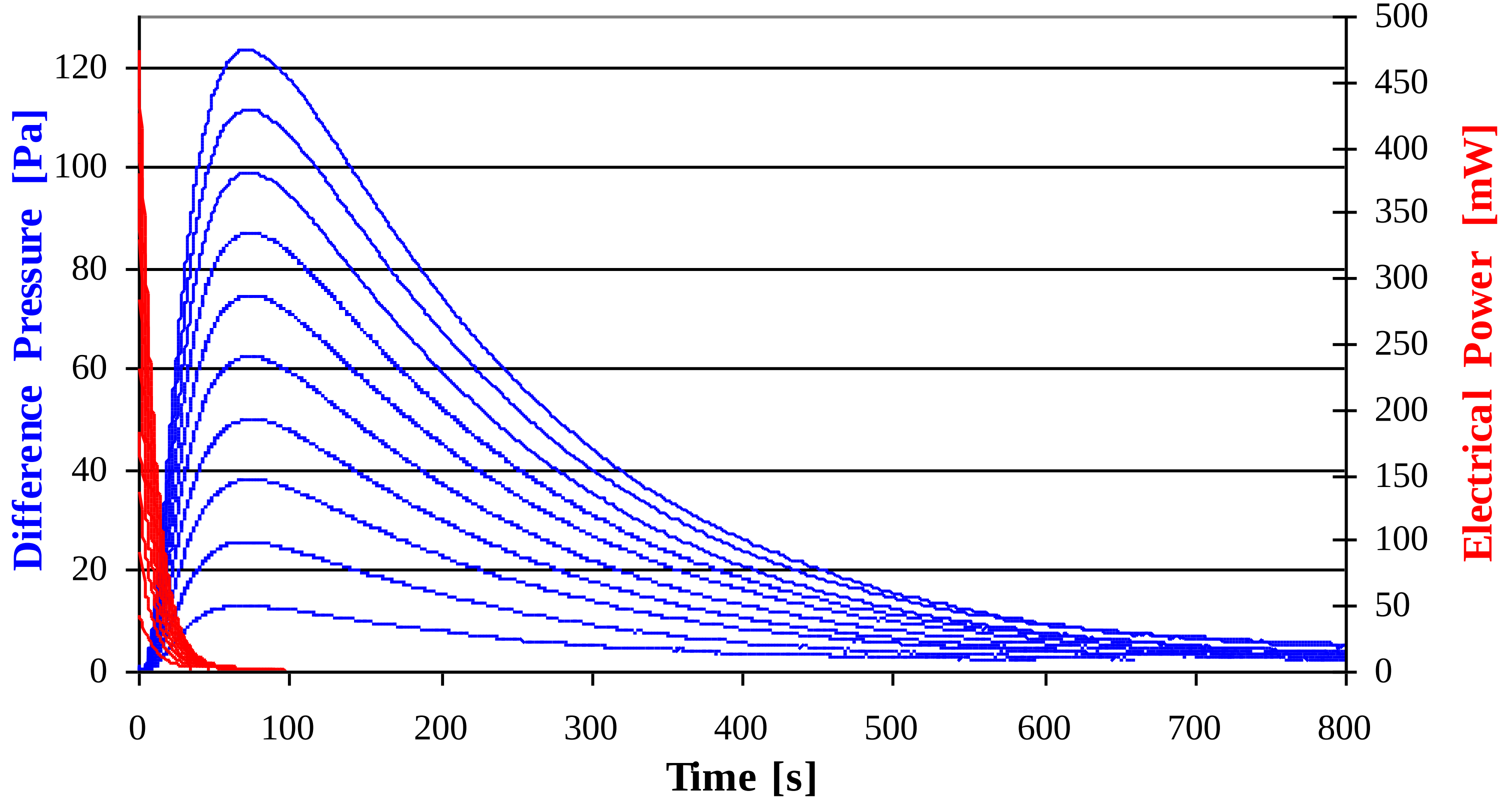
Impedance spectra of CO_2 on zeolite (DAY), T=298K



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

Schematic diagram of a Sensor Gas Calorimeter (SGC)

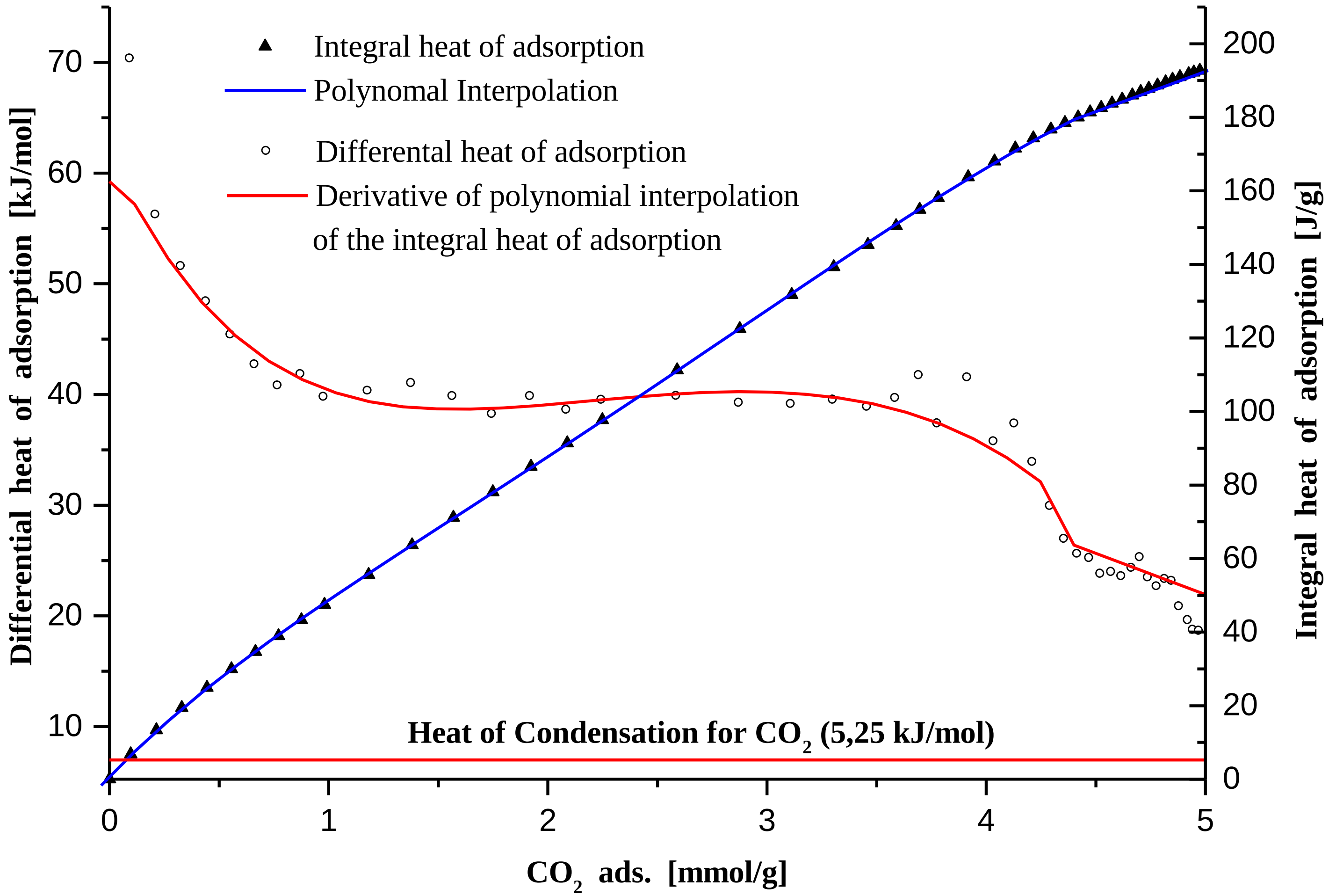




Calibration experiments in the SGC 0.5J to 5J

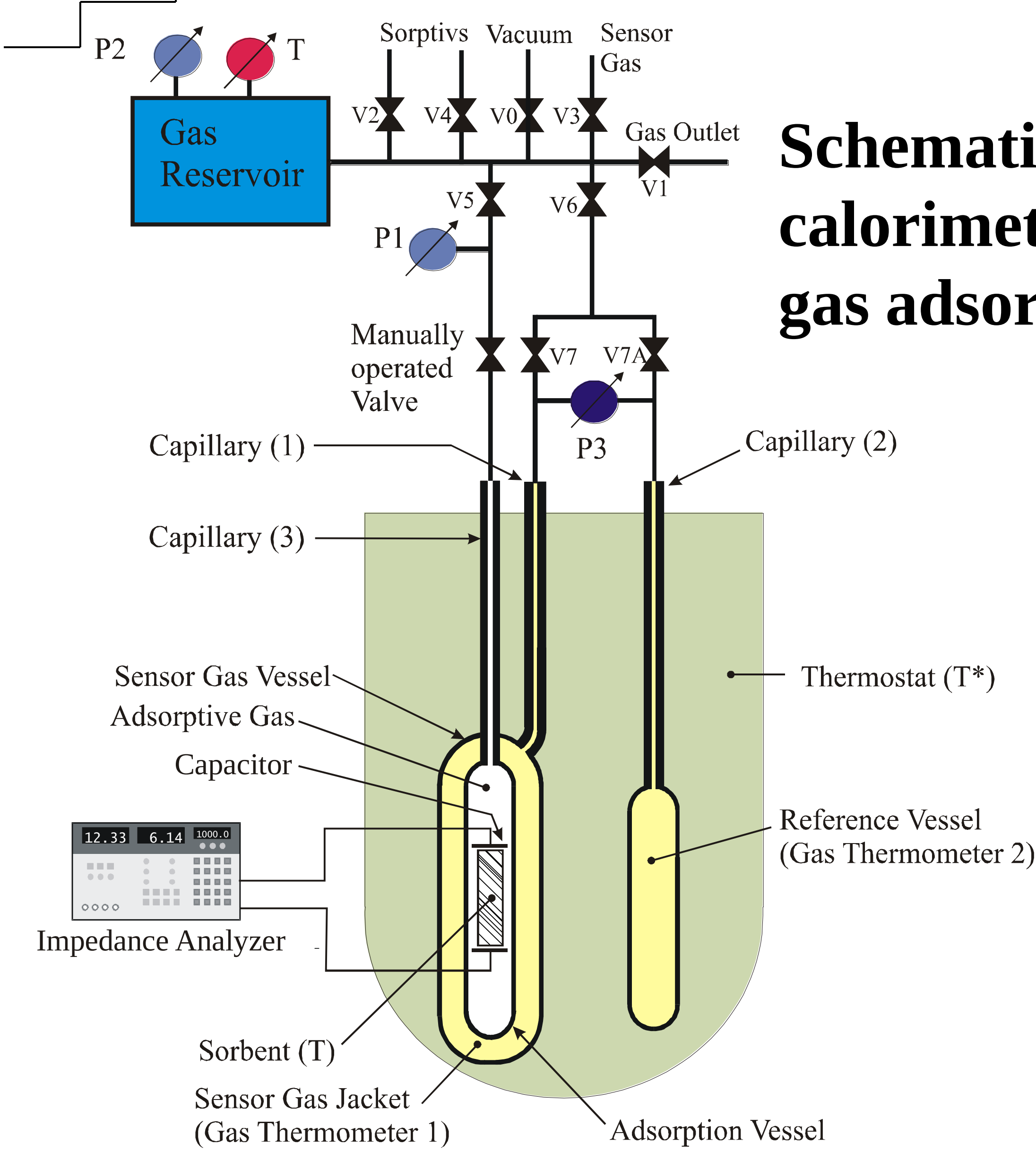
Sensor gas N_2 (1.6bar), T=298K, τ=10s

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



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

Schematics of combined calorimetric-dieletric-volumetric gas adsorption measurements



(CI) $h = h_0 + Be^{-bp}$ $\rightarrow$ $\frac{H}{m} - h_0 = B\left(\frac{(\Pi/m) - \hat{\alpha}_0}{A}\right)^{b/a}$

(DI) $\hat{\alpha} = \hat{\alpha}_0 + Ae^{-ap}$

$$m = H \Big/ \left[h_0 + B\left(\frac{(\Pi/m) - \hat{\alpha}_0}{A}\right)^{b/a} \right] \quad *)$$

$$\rightarrow \quad h - h_0 = B\left(\frac{\hat{\alpha} - \hat{\alpha}_0}{A}\right)^{b/a}$$

$$h = \frac{H}{m}$$

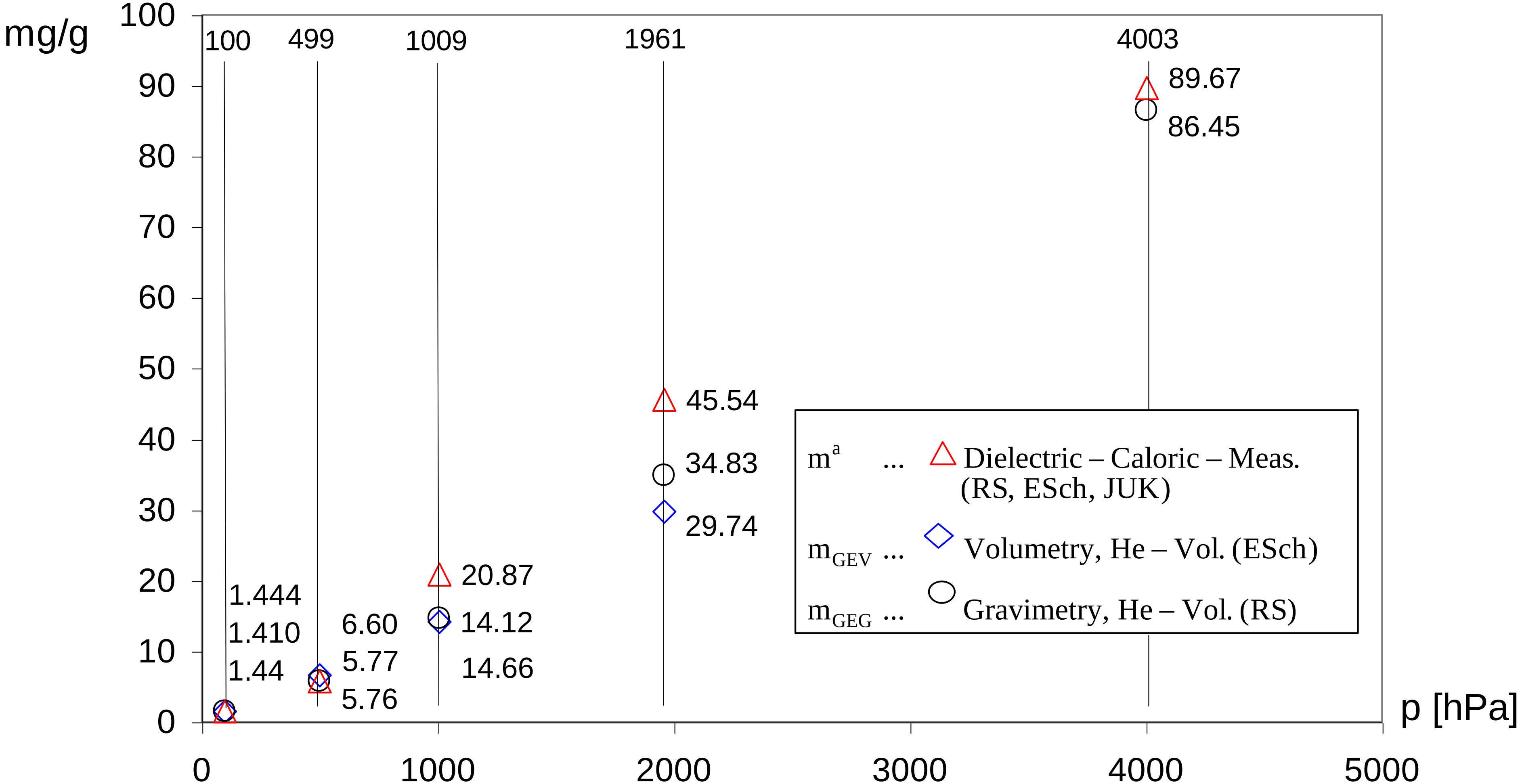
$$\hat{\alpha} = \frac{\Pi}{m}$$

$$\sum_i \left[H - h \;\; b,B \;\; m \;\; a,b,A,B,H,\Pi \right]_i^2 +$$

$$\sum_k \left[\Pi - \hat{\alpha} \;\; a,A \;\; m \;\; a,b,A,B,H,\Pi \right]_k^2 \rightarrow \text{Min}$$

$$\rightarrow a,\ A,\ b,\ B \rightarrow (*) \rightarrow m$$

Calculation of absolute adsorbed masses from DE-C-measurements



Absolute masses (m^a) and Gibbs excess masses (m_{GEV}, m_{GEG}) of CO_2 adsorbed on wessalite (DAY-zeolite) at T=298K

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	–	–	

GVC-GET Thermodynamic-Conference Würzburg, 2001