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

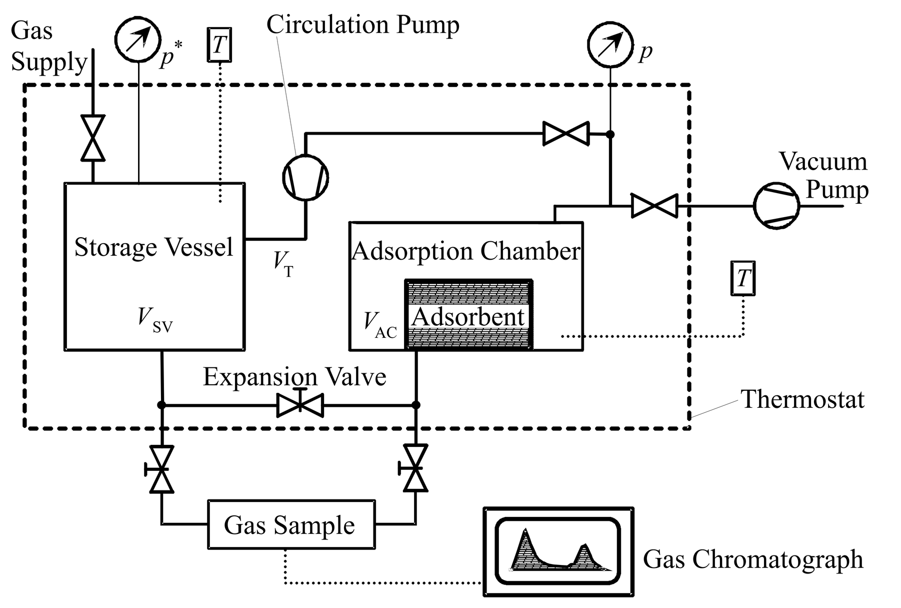
J. U. Keller[1], N. Iossifova[1], M. Seelbach[1], E. Schein[1], W. Zimmermann[1], F. Dreisbach[2], R. Staudt[3]

[1] Inst. Fluid- & Thermodynamics
University of Siegen, 57068 Siegen
e-mail: keller@ift.maschinenbau.uni-siegen.de

[2] Rubotherm Präzisionsmesstechnik GmbH
Universitätsstr. 142, 44799 Bochum
e-mail: dreisbach@rubotherm.de

[3] Center of Non-Classical Chemistry (INC)
University of Leipzig, 04318 Leipzig
e-mail: staudt@inc.uni-leipzig.de

Volumetry / Manometry (N ≥ 1)



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

Volumetry / Manometry, Theory (N ≥ 1)

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

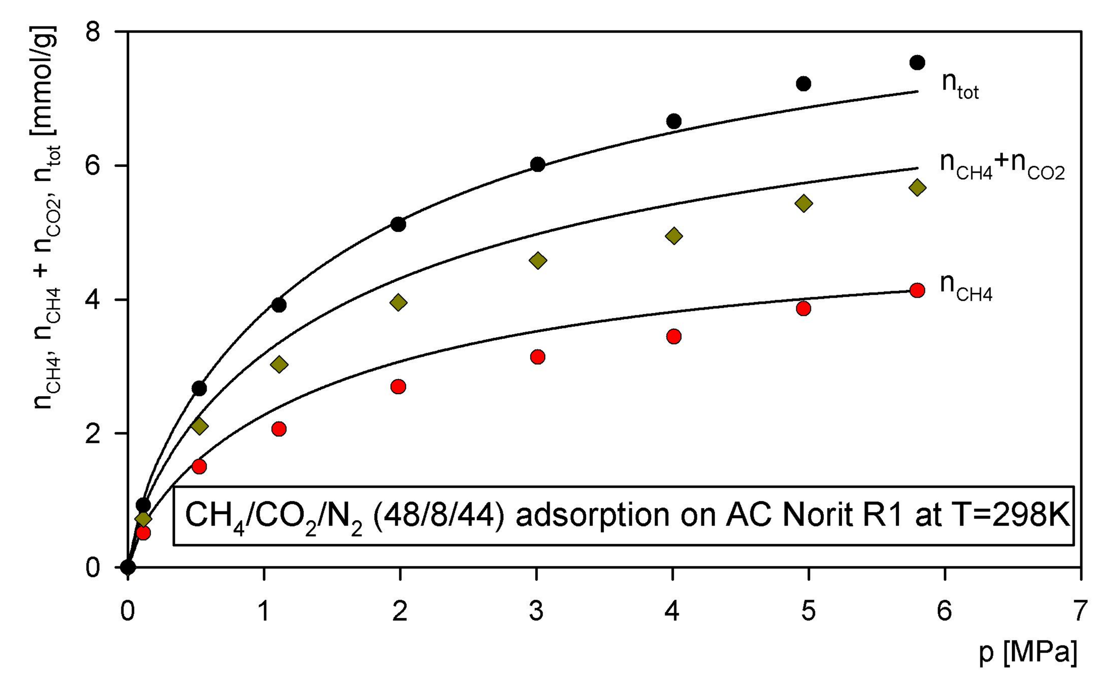
$(1-3): \Omega_i = m_i - \rho_i^f V^S$ (4)

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

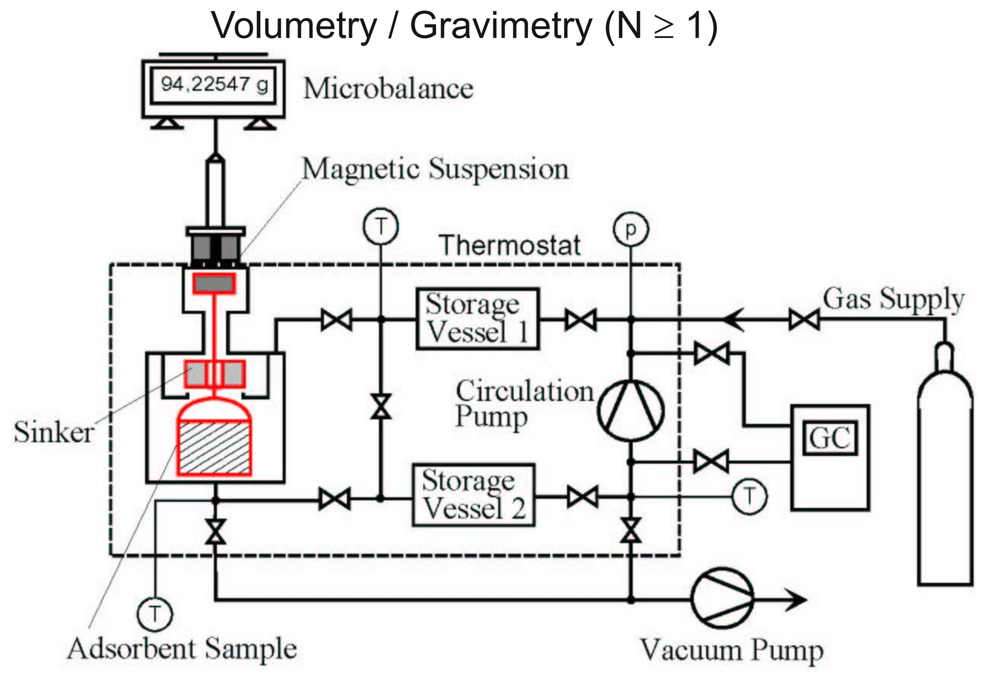
$\rho_i^f = w_i \rho^f (T, p, w, \ldots w_N), \quad w_i : GC$

$m_i \ldots$ Gibbs excess mass

Prediction of tenary adsorption data with the 2-sites AI



Volumetry / Gravimetry (N ≥ 1)



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

Gravimetry / Volumetry, Theory (N = 2)

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

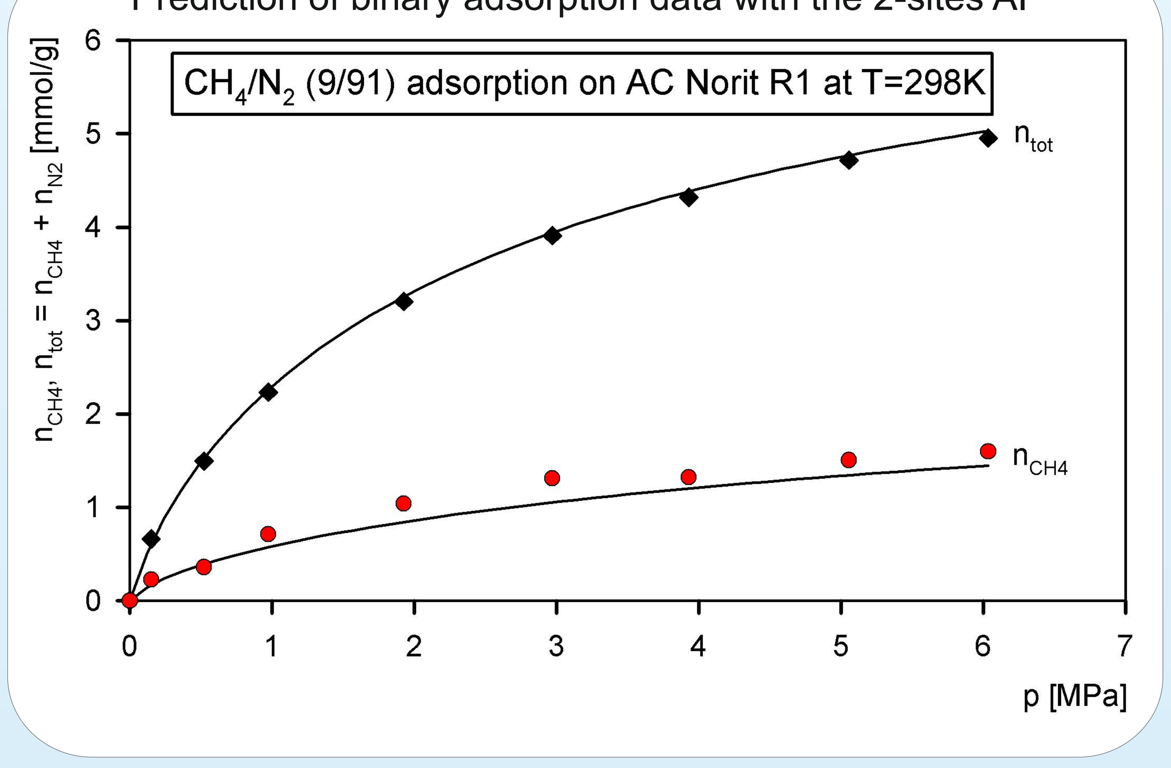
Micro-balance equation $\Omega = m_1 + m_2 - V^{as} \frac{m_1^f + m_2^f}{V^* + V^f}$

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

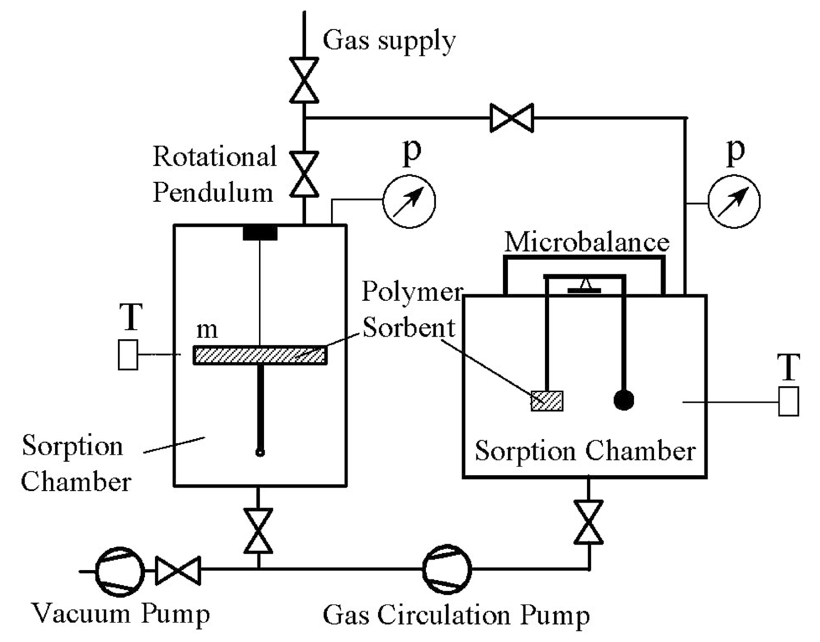
$\rightarrow m_1, m_2, m_1^f, m_2^f \ldots V^f = V - \left(1 + \frac{m_0^s}{m^s}\right) V^{as}$ if $M_1 \neq M_2$

Volume-gravimetric measurements of binary coadsorption equilibria

Prediction of binary adsorption data with the 2-sites AI



Oscillometry, Gravimetry for Swelling Sorbent Materials (Polymers)



Experimental setup for oscillometric-gravimetric measurements

Oscillometry, Theory

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)

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

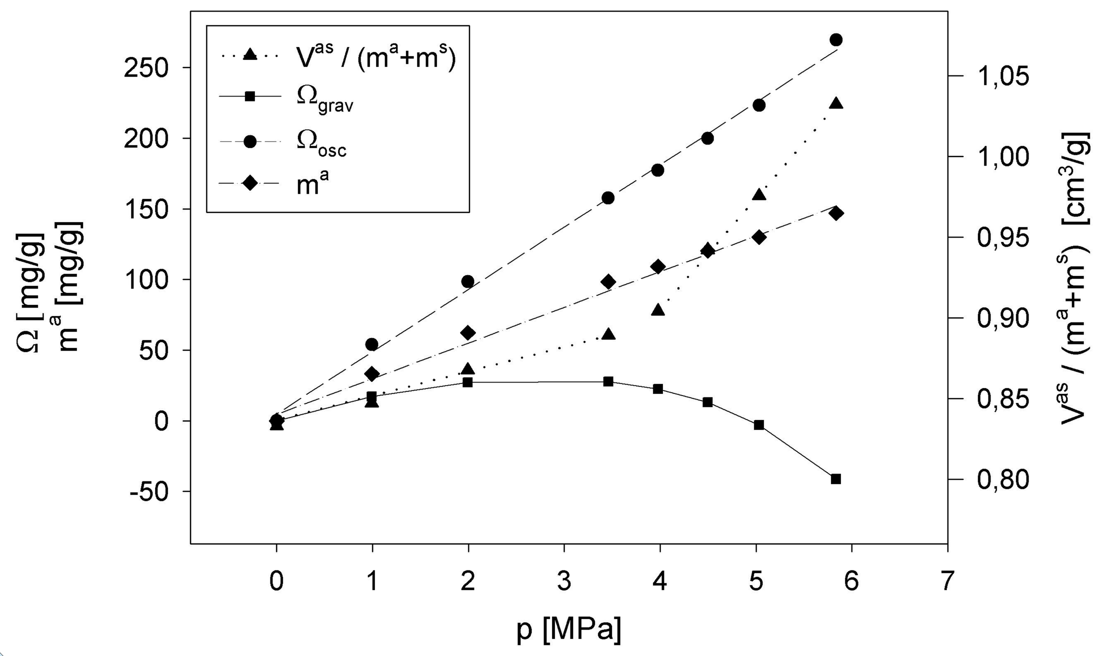
$\omega^*, \Delta^* \ldots$ empty pendulum (m^*), vacuum

$\omega_0, \Delta_0 \ldots$ pendulum and adsorbent (m^*, m^s), vacuum

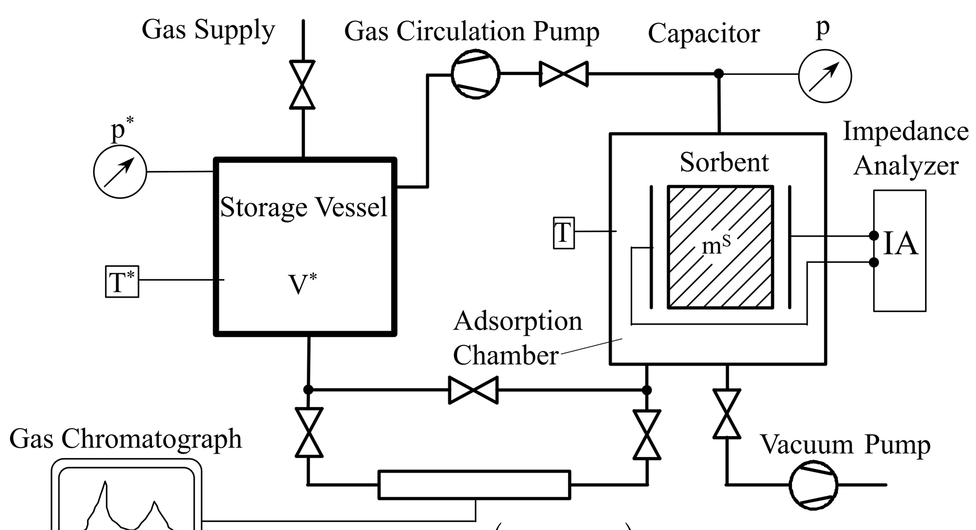
$\omega_E, \Delta_E \ldots$ pendulum, adsorbent, adsorbate (m^*, m^s, m), gas

Oscillometric measurements of gas adsorption equilibria

Swelling and sorption isotherm of polycarbonate / CO_2 at 293 K



Impedance Spectroscopy, Volumetry (N=1)

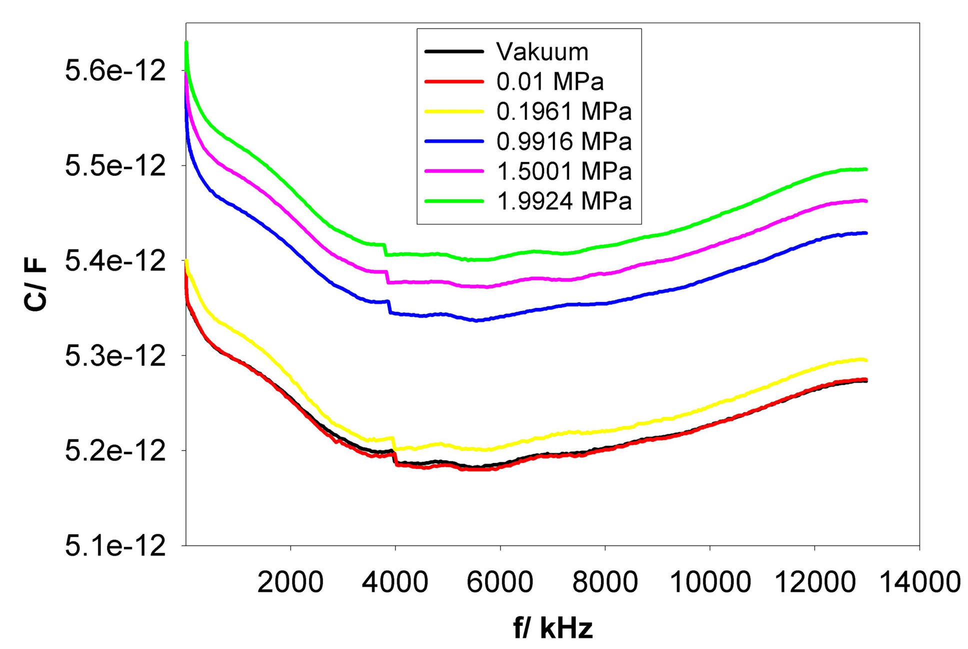


V, M $m_{MG} = m^* - (V^* - V^{as}) \rho^f (p, T), \; V^{as} \cong V_{He}$

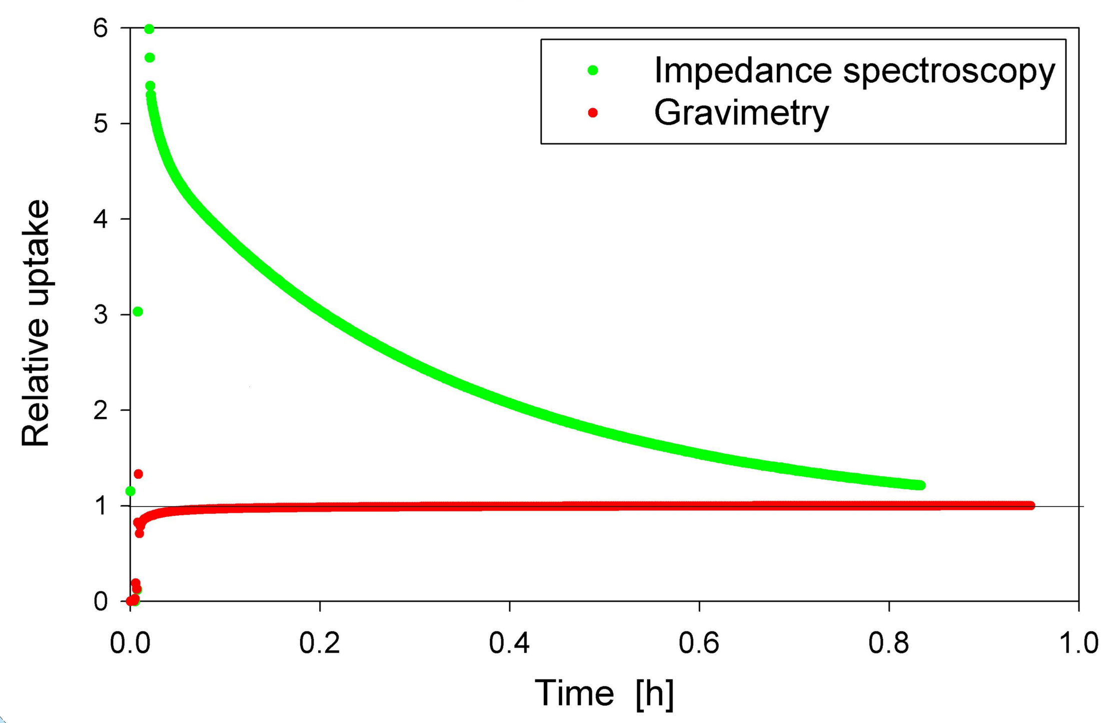
DE $\Omega_{DE} = \alpha(p, T) m_{MG}$

Experimental setup for volumetric-dielectric measurements

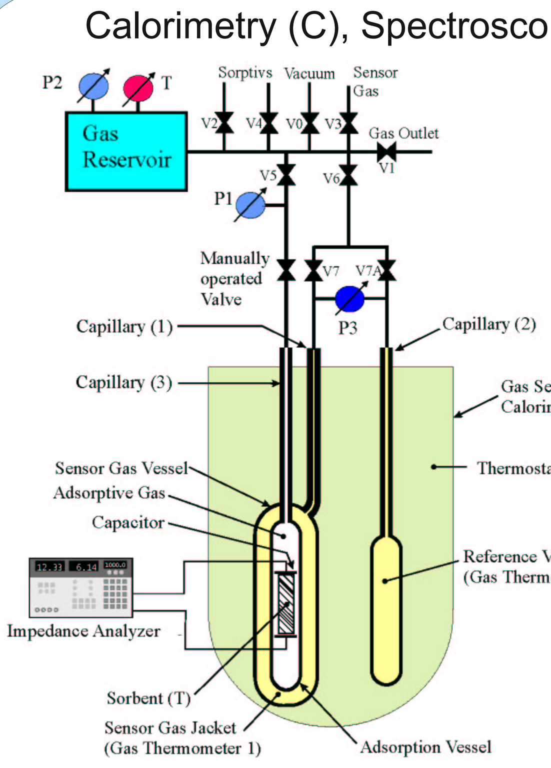
Impedance spectra of CO_2 on zeolite (DAY), T=298K



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



Calorimetry (C), Spectroscopy (SP), Volumetry (V), (N=1)



Schematics of combined calorimetric-dielectric-volumetric gas adsorption measurements

Calorimetry (C), Spectroscopy (SP), Volumetry (V), (N=1)

Example:

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

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

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

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

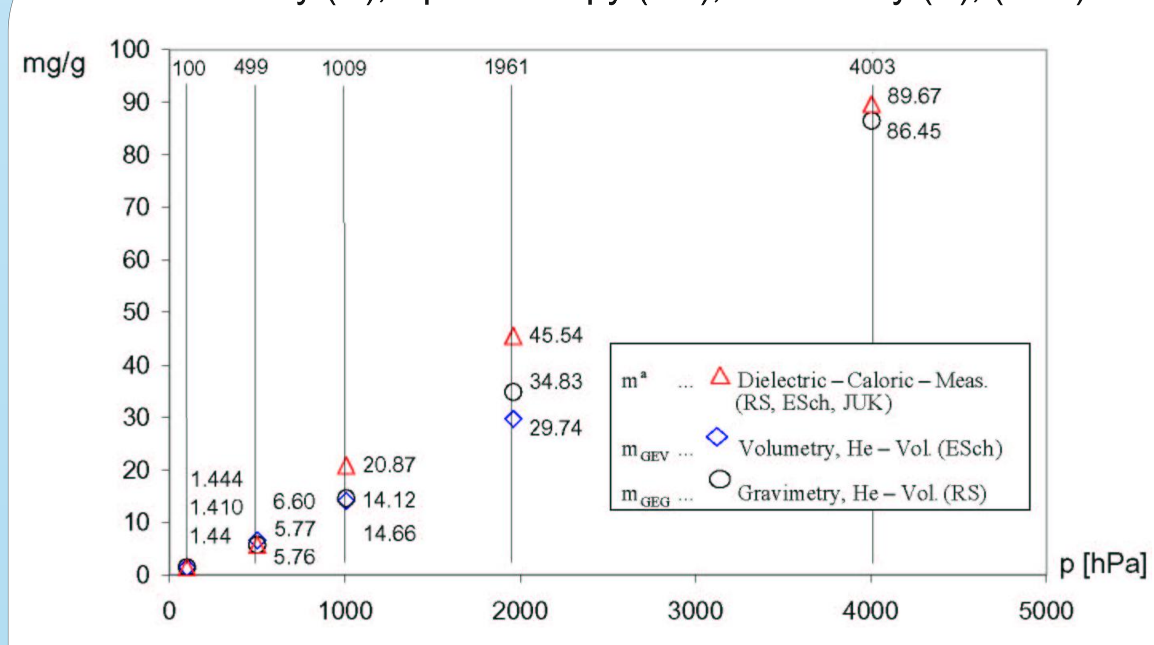
$m = H \Big/ \left[h_0 + B\left(\frac{(\Pi/m) - \hat{\alpha}_0}{A}\right)^{b/a}\right]$ *)

$\sum_i \left[H - h(b,B)\, m(a,b,A,B,H,\Pi)\right]_i^2 + \sum_k \left[\Pi - \hat{\alpha}(a,A)\, m(a,b,A,B,H,\Pi)\right]_k^2 \rightarrow \text{Min}$

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

Calculation of absolute adsorbed masses from C-SP-V- measurements

Calorimetry (C), Spectroscopy (SP), Volumetry (V), (N=1)



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