Determination of Absolute Gas Adsorption Isotherms by Combined Calorimetric and Dielectric Measurements

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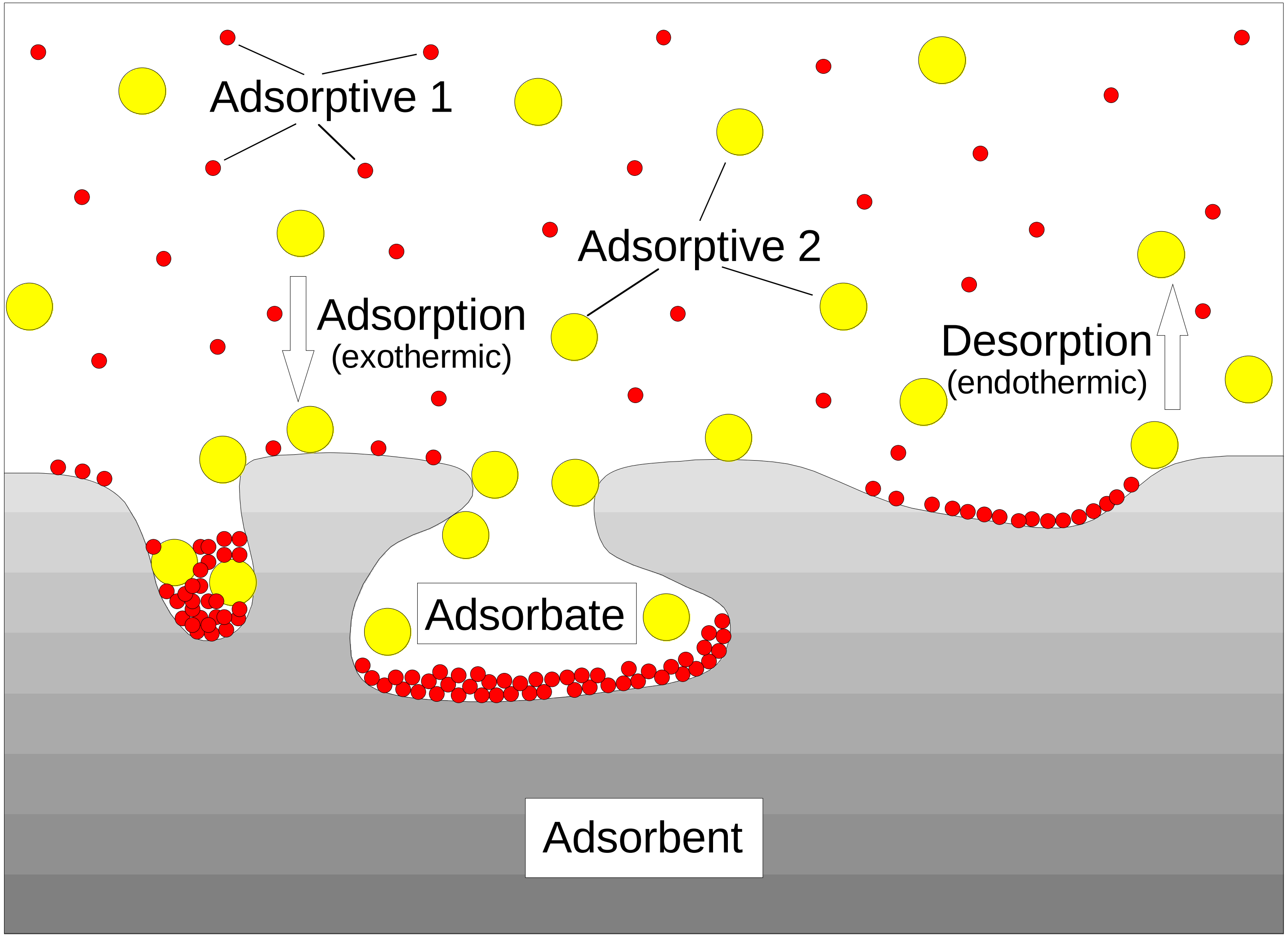
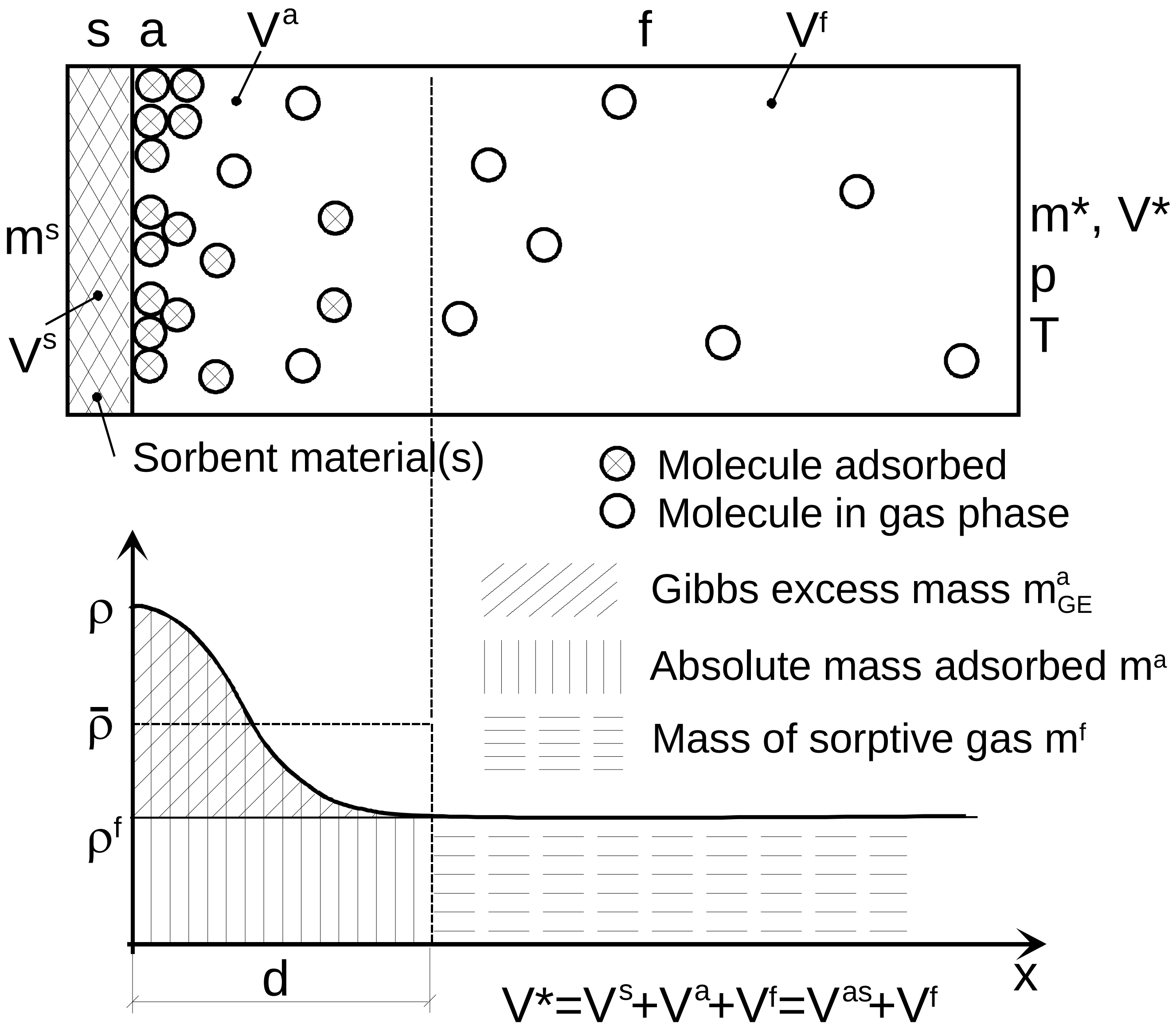
6. Example



Gas Adsorption Systems, Basic Concepts

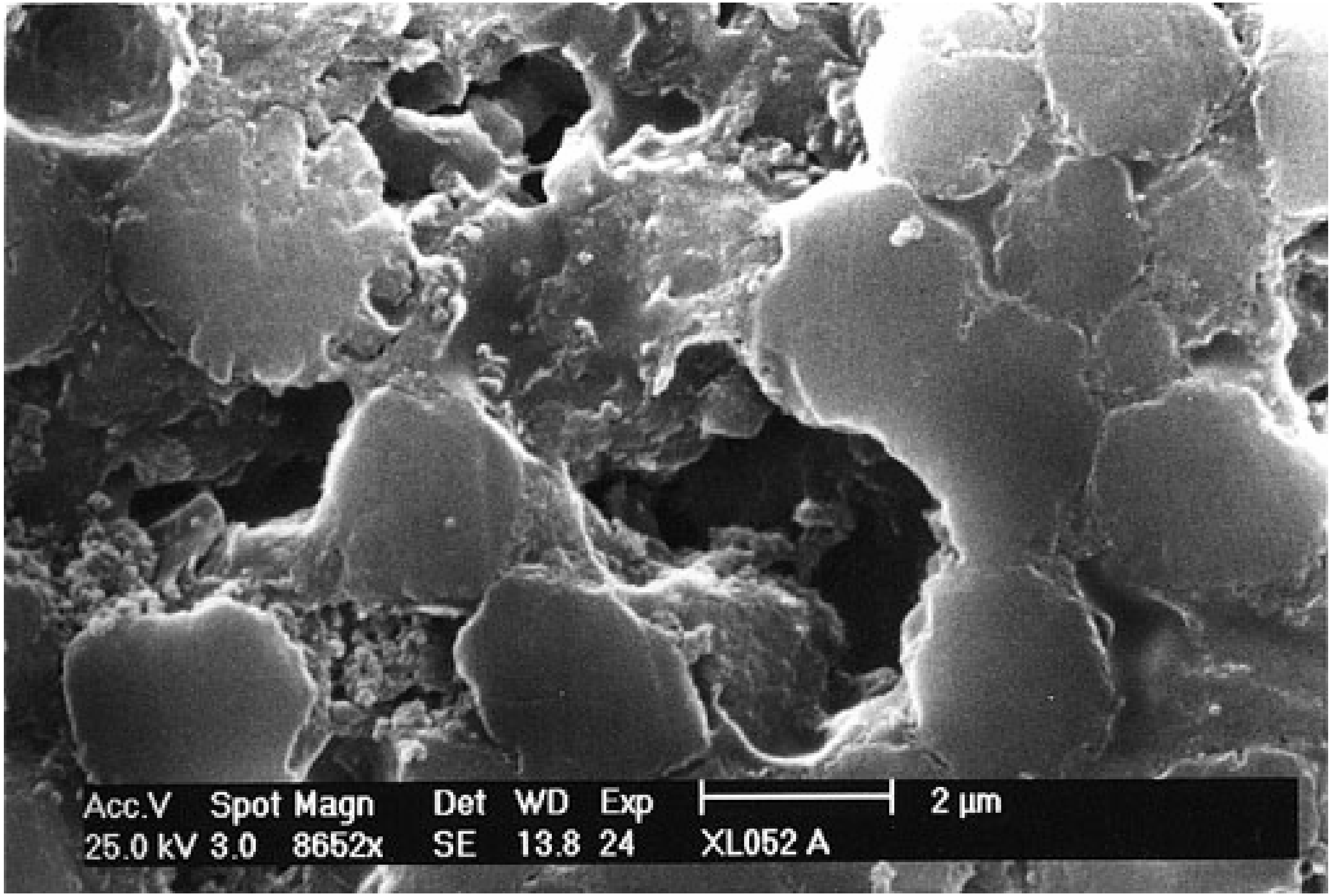
Plane Surface Sorption System: Absolute/Excess Mass

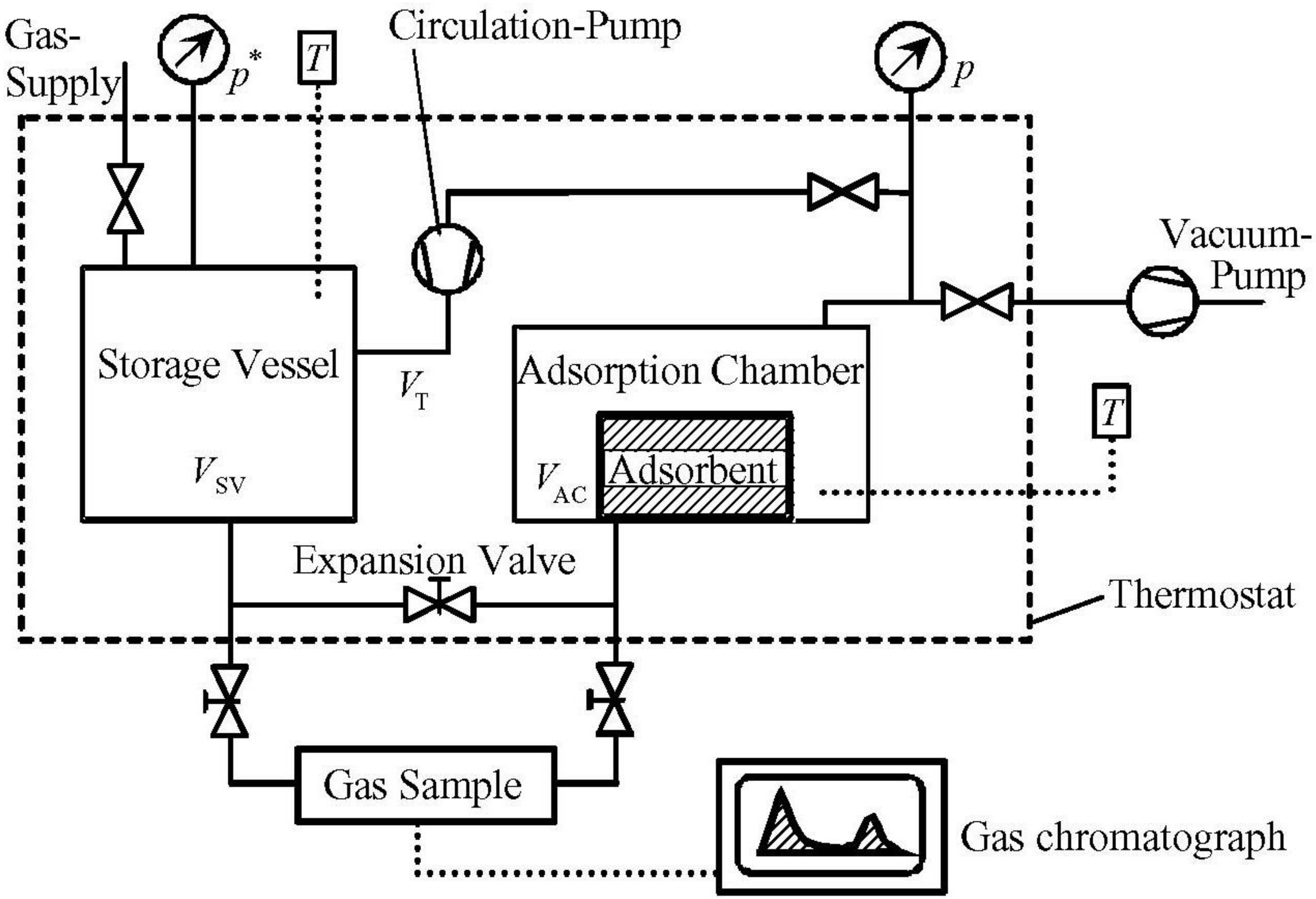


$$V^* = V^s + V^a + V^f = V^{as} + V^f$$

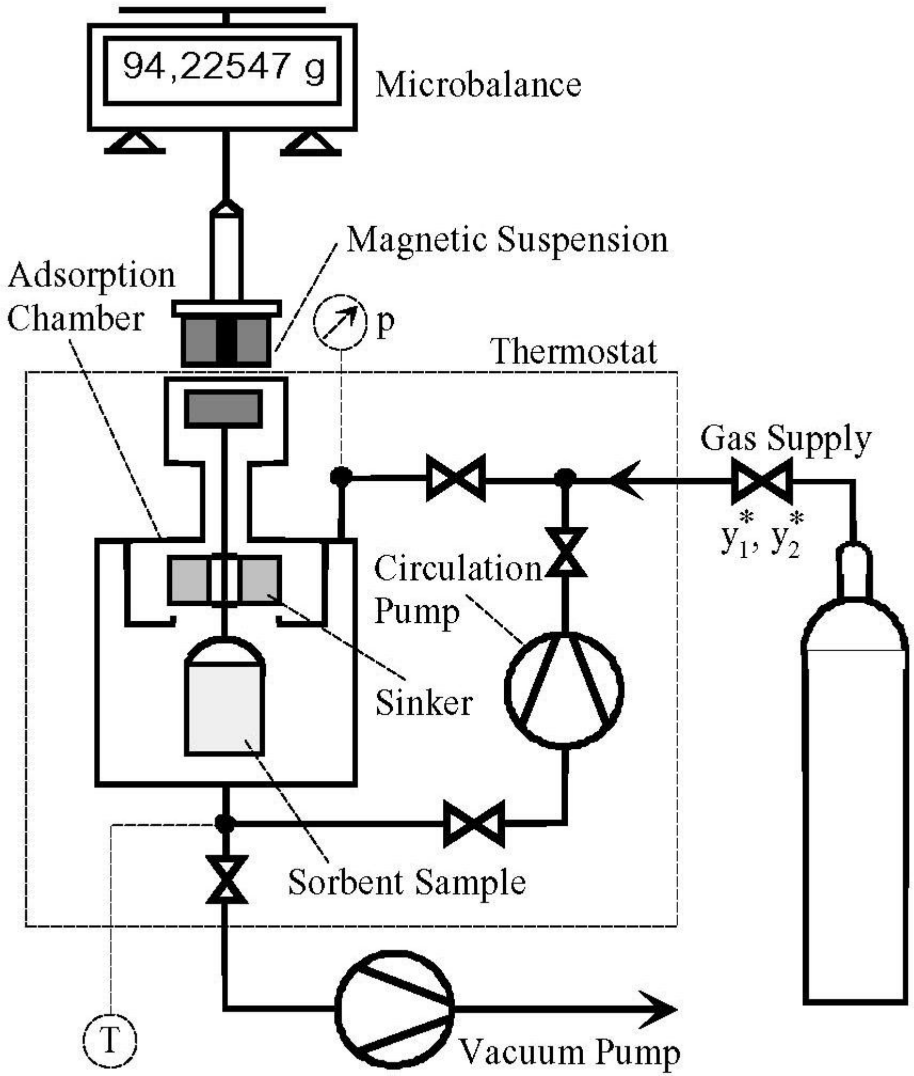
Zeolite Molecular Sieve UOP/Linde MS13X

Capillaries/Macropores, Mesopores,Micropores





Experimental Setup for Volumetric- Chromatographic Measurements of Gas Adsorption Equilibria



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

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Measurement Methods of Masses of Adsorbed Phases

1.Volumetry / Manometry

Result of measurements:

$$\Omega = m^{a} - \rho^{f} V^{as}$$

2.Gravimetry

Gas Adsorption System

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

Approximations:

1.Gibbs excess mass

$$V^{as} \cong V_{He}^{s}, \quad V^{a} = 0$$

$$m_{GE}^{a} = \Omega + \rho^{f} V_{He}^{s}$$

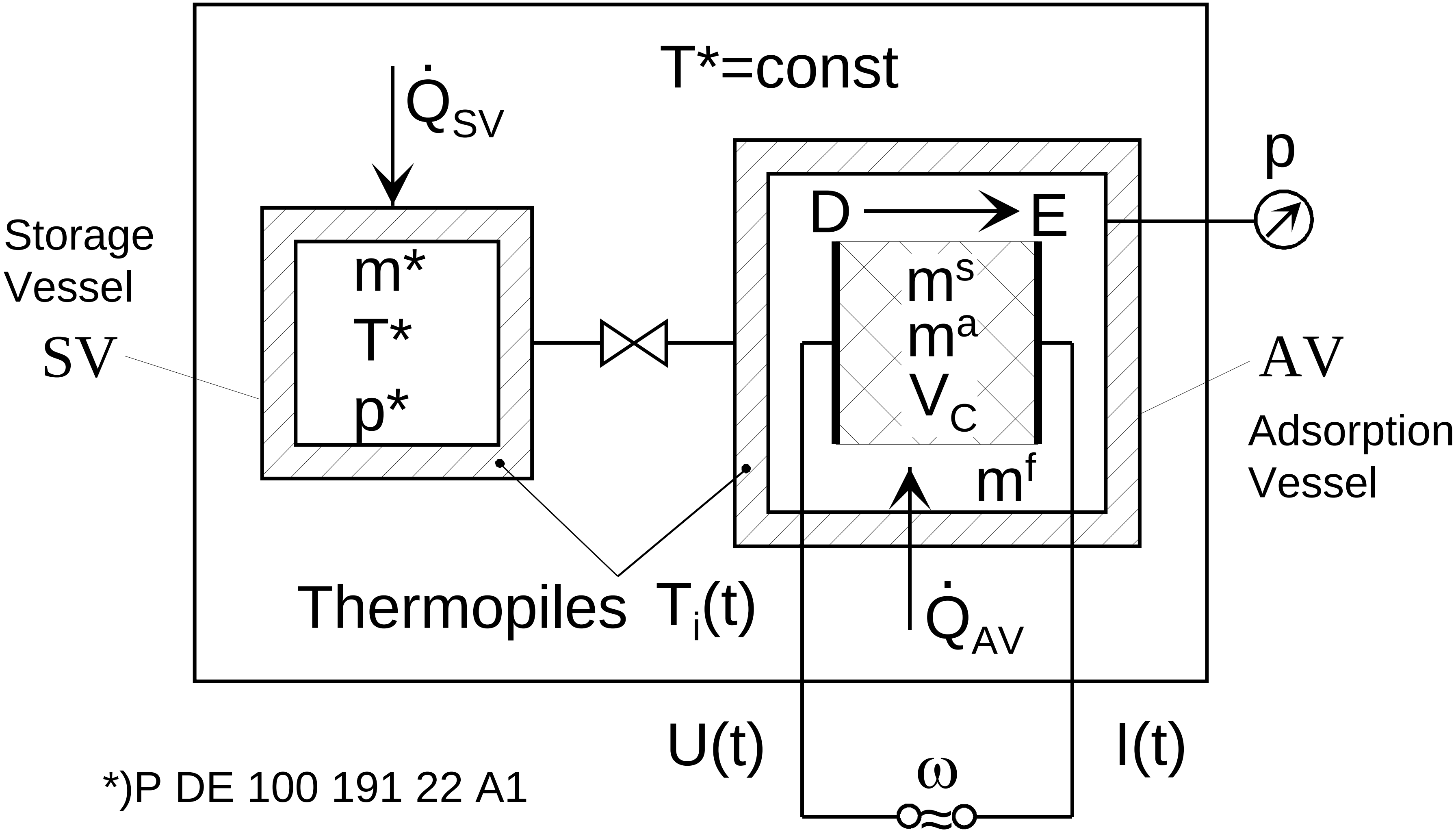
2.Absolute mass adsorbed

$$V^{as} \cong V_{He}^{s} + (m^{a} / \rho_{0}^{L})$$

$$m^{a} = \frac{m_{GE}^{a}}{1 - (\rho^{f} / \rho_{0}^{L})} \geq m_{GE}^{a}$$

Impedance Calorimeter*

Experimental setup for calorimetric - dielectric measurements of gas adsorption equilibria.



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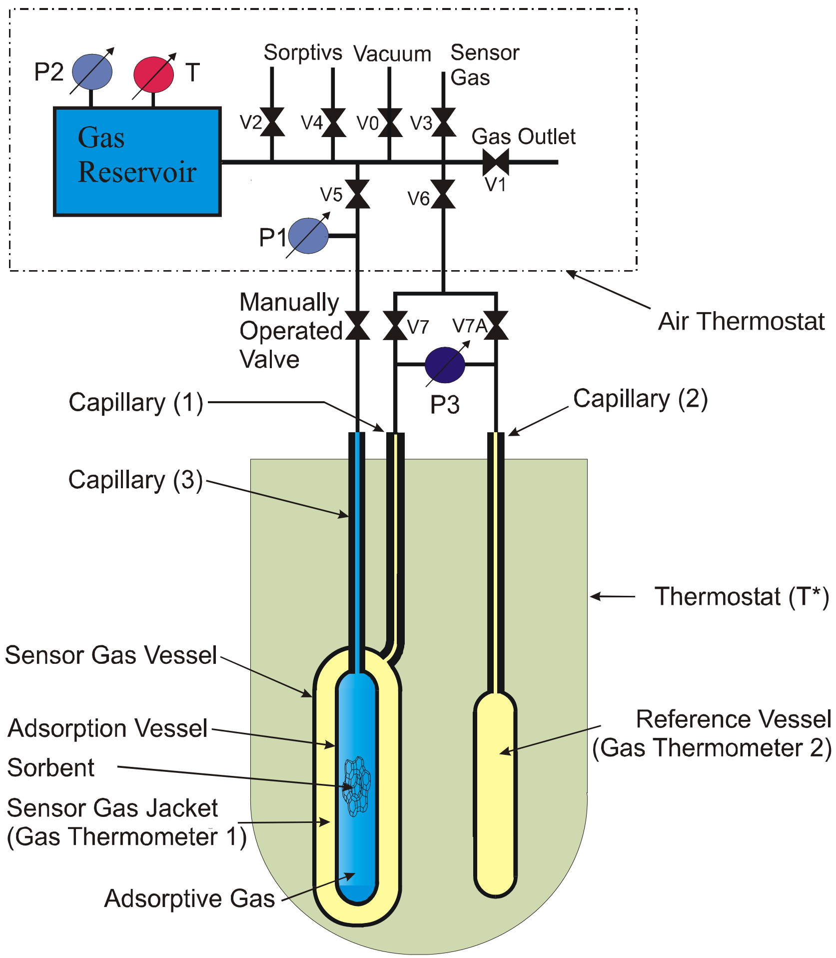
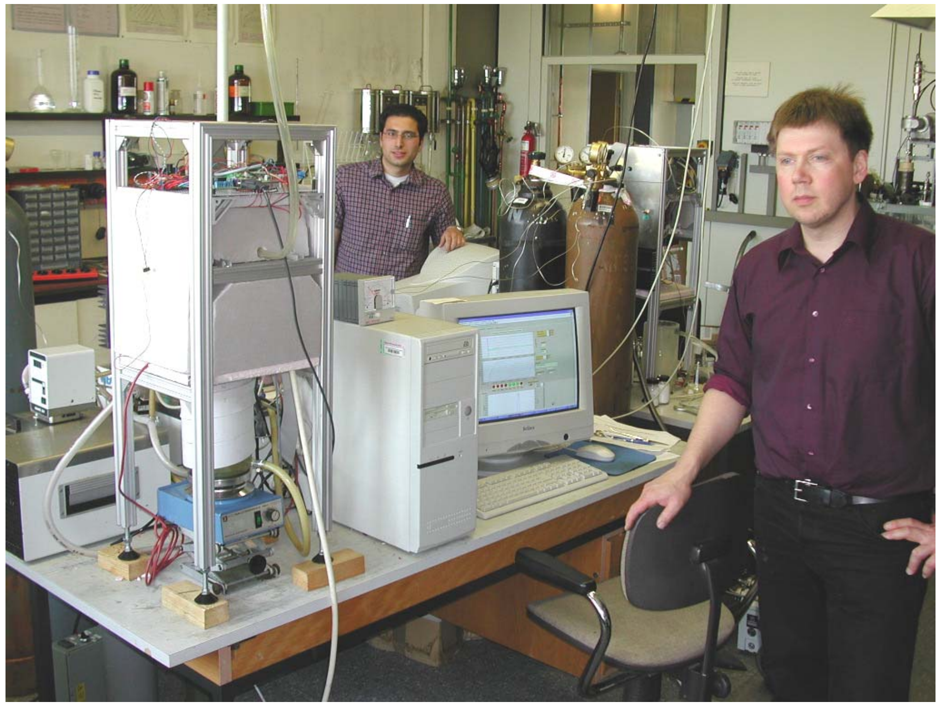
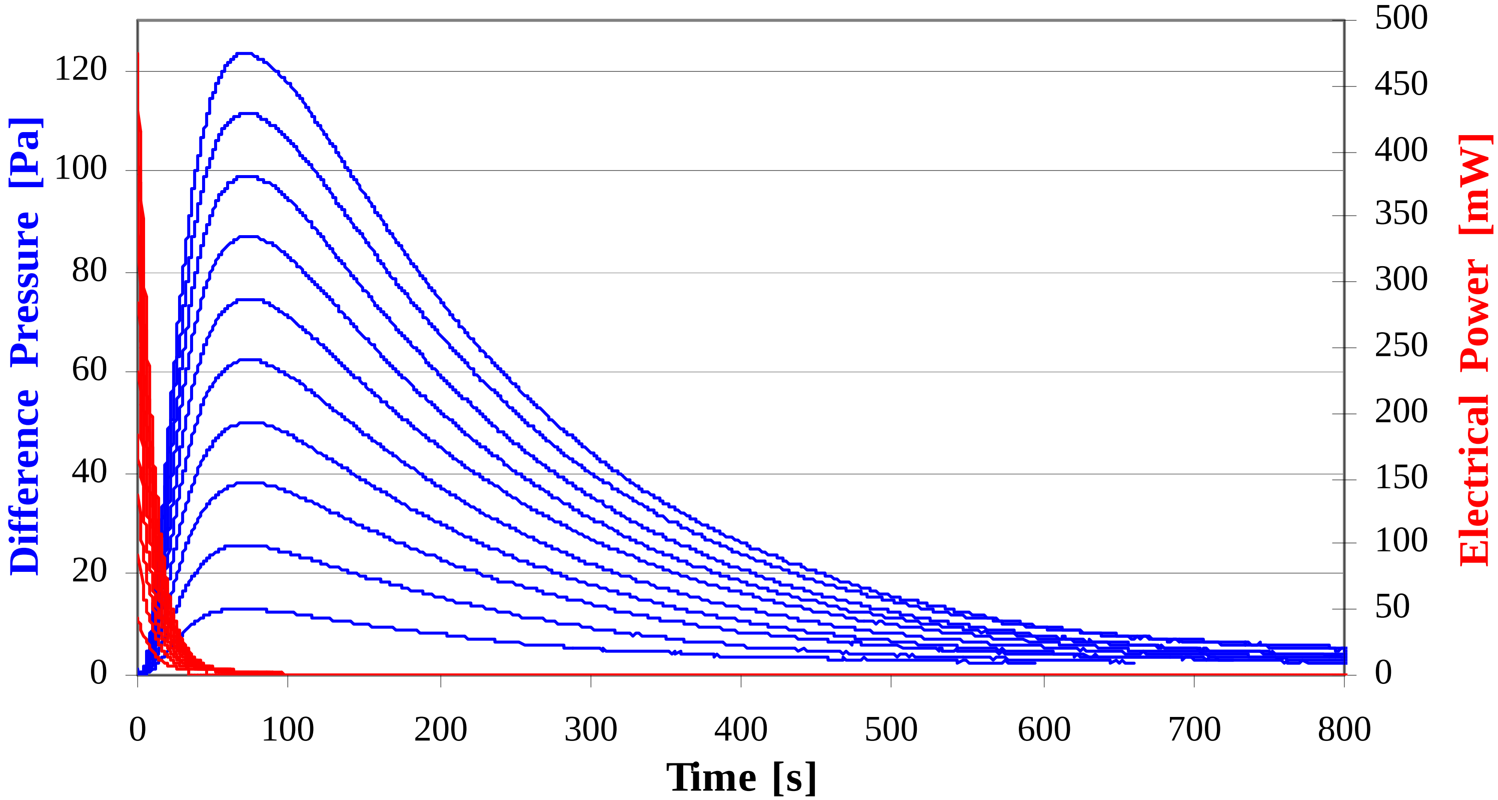


Schematic diagram of a sensor gas calorimeter (SGC)



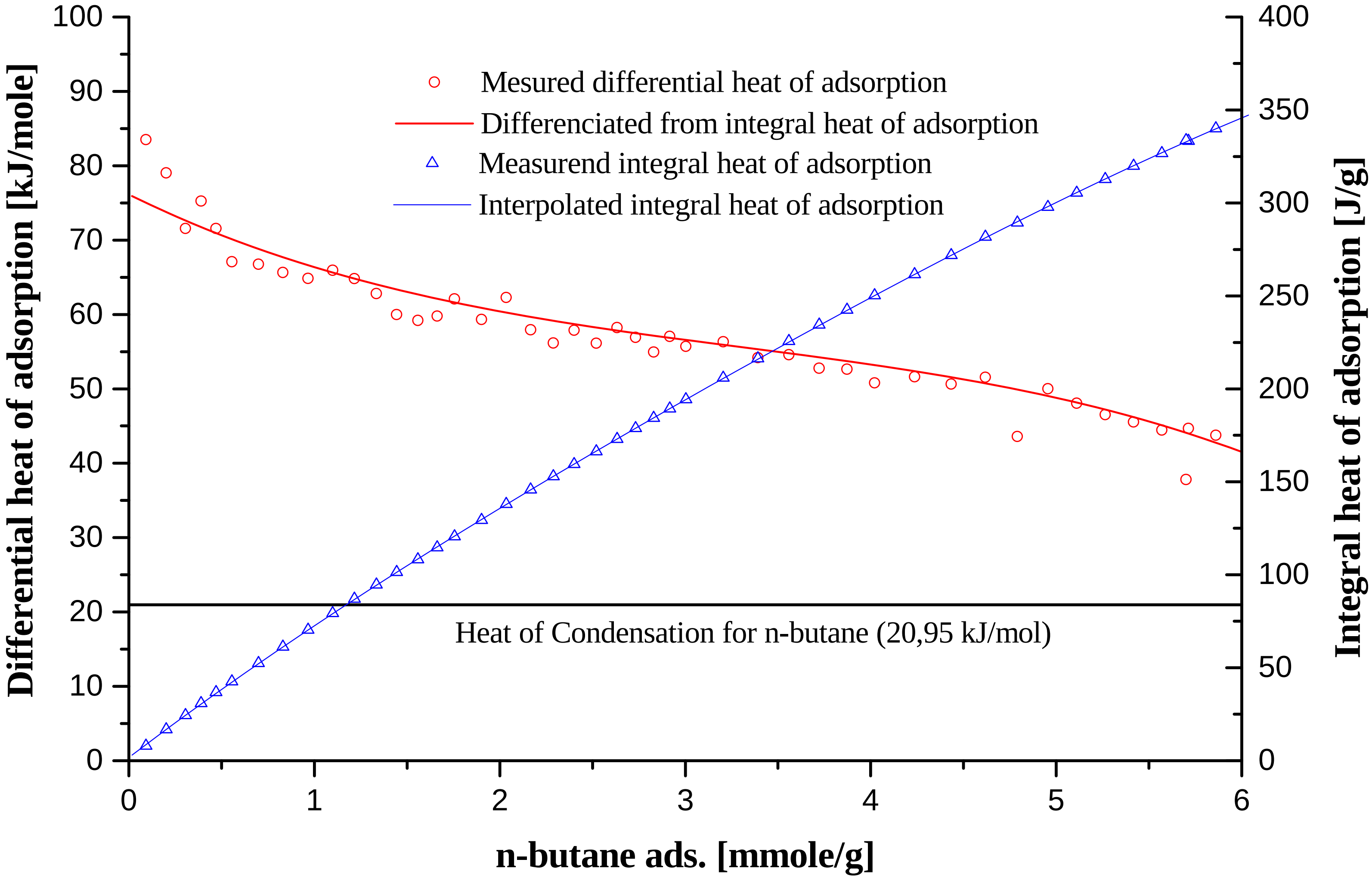
Sensor gas calorimeter (SGC) for simultaneous measurements of adsorption isotherms and enthalpies.



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)



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

Calorimetric - Dielectric Measurements (1)

1.Dielectric polarizability of the adsorbed phase (a)

$$\Omega^{a}_{DE} = \Omega^{a}_{DE}(p, T, m^{s}, m^{a})$$

Asm/(V/m) DEOS

$$\Omega^{a}_{DE} = \alpha^{a}\left(p, T, \frac{m^{a}}{m^{s}}\right)m^{a}$$

2.Enthalpy of adsorbed phase (a)

$$\Delta H = H^{f} - H^{a}$$

$$\Delta H = \Delta H(p, T, m^{a}, m^{s})$$

J, kJ CEOS

$$\Delta H = \Delta h(p, T, \tfrac{m^{a}}{m^{s}}).m^{a}$$

Calorimetric - Dielectric Measurements (2)

Inversion of (DEOS)

$$p = p\left(\alpha^a, T, \frac{m^a}{m^s}\right)$$

Insert in CEOS

$$\Delta H = \Delta h\left(p\left(\alpha^a, T, \frac{m^a}{m^s}\right), T, \frac{m^a}{m^s}\right) m^a$$

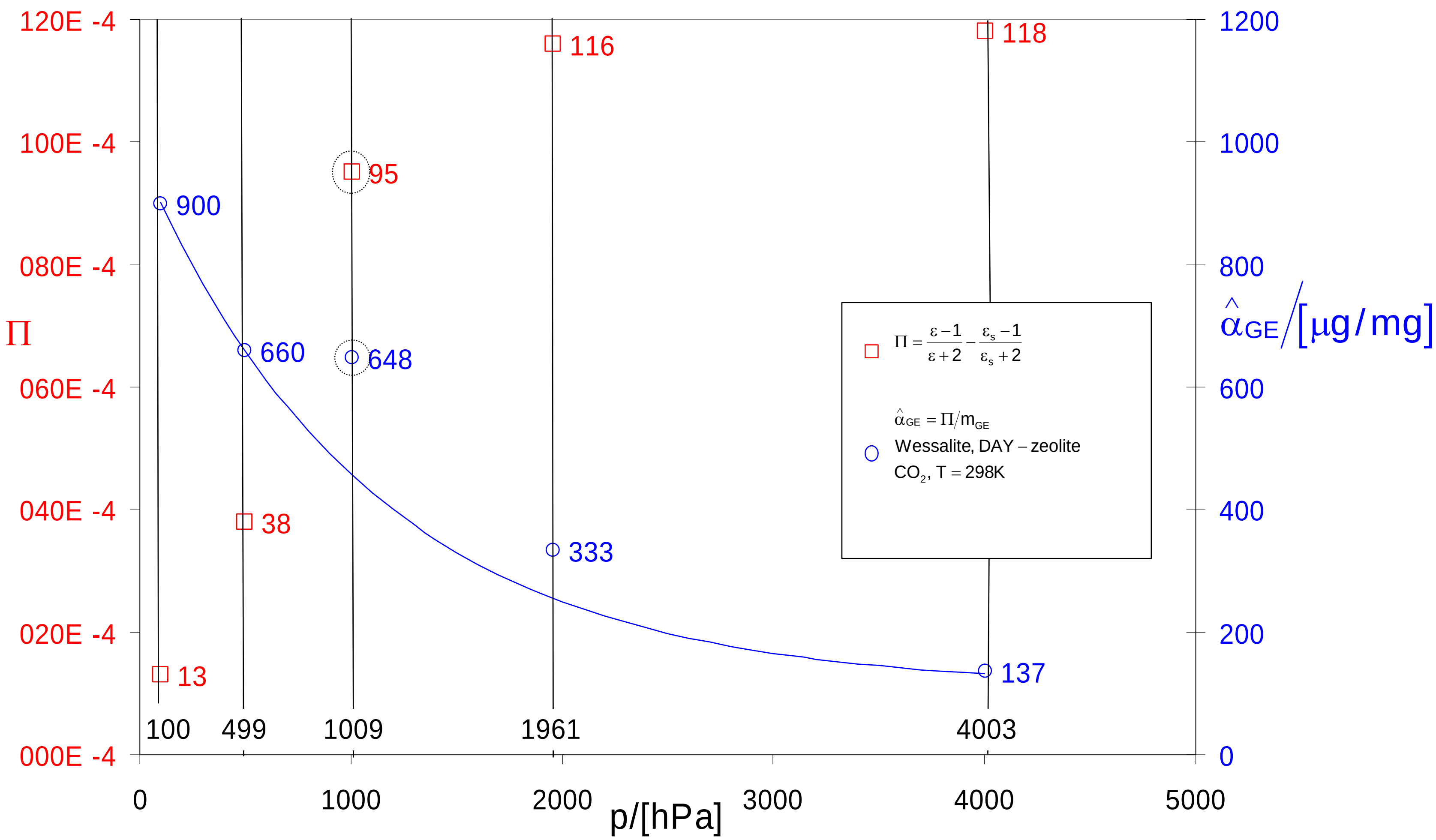
Extensivity relation

$$\alpha^a = \Omega_{DE}^a / m^a$$

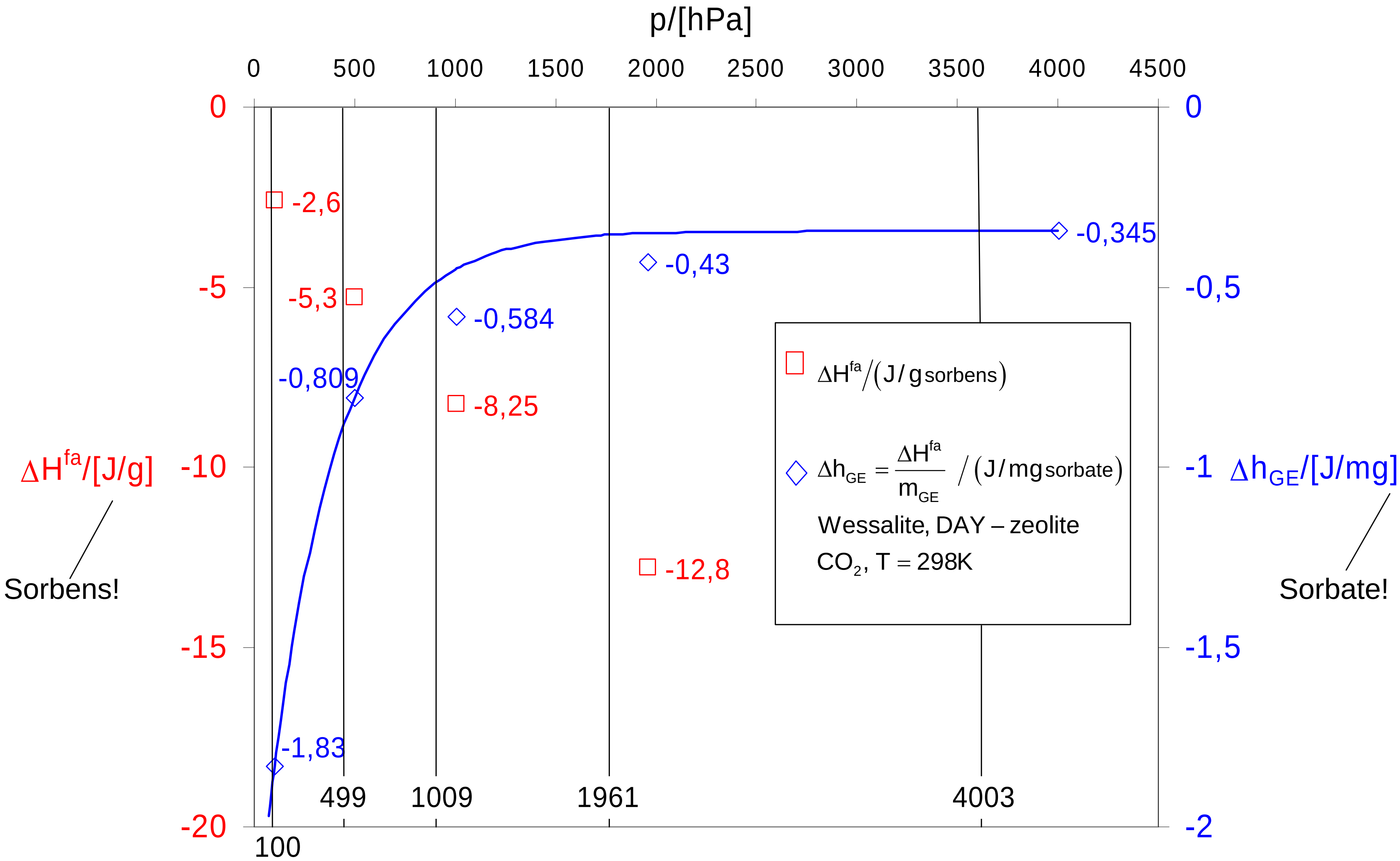
Dielectric - caloric equation of state (DCEOS)

$$\frac{\Delta H}{m^a} = \Delta h\left(\frac{\Omega_{DE}^a}{m^a}, T, \frac{m^a}{m^s}\right)$$

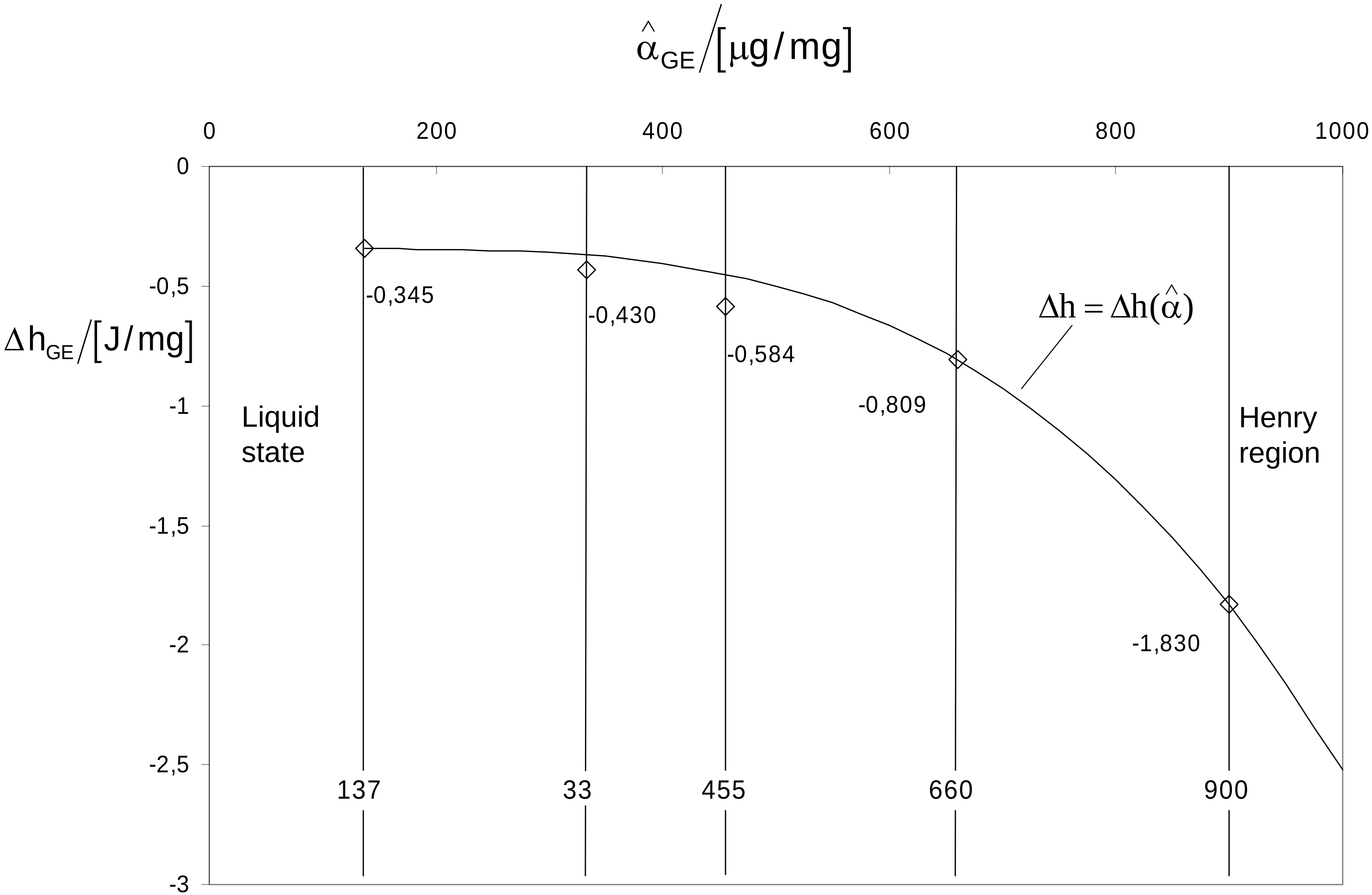
Experimental data: $\Delta H, \Omega_{DE}^a, T, m^s$ Calculated quantity: m^a



Reduced dielectric polarizability (Π) and Gibbs excess specific polarizability ($\hat{\alpha}$=Π/mGE) of CO_2 on DAY-zeolite at T = 298K.

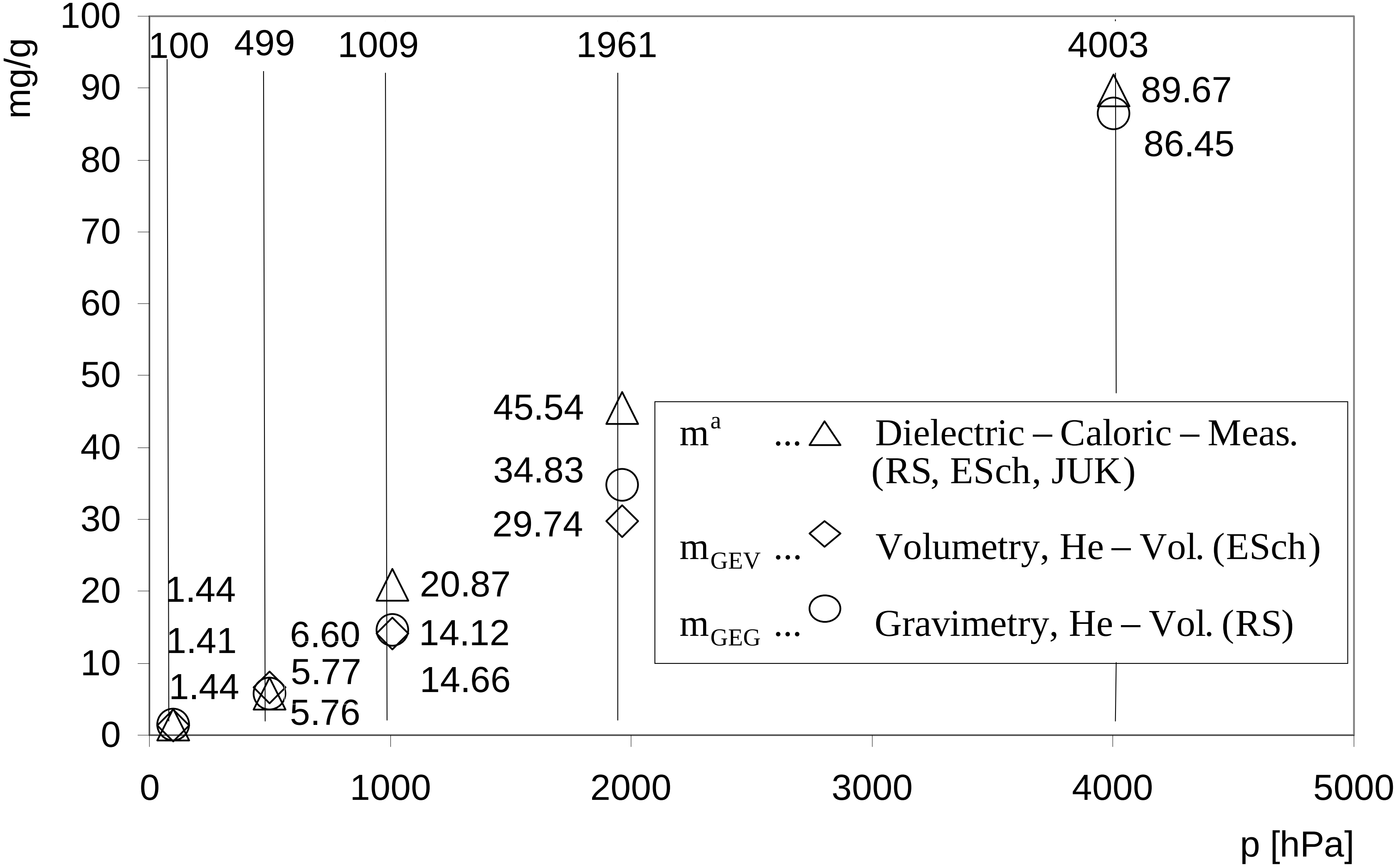


Enhalpy (ΔH^{fa}) and Gibbs excess specific enthalpy ($\Delta h_{GE}=\Delta H^{fa}/m_{GE}$) of CO_2 adsorbed on DAY-zeolite at T=298K.



Gibbs excess specific enthalpy ($\Delta h_{GE}=\Delta H^{fa}/m_{GE}$) - reduced Gibbs excess specific polarizability ($\hat{\alpha}_{GE}=\Pi/m_{GE}$) - diagram of CO_2 on DAY-zeolite at T=298K.
Curve: $\Delta h=\Delta h(\hat{\alpha})$, $\hat{\alpha}=P/m^a$, $\Delta h=\Delta H^{fa}/m^a$.

Absolute and Excess Masses of CO2 Adsorbates on Wessalite (DAY -Zeolite) at T=298K



Conclusions (1)

0. Gas adsorption phenomena on porous solids (zeolites,activated carbons) provide the basis for a still growing number of separation / purification processes for air and other technical gases.

1. Traditional measurement methods for the mass of gas adsorbed on a porous solid like **volumetry** and **gravimetry** need auxiliary model assumptions on the sorbent/sorbate system and hence deliver only approximate values of that mass.

   Deviations between apparent and true values of masses are expected to increase with increasing preasure and decreasing temperature.

Conclusions (2)

2. Combined calorimetric-dielectric measurements of gas adsorption systems allow on principle to **calculate** the mass adsorbed from the dielectric - caloric equation of state (DCEOS) of the adsorbate.

3. Measurements are presently laborious and cumbersome.

   Hence development of a (fully automated) instrument,probably based on a gas sensor calorimeter (SGC) would be desirable and useful.

References:
(1) Keller,J.U.,Staudt R.
Gas Adsorption Equilibria, Experimental Methods and Adsorption Isotherms, Springer, New York, 2004.

(2) Keller J.U.,Zimmermann W., Schein E.
Determination of absolute gas adsorption isotherms by combined calorimetric and dielectric measurements, Adsorption 9(2003),p.177-188.