

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

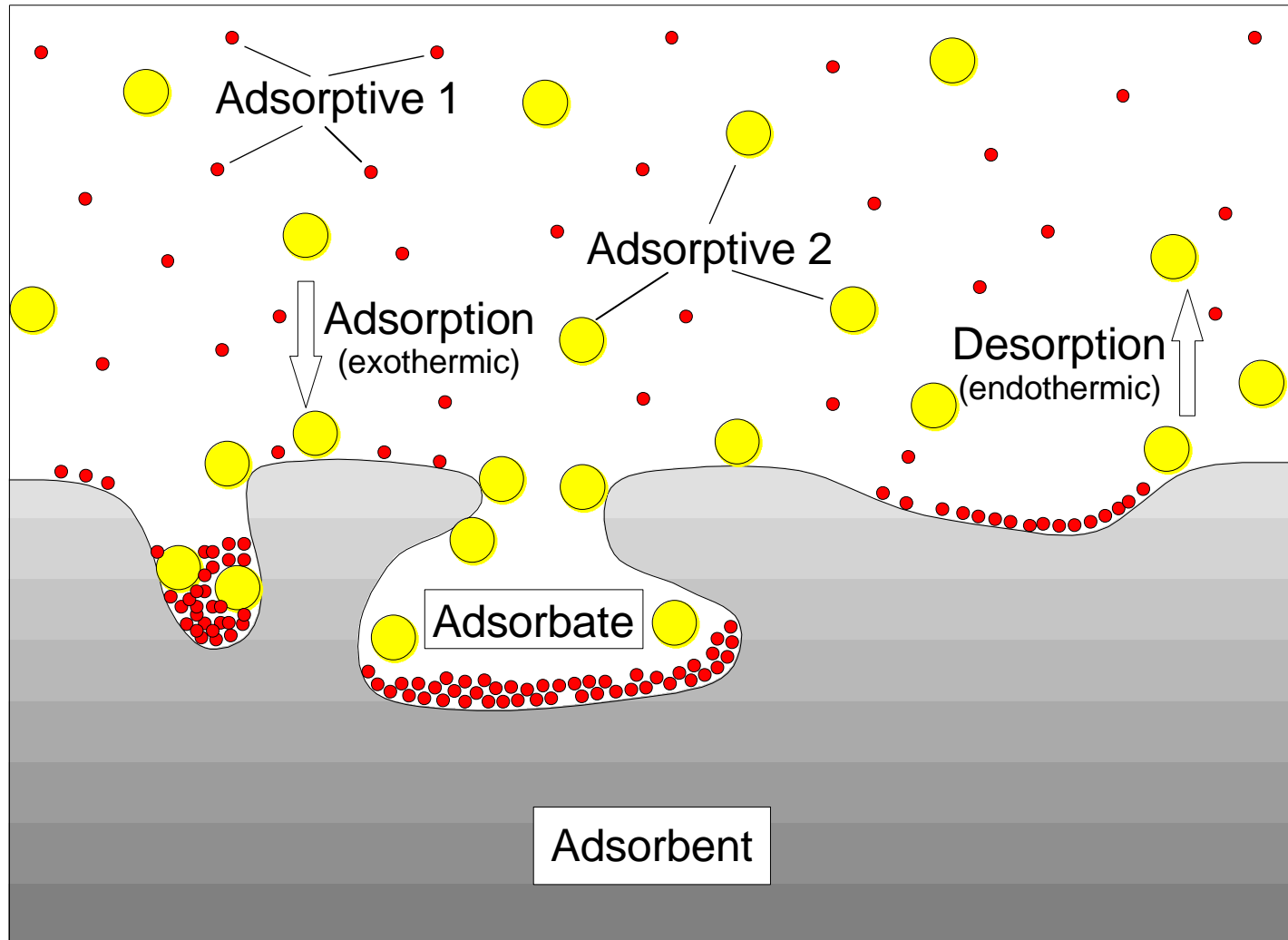
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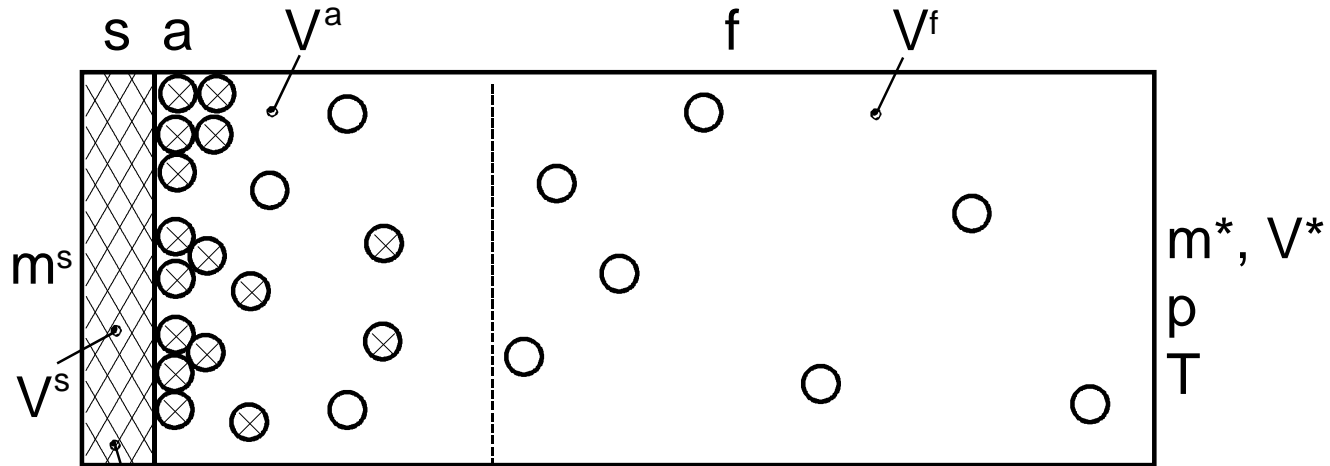
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1. Gas Adsorption Systems, Basic Concepts
2. Masses of Adsorbed Phases (Adsorbates)
Definition, Measurements Methods (Volumetry, Gravimetry)
3. Calorimetric Measurements of Pure Gas Adsorption
Equilibria
4. Dielectric Measurements of Pure Gas Adsorption Equilibria
5. Calculation of the Absolute Mass of the Adsorbate
6. Example



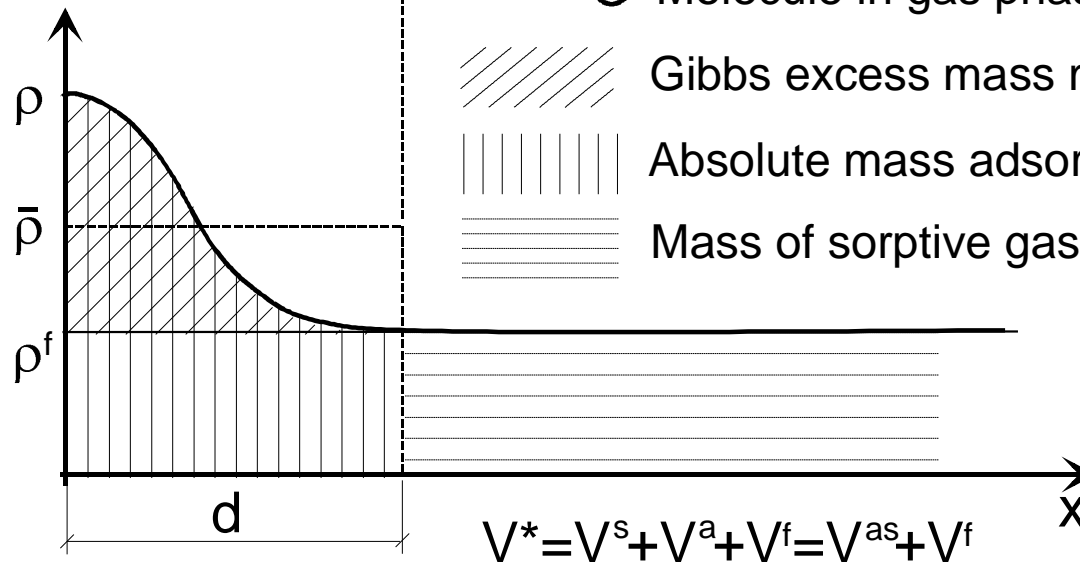
Gas Adsorption Systems, Basic Concepts

Plane Surface Sorption System: Absolute/Excess Mass



Sorbent material(s)

- ⊗ Molecule adsorbed
- Molecule in gas phase

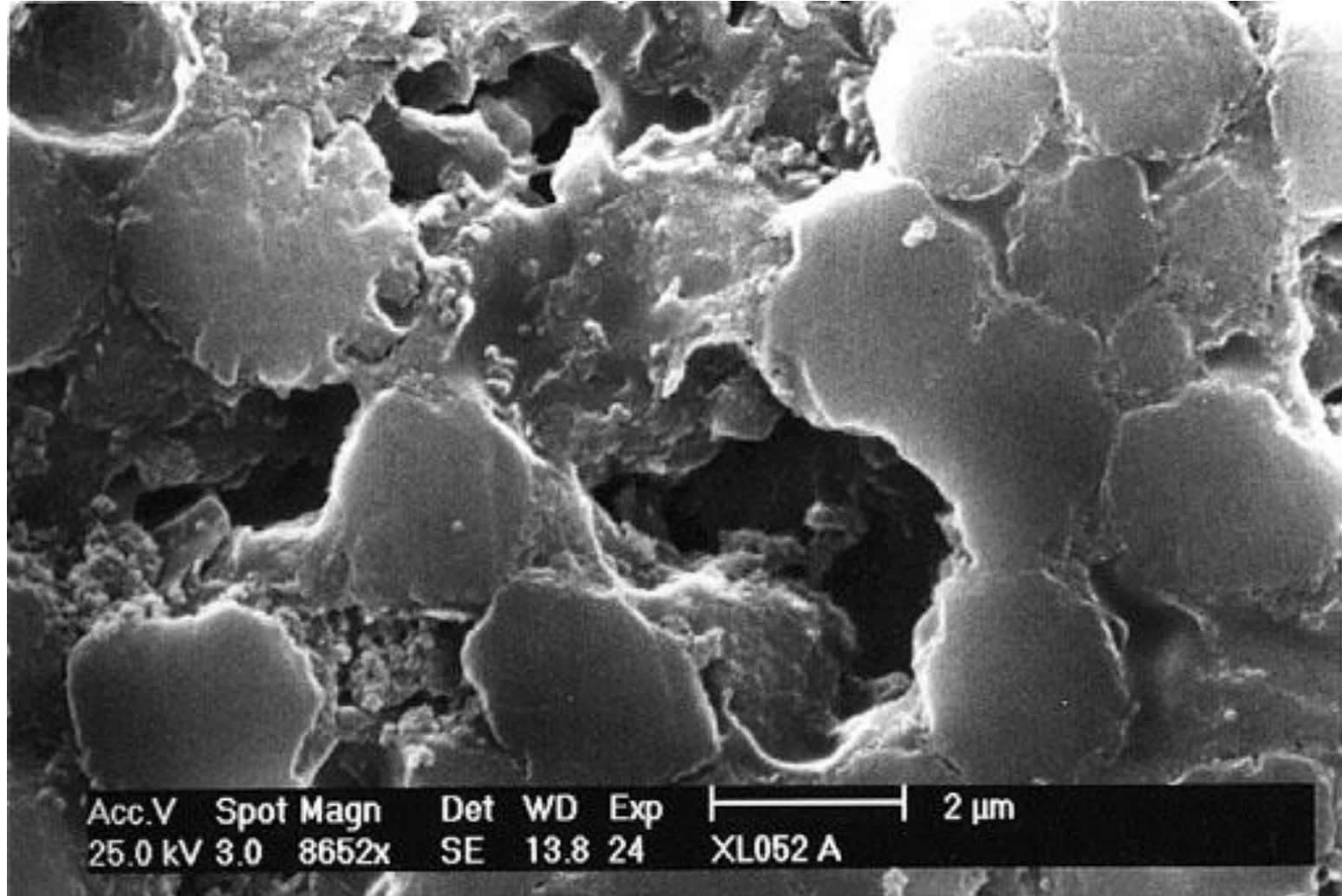


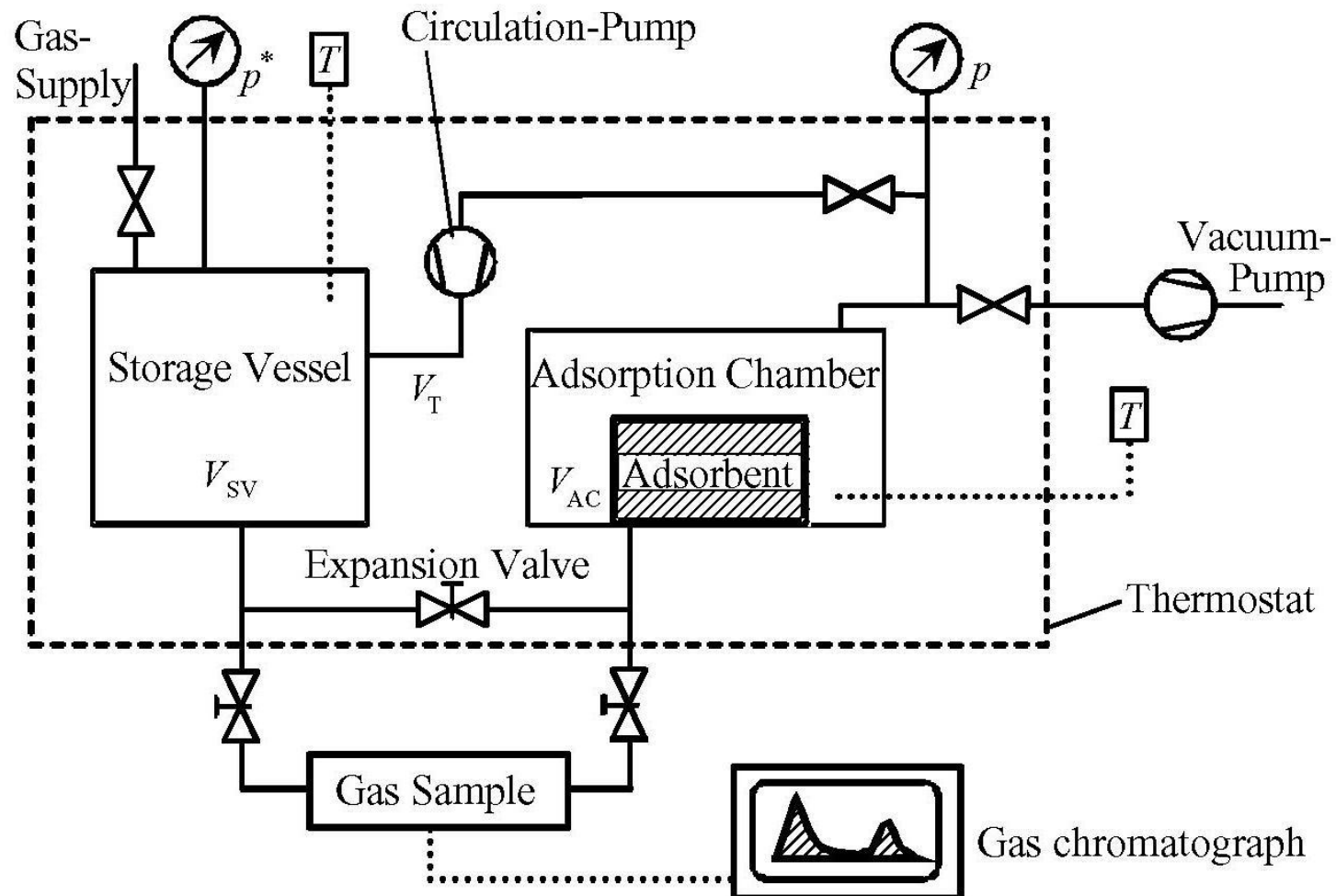
- Gibbs excess mass m_{GE}^a
- Absolute mass adsorbed m^a
- Mass of sorptive gas m^f

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

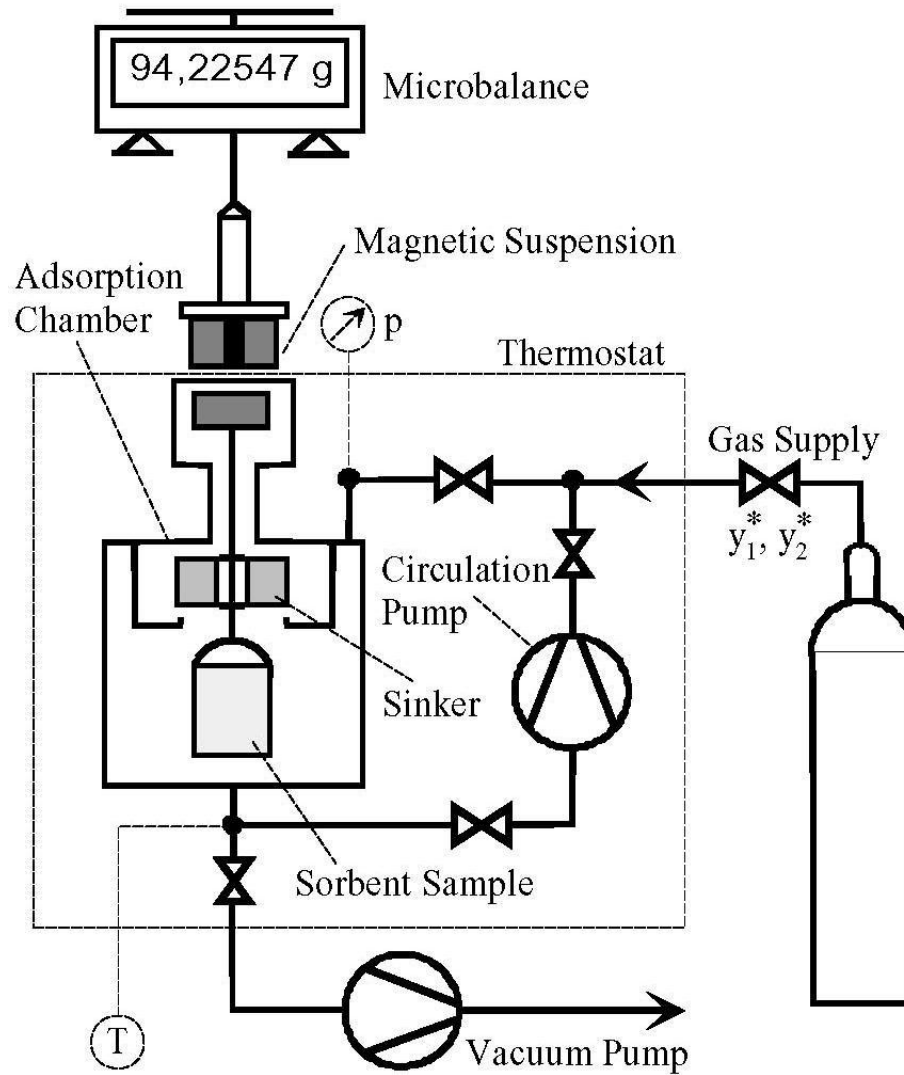
Zeolite Molecular Sieve UOP/Linde MS13X

Capillaries/Macropores, Mesopores, Micropores





Experimental Setup for Volumetric- Chromatographic Measurements of Gas Adsorption Equilibria



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

Measurement Methods of Masses of Adsorbed Phases

1. Volumetry / Manometry

2. Gravimetry

Result of measurements:

Gas Adsorption System

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

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

Approximations:

1. Gibbs excess mass

2. Absolute mass adsorbed

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

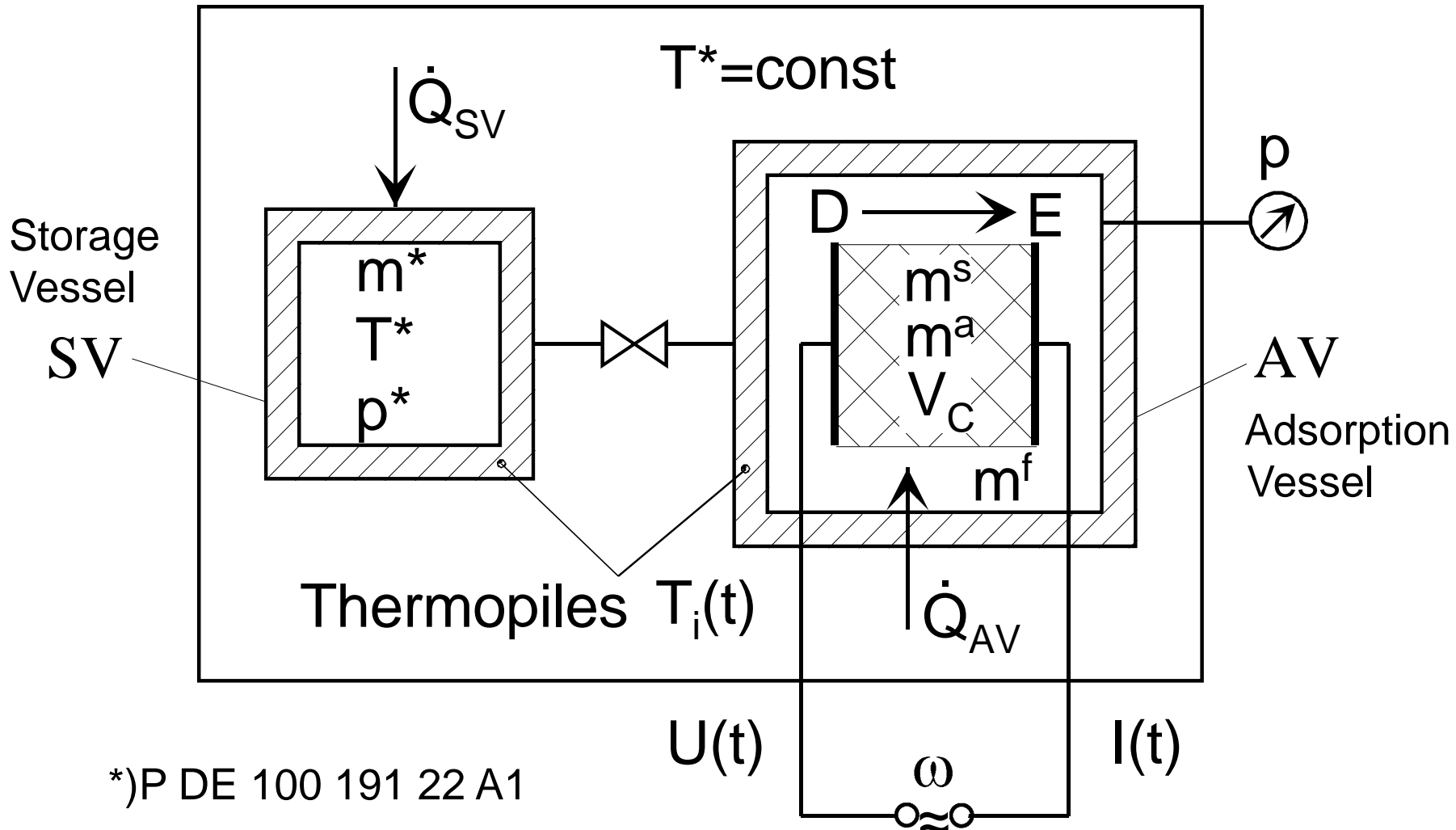
$$V^{as} \cong V_{He}^s + (m^a / \rho_0^L)$$

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

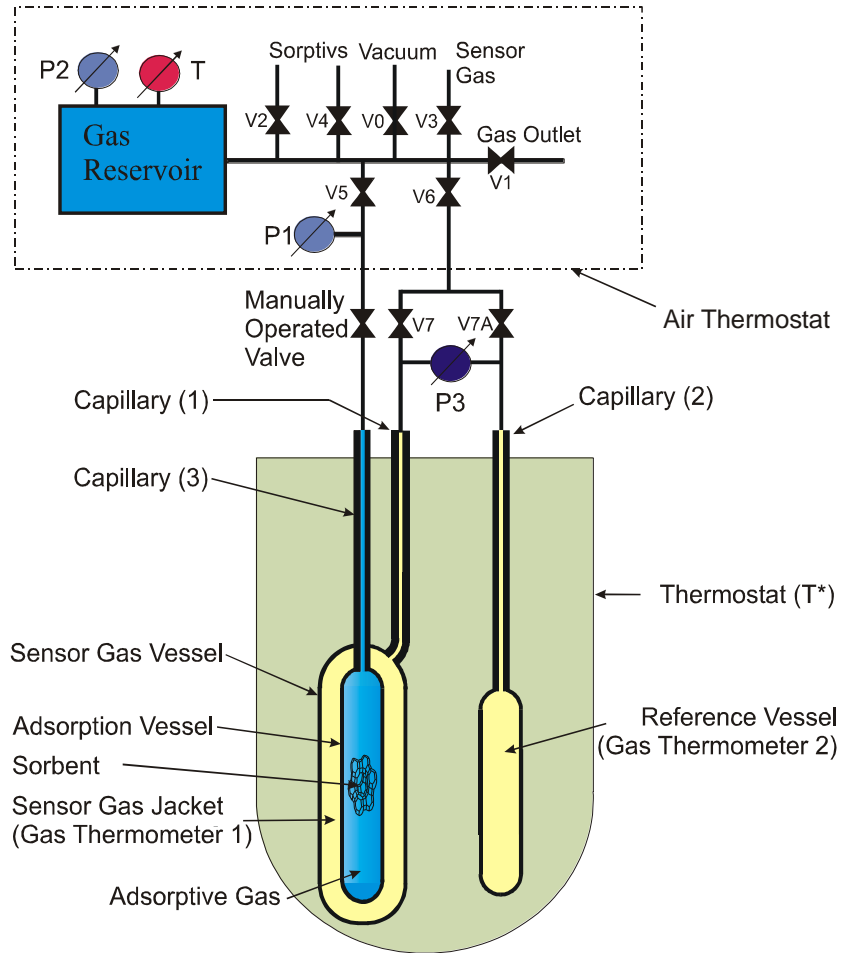
$$m^a = \frac{m_{GE}^a}{1 - (\rho^f / \rho_0^L)} \geq m_{GE}^a$$

Impedance Calorimeter*

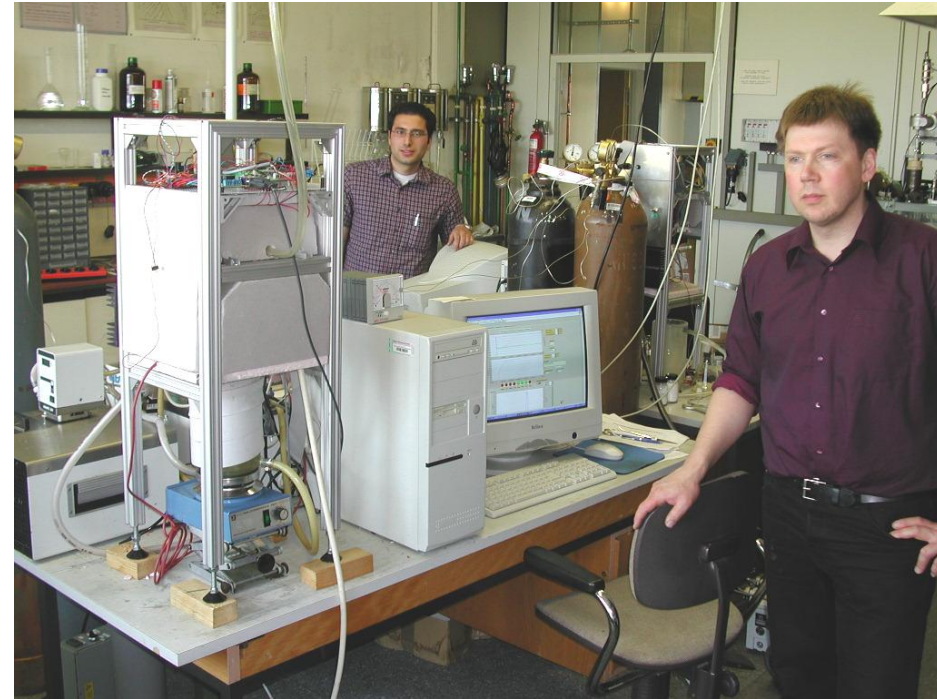
Experimental setup for calorimetric - dielectric measurements of gas adsorption equilibria.



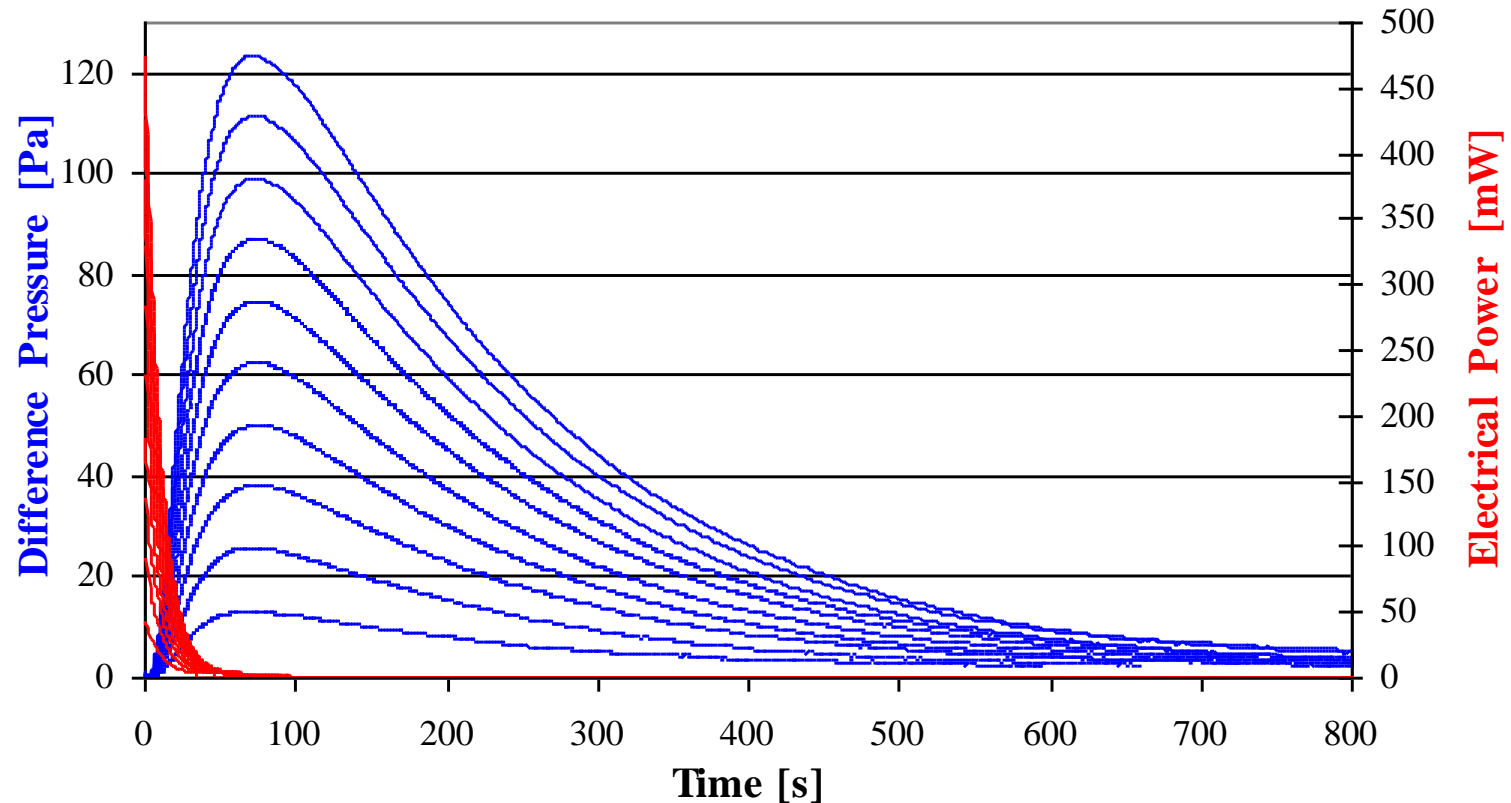
*)P DE 100 191 22 A1



Schematic diagram of a sensor gas calorimeter (SGC)



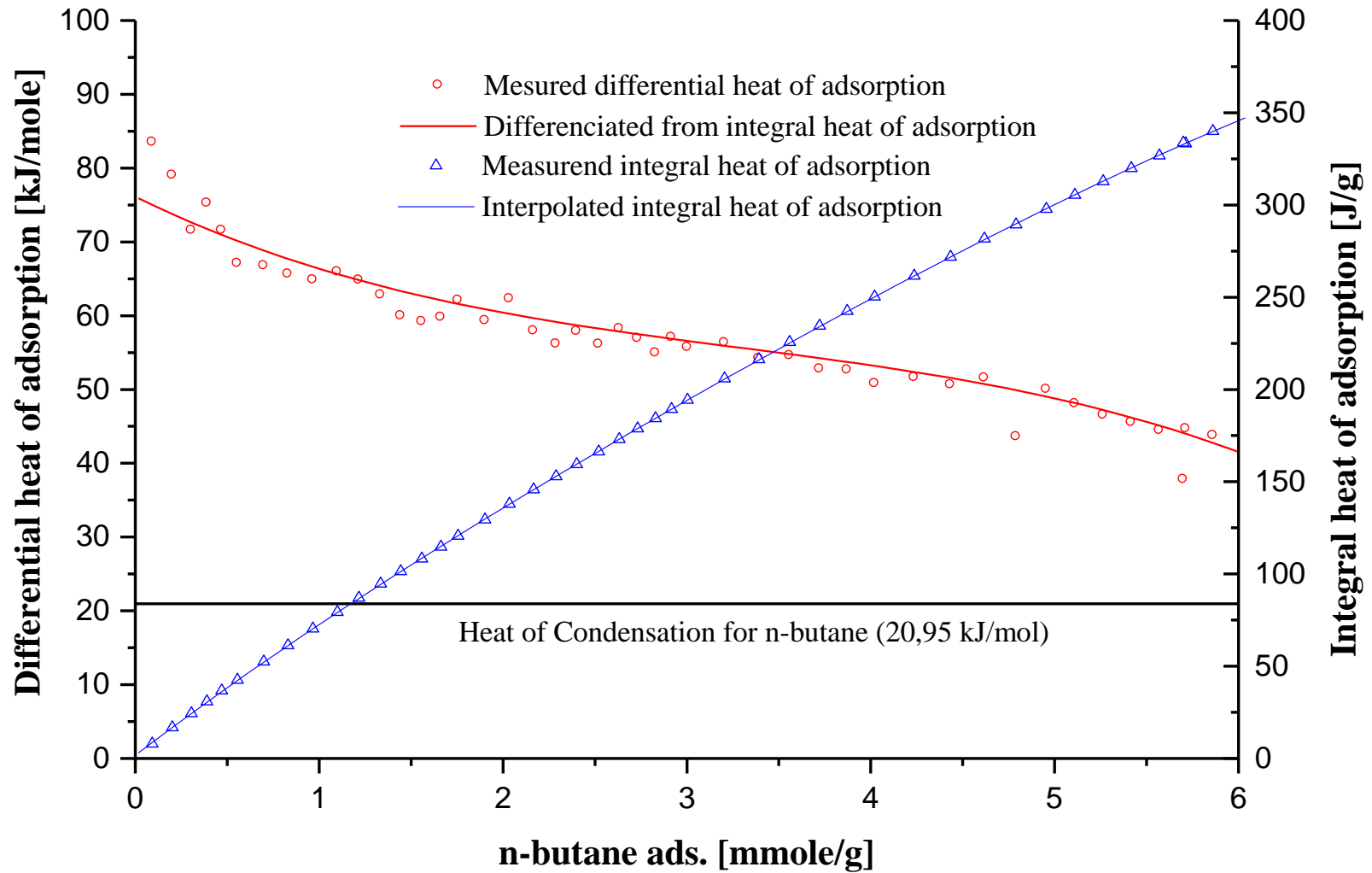
Sensor gas calorimeter (SGC) for simultaneous measurements of adsorption isotherms and enthalpies.
 © IFT, University of Siegen, 2003.



Calibration experiments in the SGC 0.5J to 5J

Sensor gas N_2 (1.6bar), $T=298K$, $\tau=10s$

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 (C₄H₁₀) at 298K.

Calorimetric - Dielectric Measurements (1)

1. Dielectric polarizability of the adsorbed phase (a)

$$\Omega_{DE}^a = \Omega_{DE}^a(p, T, m^s, m^a) \quad \text{Asm/(V/m)} \quad \text{DEOS}$$

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

2. Enthalpy of adsorbed phase (a)

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

$$\Delta H = \Delta H(p, T, m^a, m^s) \quad \text{J, kJ} \quad \text{CEOS}$$

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

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

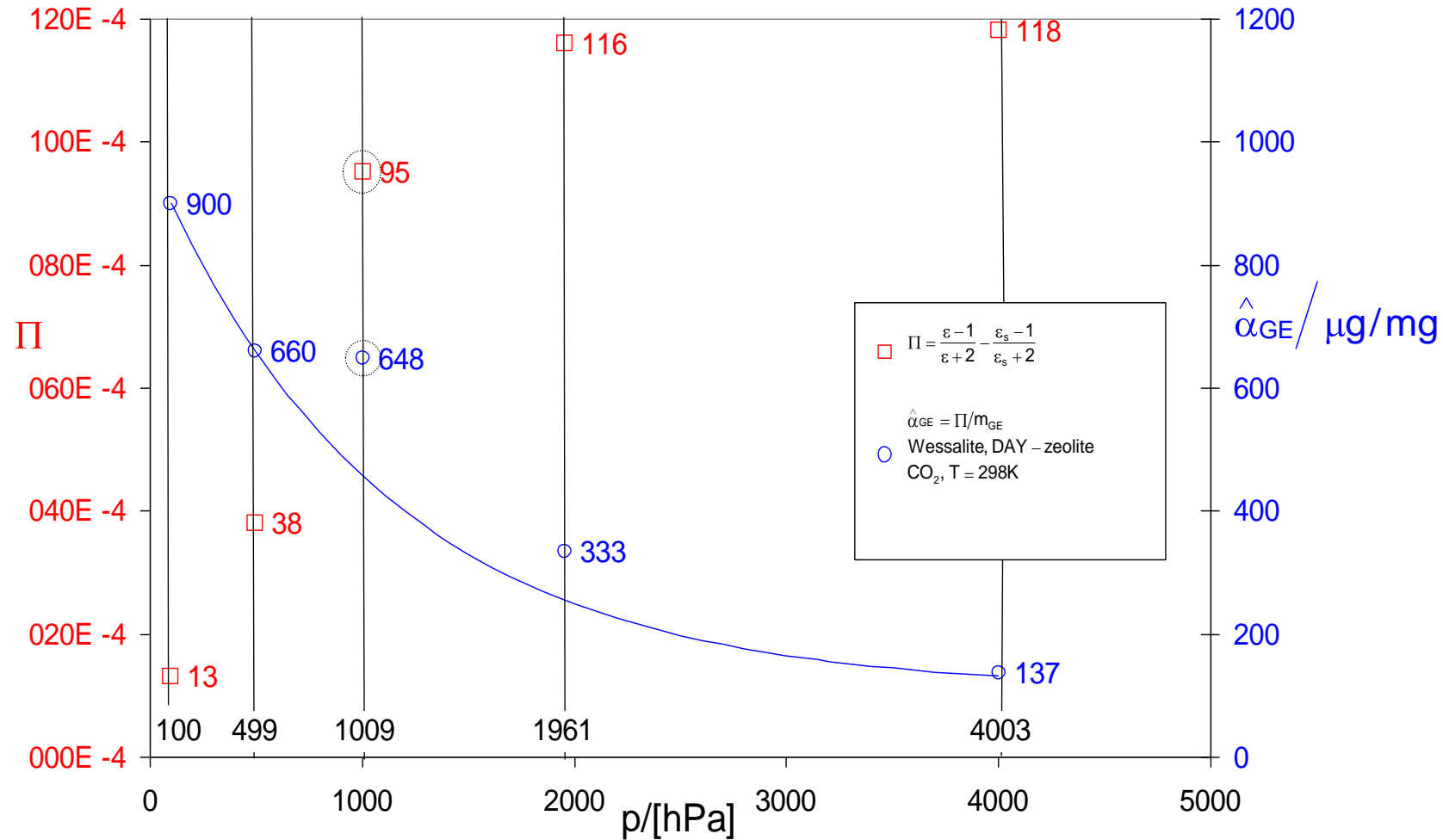
$$\alpha^a = \Omega_{DE}^a / m^a$$

Dielectric - caloric equation of state (DCEOS)

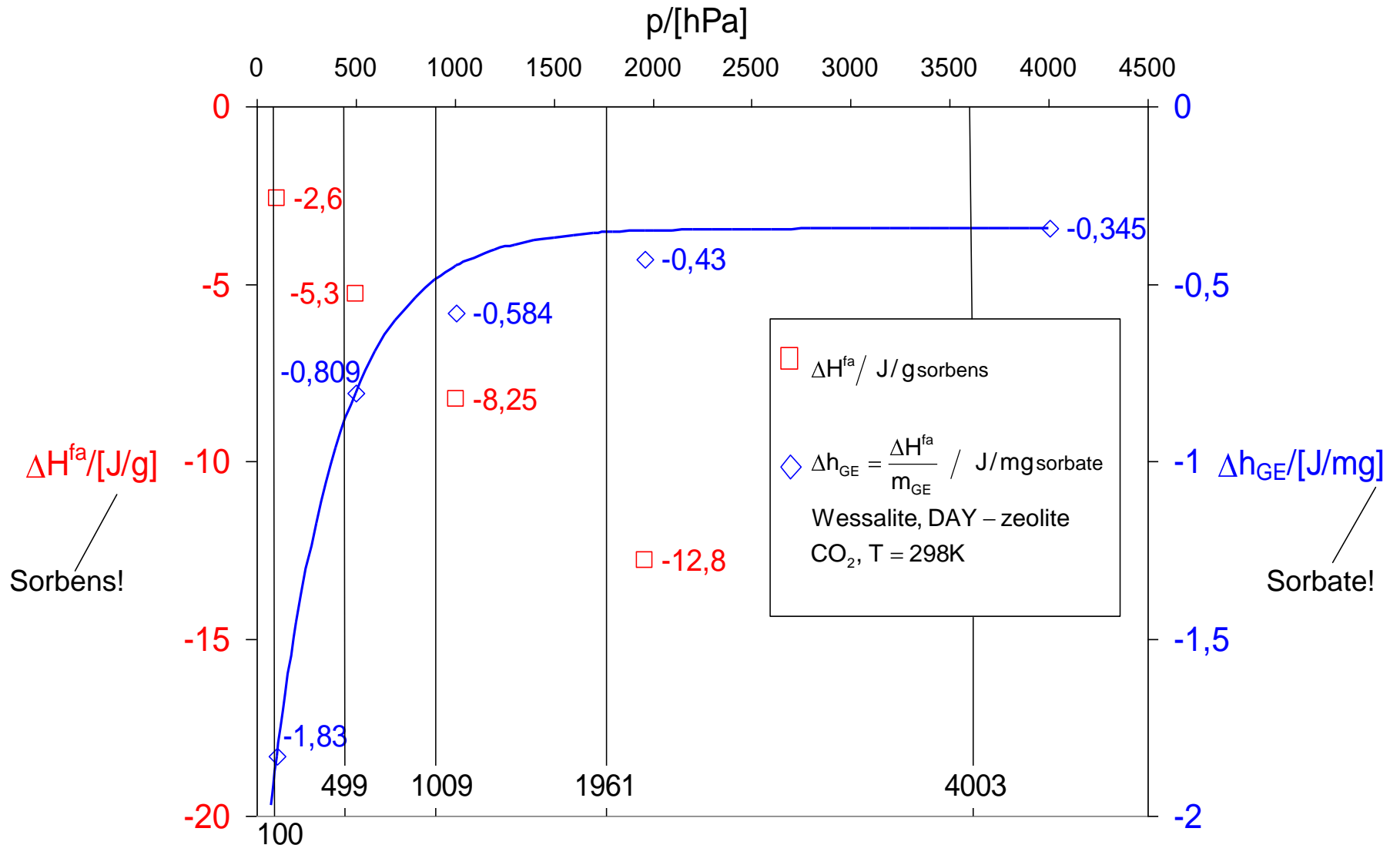
$$\frac{\Delta H}{m^a} = \Delta h\left(\frac{\Omega_{DE}^a}{m^a}, T, \frac{m^a}{m^s}\right)$$

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

Calculated quantity: m^a

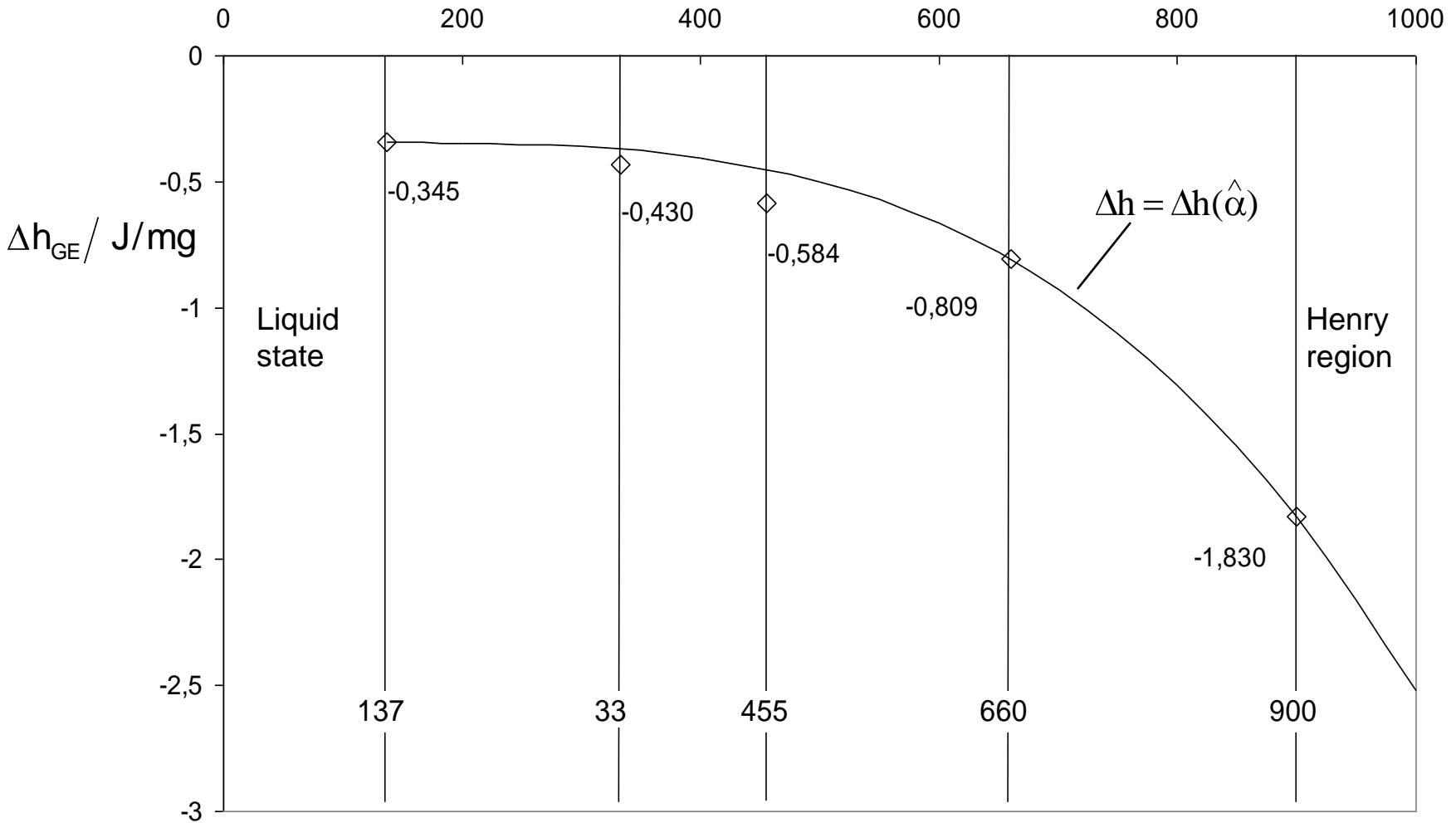


Reduced dielectric polarizability (Π) and Gibbs excess specific polarizability ($\hat{\alpha} = \Pi / m_{GE}$) of CO_2 on DAY-zeolite at $T = 298\text{K}$.



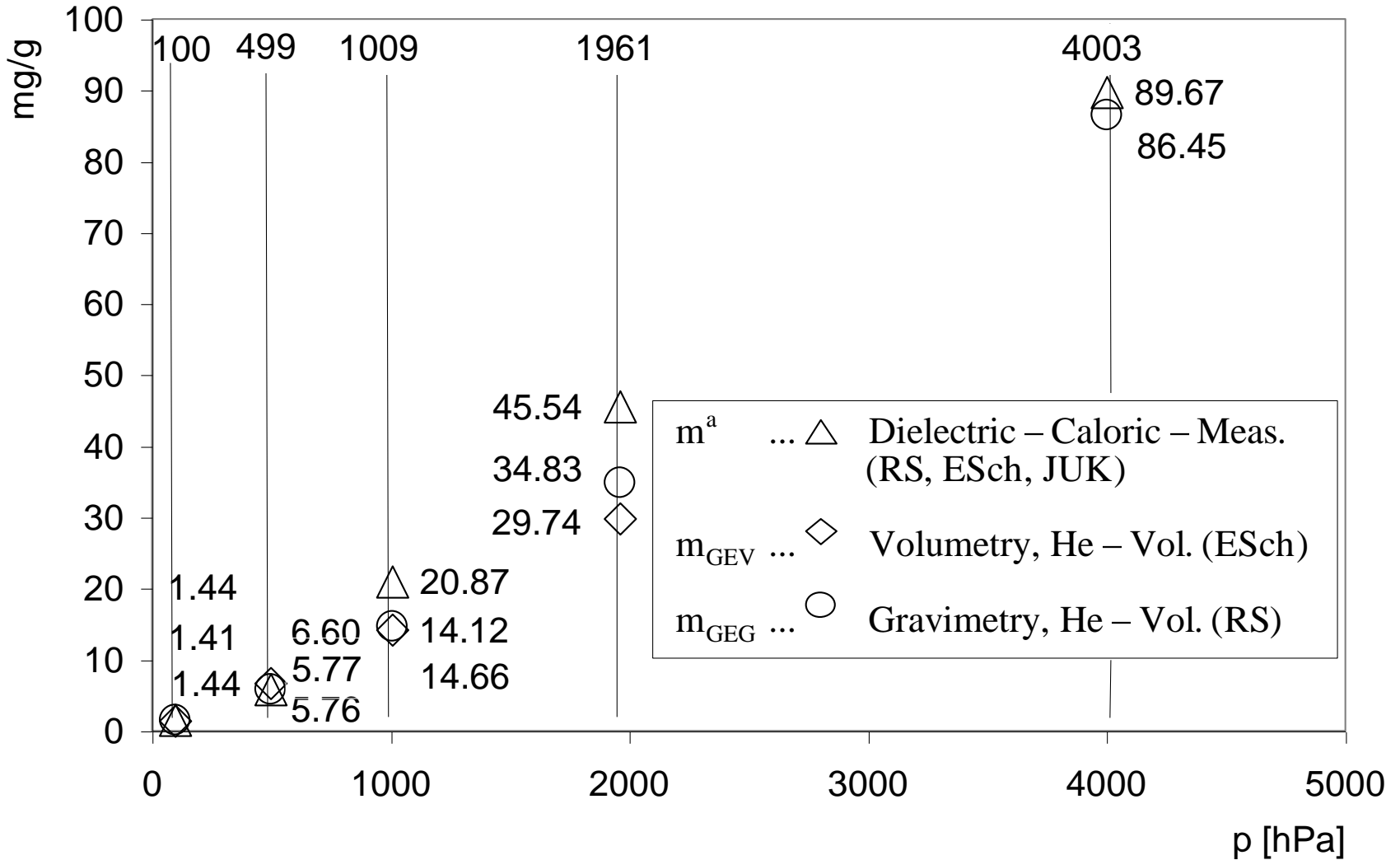
Enthalpy (ΔH^{fa}) and Gibbs excess specific enthalpy ($\Delta h_{GE} = \Delta H^{fa} / m_{GE}$) of CO_2 adsorbed on DAY-zeolite at $T = 298\text{K}$.

$$\hat{\alpha}_{GE} / \mu\text{g}/\text{mg}$$



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 $T = 298\text{K}$.
 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 pressure 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.