Oscillometric-Gravimetric Measurements of Pure Gas Adsorption Equilibria Without the Non-Adsorption of Helium Hypothesis

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Abstract

A new method is presented to measure pure gas-adsorption equilibria on porous solids or powders without using a hypothesis on the void volume of the solid sorbens, as for example the non-adsorption-of-helium hypothesis [1].

The method consists of combined gravimetric and dynamic measurements, namely observations of the frequency of small adiabatic oscillations of the sorptive gas being in equilibrium with the adsorbed phase or adsorbate.
The oscillations of the sorptive gas are initiated by small oscillations of a sphere or a cylinder positioned in a vertical tube above the vessel containing the gas and sorbens (reversion of experiment by Ruechardt (1929) - Flammersfeld (1972)), [2].

Experiments show that adsorbates of gases include two different phases consisting respectively of molecules which are only weakly bound to sorbent's atoms so that they can participate in the low frequency gas oscillations (< 10 Hz) and other molecules being strongly bound to sorbent's atoms so that they are "stiff", i.e. cannot participate in the gas oscillations, eigenfrequencies being in the range of (10*10 – 10*12)Hz.

The theory of these measurements will be presented and data of adsorption equilibria of CO_2 on activated carbon BAX 1100 at near ambient conditions (1040.5 mbar, 296.4 K) will be given and discussed to a certain extend.

Volumetry, Gravimetry: The Void Volume Problem

Volume balance:

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

Mass balance:

$$m^* = m^f + m^a$$

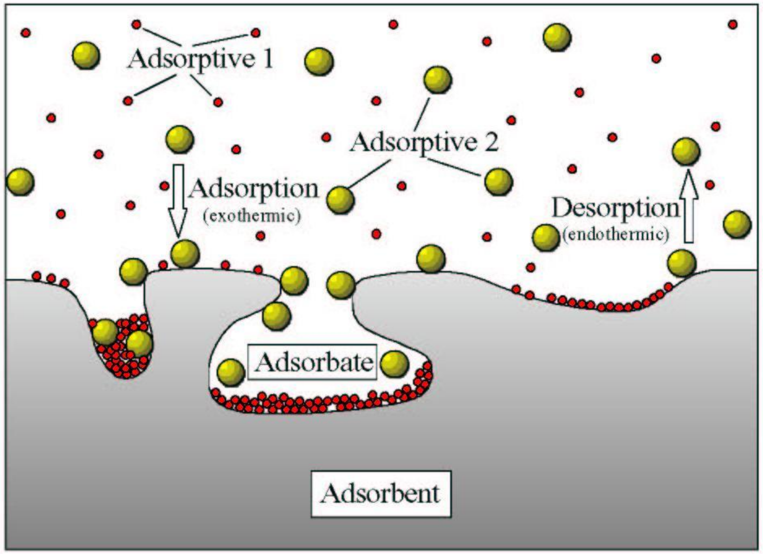
Volumetry, Gravimetry $\Rightarrow$

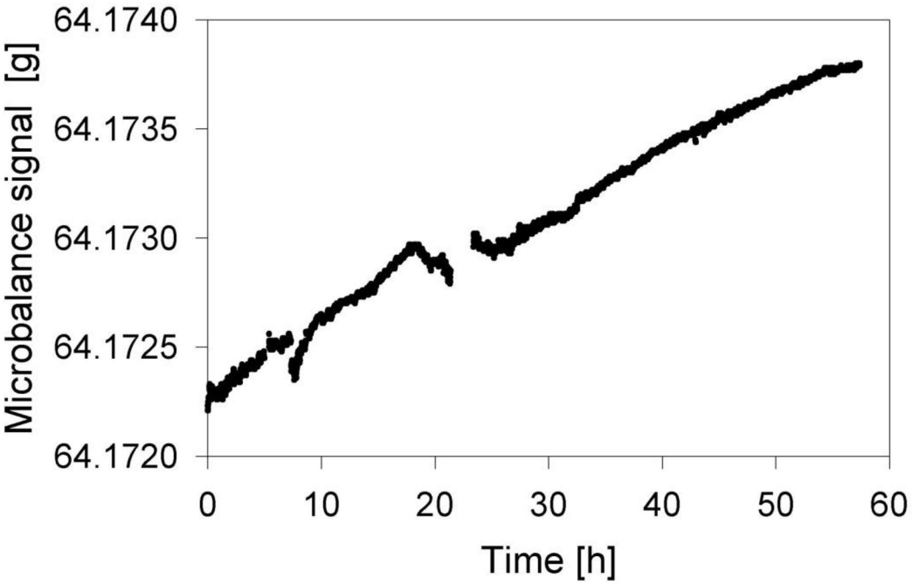
$$\Omega = m^a - \rho^f V^{as}$$

Helium hypothesis:

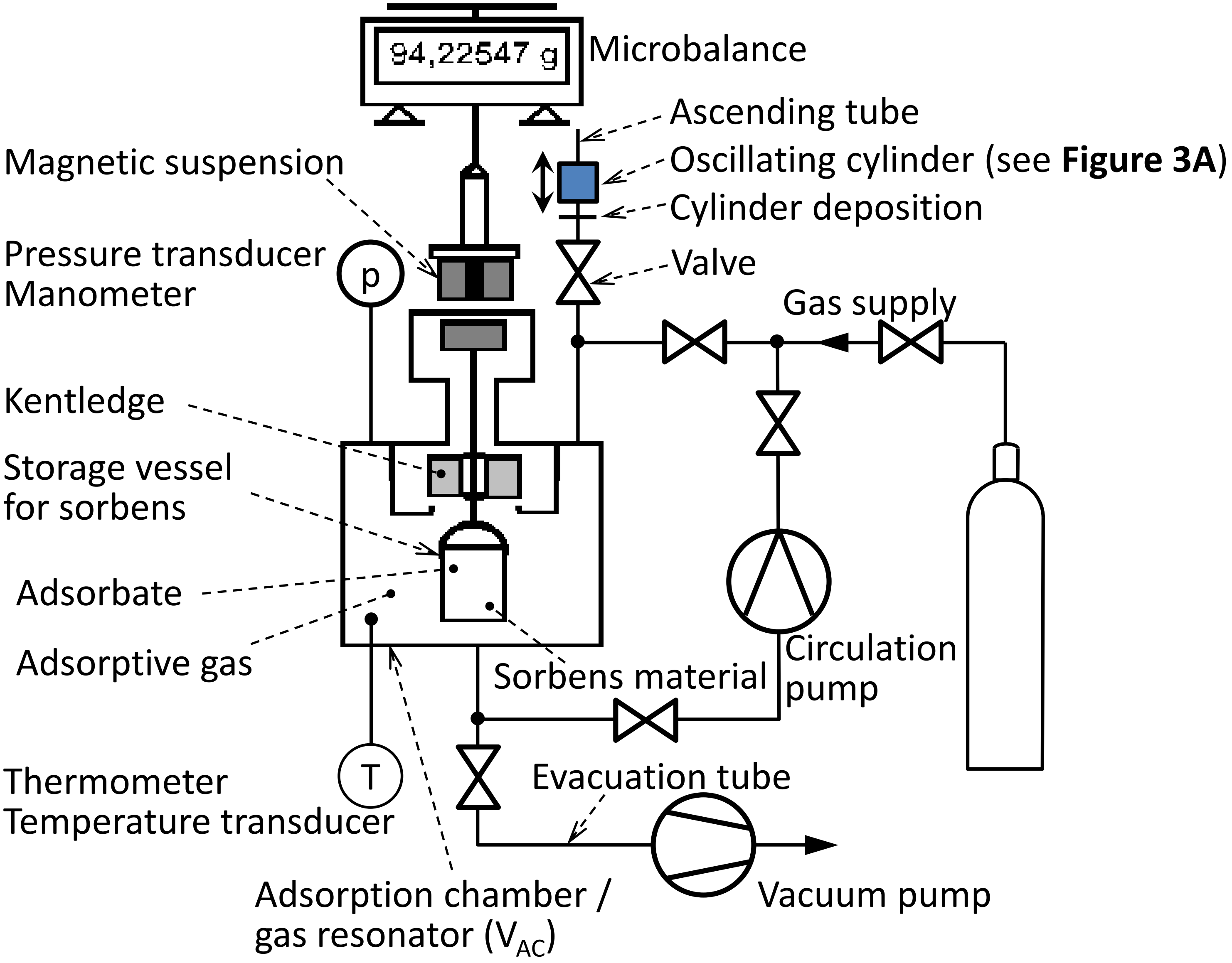
$$m_{He}{}^a = 0 \quad V^{as} \cong V^s_{He},$$

$$\rightarrow m^a_{GE} = \Omega + \rho^f V^s_{He}$$





Oscillometric-Gravimetric Measurements of Gas Adsorption



Microbalance

Ascending tube

Oscillating cylinder (see **Figure 3A**)

Cylinder deposition

Valve

Gas supply

Magnetic suspension

Pressure transducer
Manometer

Kentledge

Storage vessel
for sorbens

Adsorbate

Adsorptive gas

Sorbens material

Circulation
pump

Thermometer
Temperature transducer

Evacuation tube

Adsorption chamber /
gas resonator (V_{AC})

Vacuum pump

The Flammersfeld Oscillator

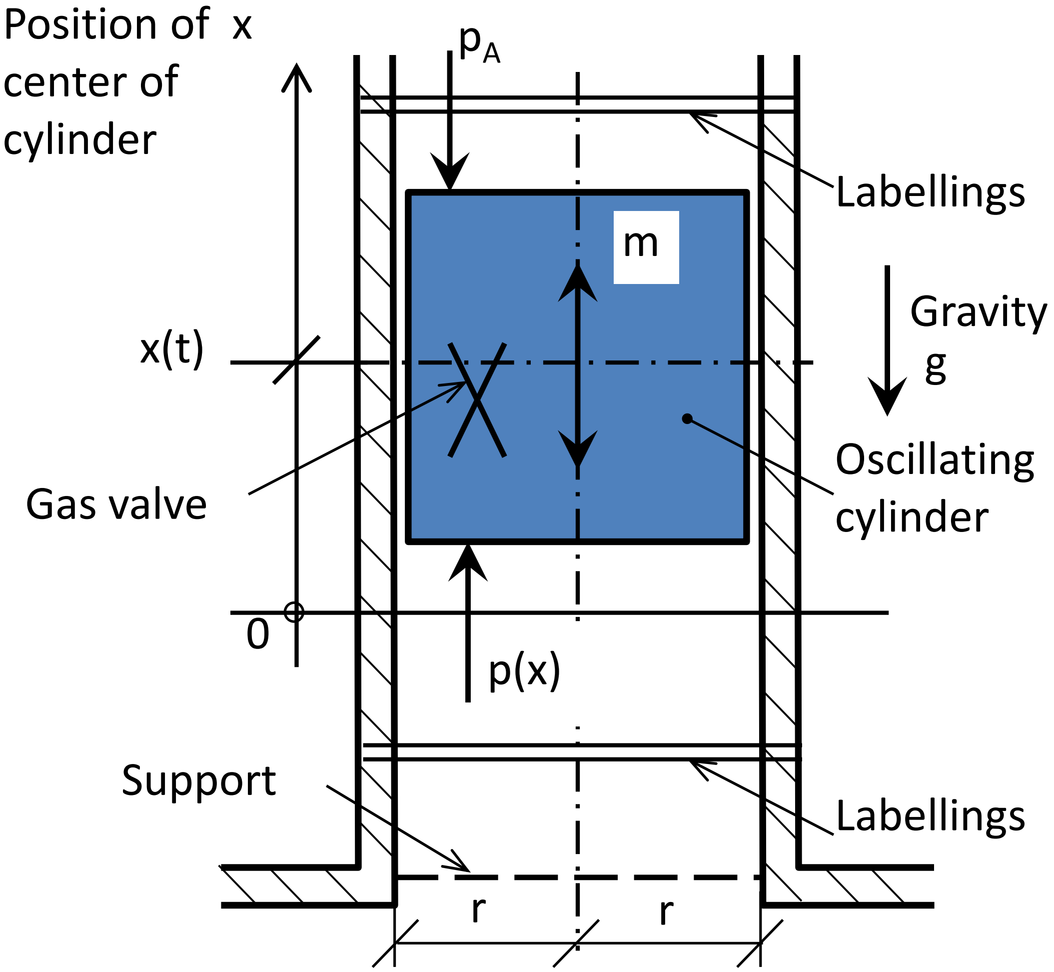


Figure 3A

$$m\ddot{x} - F_R - \left(p(x) - P_A\right)F + mg = 0$$

$$p(x)V(x)^{\kappa} = p(0)V(0)^{\kappa}$$

Eigenfrequency
Gas-Oscillator-System

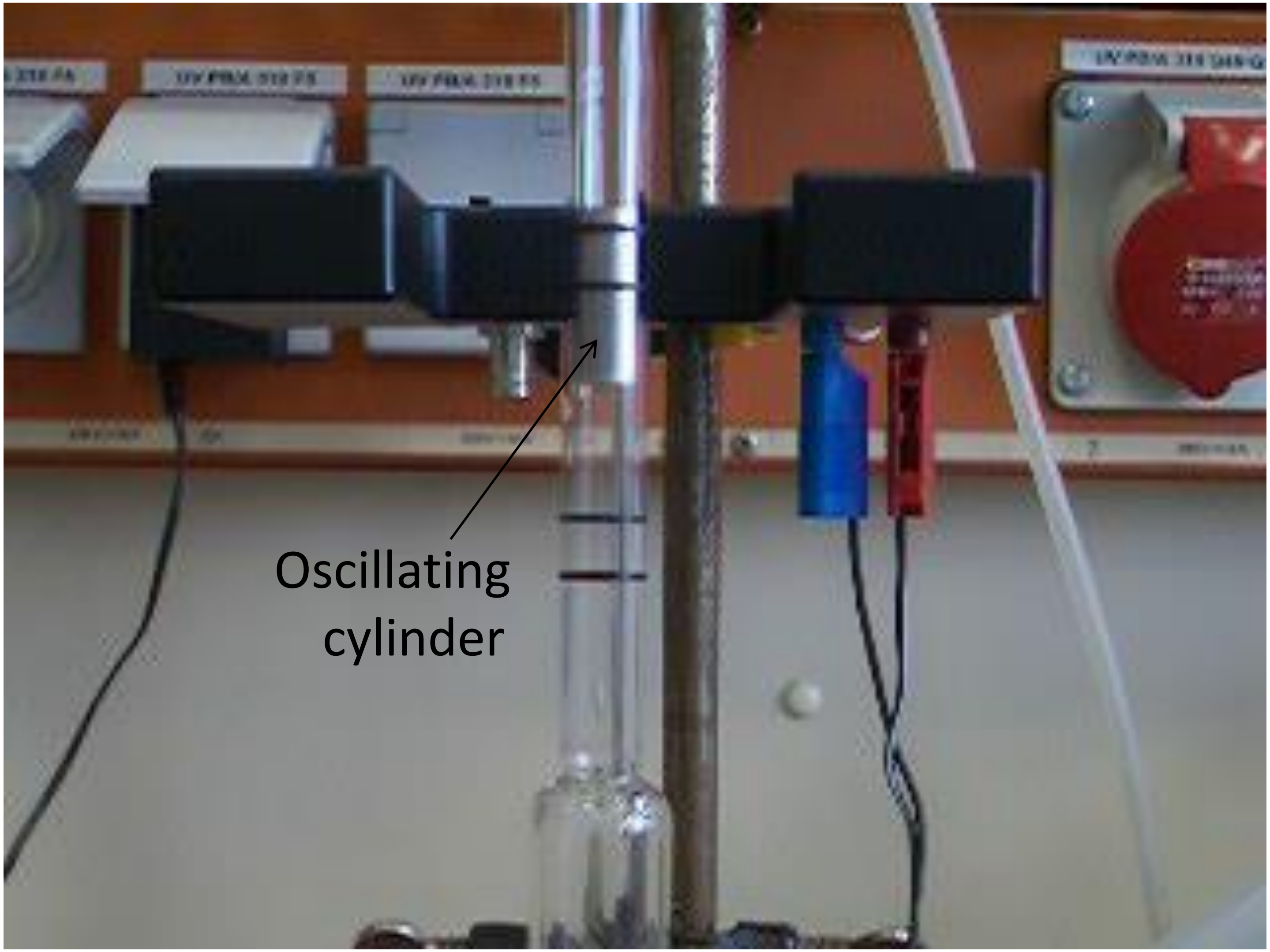
$$\omega^2 = \kappa \frac{F^2}{m} \cdot \frac{p(0)}{V(0)} - \left(\frac{f}{2m}\right)^2$$

$$V(0) \equiv V_{os} \qquad \alpha = \frac{m}{\kappa p F^2}$$

Mass of Oscillating Gas

$$\frac{1}{m_{os}} = \left(\frac{1}{V_{AC}} + \alpha\left(\omega^2 - \omega_0^2\right)\right)\frac{RT}{p}$$

Experiment by Ruechardt & Flammersfeld
Measurement of Gas – Oscillations



Oscillating cylinder

Oscillometric Measurements of Gas-Adsorption-Equilibria

Inversion of the experiment by Ruechardt – Flammersfeld

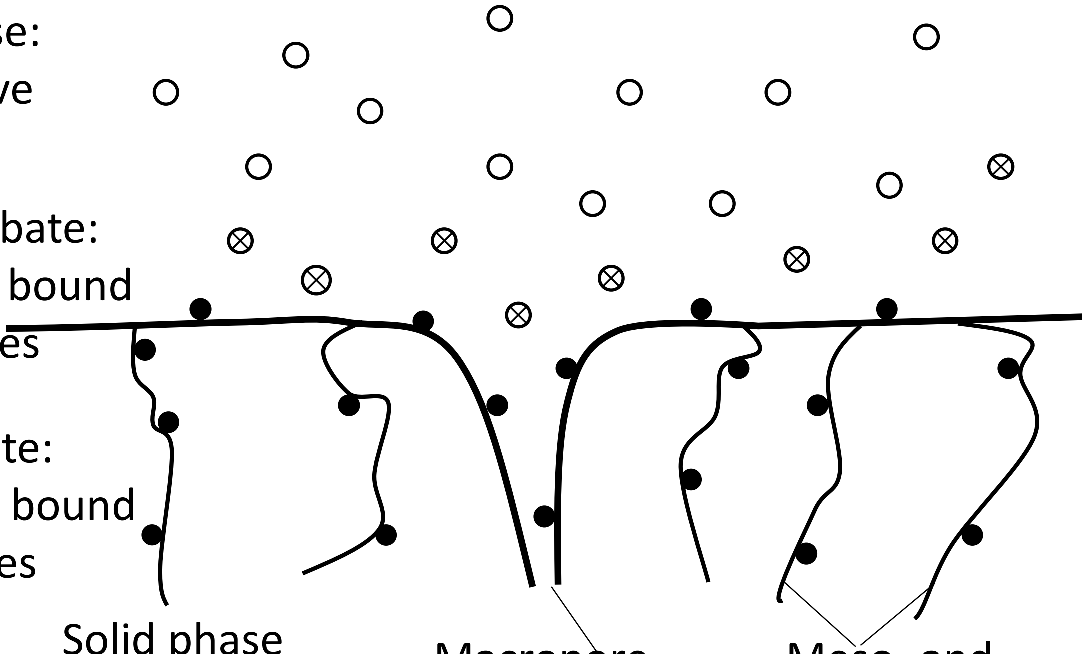
Eigenfrequencies of an oscillator-gas-system ⇒ Mass of all oscillating gas molecules:

Bulb empty

$$\frac{1}{m_{os}} = \left(\frac{1}{V_{AC}} + \alpha \left(\omega^2 - \omega_0^2 \right) \right) \frac{RT}{p}$$

Bulb filled with AC

Adsorption Model



○ Gasphase:
Adsoptive

⊗ Semisorbate:
Weakly bound
molecules

● Adsorbate:
Strongly bound
molecules

Solid phase
Sorbens

Macropore

Meso- and
micropores

Adsorptive model:

$$V^f = V_{AC} - v_B^s m^s$$

$$m^f = \frac{pV^f}{RT}$$

Bulk volume
of sorbent

Adsorbate

$$m^a = m_{os}^a + m_{nos}^a$$

Gravimetry:

$$\Omega = m^a - \rho^f V_B^s$$
$$= m_{os}^a + m_{nos}^a - \rho^f V_B^s$$

$$\Rightarrow$$

$$m_{nos}^a = \Omega - m_{os}^a + \rho^f V_B^s$$

$$m_{os}^a = m_{os} - m^f$$

Oscillometry:

$$m_{os} = m^f + m_{os}^a$$

Theory of Adsorption Measurements (1)

Parameters

Sorptive gas:

$$m^f, \; V^f, \; \rho^f = \frac{m^f}{V^f} = \rho^f(p, T)$$

Adsorbate:

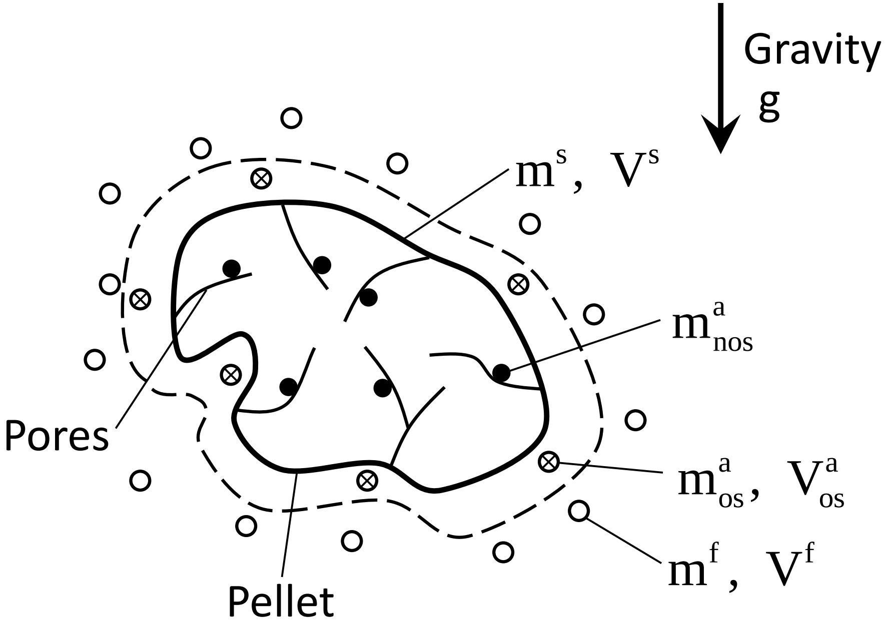
$$m^a = m^a_{os} + m^a_{nos}, \; V^a_{os}, \; V^a_{nos}$$

Sorbent:

$$m^s, \; V^s, \; V^s_{B(ULK)}$$

Buoyancy - equilibrium condition:

$$\left(\rho^a_{os} - \rho^f\right) V^s = \rho^f V^a_{os}$$



Theory of Adsorption Measurements (2)

Gravimetry (Magnetic Suspension Balance)

Weighing data:

G_o ... empty balance in vacuum

G_o^s ... balance filled with sorbens in vacuum

G_f ... empty balance in sorptive gas

G_f^{as} ... balance filled with sorbens in sorptive gas

Gravimetry

$$\Omega = \frac{1}{g}\left(G_f^{as} - G_o^s - G_f + G_o\right) \quad (*)$$

$$\Omega = m^a - \rho^f V_B^s$$

$$= m_{os}^a + m_{nos}^a - \rho^f V_B^s \qquad (1)$$

Oscillometry

$$m_{os} = m^f + m_{os}^a \qquad (2)$$

Volume balance

$$V_{AC} = V^f + V_B^s \qquad (**)$$

$$V_B^s = V_{os}^a + V_{nos}^a$$

Buoyancy condition

$$\left(\rho_{os}^a - \rho^f\right)V^s = \rho^f V_{os}^a \qquad (3)$$

Mass of adsorptive

$$m^f = \frac{pV^f}{RT} \qquad (4)$$

Model bulk volume of sorbent

$$V_B^s = V_{os}^a + V^s \qquad (5)$$

$$\left(V^s = V_{nos}^a\right) \qquad (6)$$

$$(2-5): \quad V_{os}^a = \frac{V_B^s}{1 + \rho^f V_B^s / m_{os}^a} < V_B^s \qquad (7)$$

Volume of semi-sorbate or weak adsorbate

Theory of Adsorption Measurements (3)

Unknown quantities

Phase	Volume	Mass
Sorptive gas	V^f	m^f
Semi adsorbate	V^a_{os}	m^a_{os}
Strong adsorbate	$V^s_{nos} = V^s$	m^a_{nos}

Experimental data

m_{os} , G^s_o , $G^{as}_f \Rightarrow \Omega$

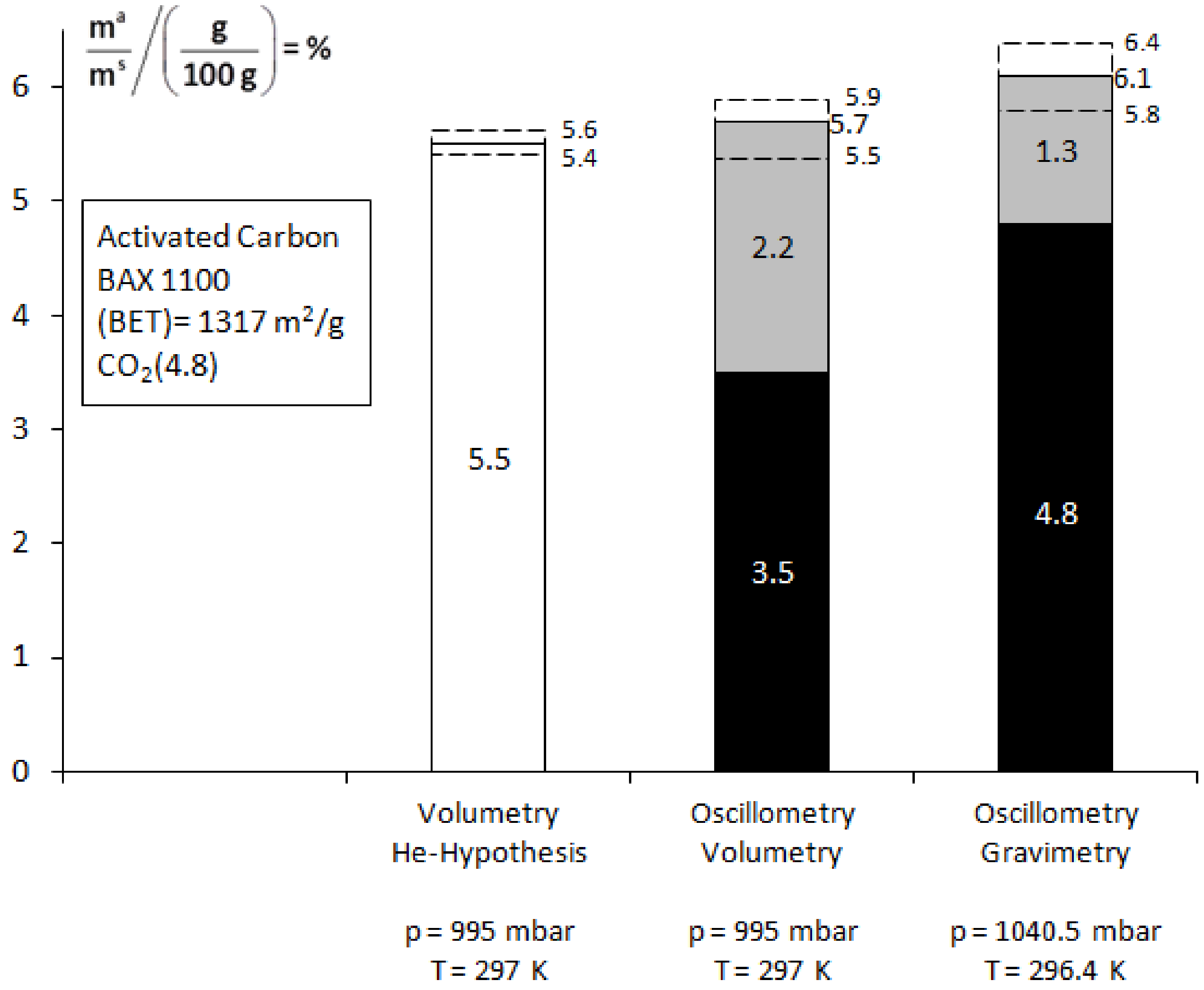
m^s , p , T , $\rho^f(p,T)$

System data

V_{AC} , G_o , G_f , g

Equation	Solutions
(**)	$V^f = V_{AC} - v^s_B m^s$ $m^f = \rho^f(p,T) V^f$
(2)	$m^a_{os} = m_{os} - m^f$
(7)	$V^a_{OS} = \dfrac{V^s_B}{1 + \dfrac{\rho^f V^s_B}{m^a_{os}}} < V^s_B$
(1)	$m^a_{nos} = \Omega + \rho^f V^s_B - m^a_{os}$
(5)	$V^a_{nos} = V^s_B - V^a_{os} \equiv V^s$

Adsorption of CO_2 on AC BAX 1100 at near ambient conditions



Summary

The adsorbate of a gas on the surface of a porous solid can be split into two sets of molecules consisting of

A strongly adsorbed molecules sticking to the (external or intenal) surface of the solid and having high eigenfrequencies of oscillations (~ 10*(12-14)Hz); **(adsorbate**)

B weakly adsorbed molecules being in the gaseous boundary layers near the surface of the sorbent pellets and having very low eigenfrequencies of oscillations in the bulk gas phase (<10Hz) (**semi-adsorbate**)

The mass of both phases can be determined by observing eigenoscillations of the oscillating sorptive gas phase system and combining the results with those of gravimetric measurements.

The non-adsorption of Helium hypothesis is not used .

References: Characterization Porous solids

[1] **Keller J.U., Staudt R.**
Gas Adsorption Equilibria, Experimental Methods and Adsorption Isotherms, p. 420, Kluwer/Springer, 2005.

[2] **Keller J.U.,** Göbel M.U.
Oscillometric-Volumetric Measurements of Pure Gas Adsorption Equilibria Devoid of the Non-Adsorption of Helium Hypothesis, Adsorption Science&Technology, Vol. 33 No. 9, 2015, p. 793-818.

[3] **Kaneko K., Setoyama N., Suzuki T.**
Ultramicropore characterization by the adsorption, Proceedings Conference on Porous Solids 3, Marseille, May 1993, J. Rouquerol, Ed. Elsevier, Amsterdam, 1994, p. 593-602.

[4] **Robens E., Keller J.U., Massen C.H., Staudt R.**
Sources of Error in Sorption and Density Measurements, J. of Thermal Analysis and Calorimetry, 55 (1999), 383-387.