To What Extend is Helium Adsorbed on Porous Solids at Ambient Temperatures?

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Introduction

Volumetric or gravimetric measurements of porous solids in helium atmosphere are used to determine the so-called helium-volume, i. e. the skeletal volume of the material impenetrable to helium atoms [1, Chap. 1, Sect. 4.2]. This volume (V^{s}_{He}) can be considered as a lower boundary to the volume of the material being impenetrable for other (bigger) molecules. As V^{s}_{He} is normally be determined under the assumption that helium is neither adsorbed nor absorbed within the material, the question arises how this can be checked.

A variety of helium sorption experiments have been performed at the institute of Fluid- and Thermodynamics of the University of Siegen during the years 1994 - 2002. The main results of these are:

1. Helium is adsorbed or sorbed in all porous materials even at low pressures and high temperatures. The adsorption process is very quick, i. e. a preliminary type of saturation is reached within few seconds, sometimes minutes.

2. If preliminary saturation is reached, increase of the helium gas pressure does not lead to gravimetrically measurable increase of adsorption within several hours.

3. However, long time adsorption experiments lasting days and months show a slow but steady increase of helium being sorbed in the material. This also was observed for nonporous sorbent materials like dense polymers.

4. Helium adsorption experiments in gas adsorption systems which are in equilibria states show that the volume (V^{as}) of the combined sorbent/sorbate phase is not constant but depends, i. e. increases with the amount of gas adsorbed.

These statements will be verified by presenting respective experimental data. Consequently, the helium volume (V^s_{He}) of a porous material can be considered as one of its characteristic quantities serving as approximation for the void volume of the material impenetrable for other molecules. For adsorption isotherm measurements this approximation seems to hold reasonably well for low gas pressures ($p < 0.1\ p_s(T)$). However, for high sorptive gas pressures, other models for (V^{as}) should be used taking into account the sorption of helium in the material and also the difference in size between the helium atom and the sorptive gas molecule actually used.

References

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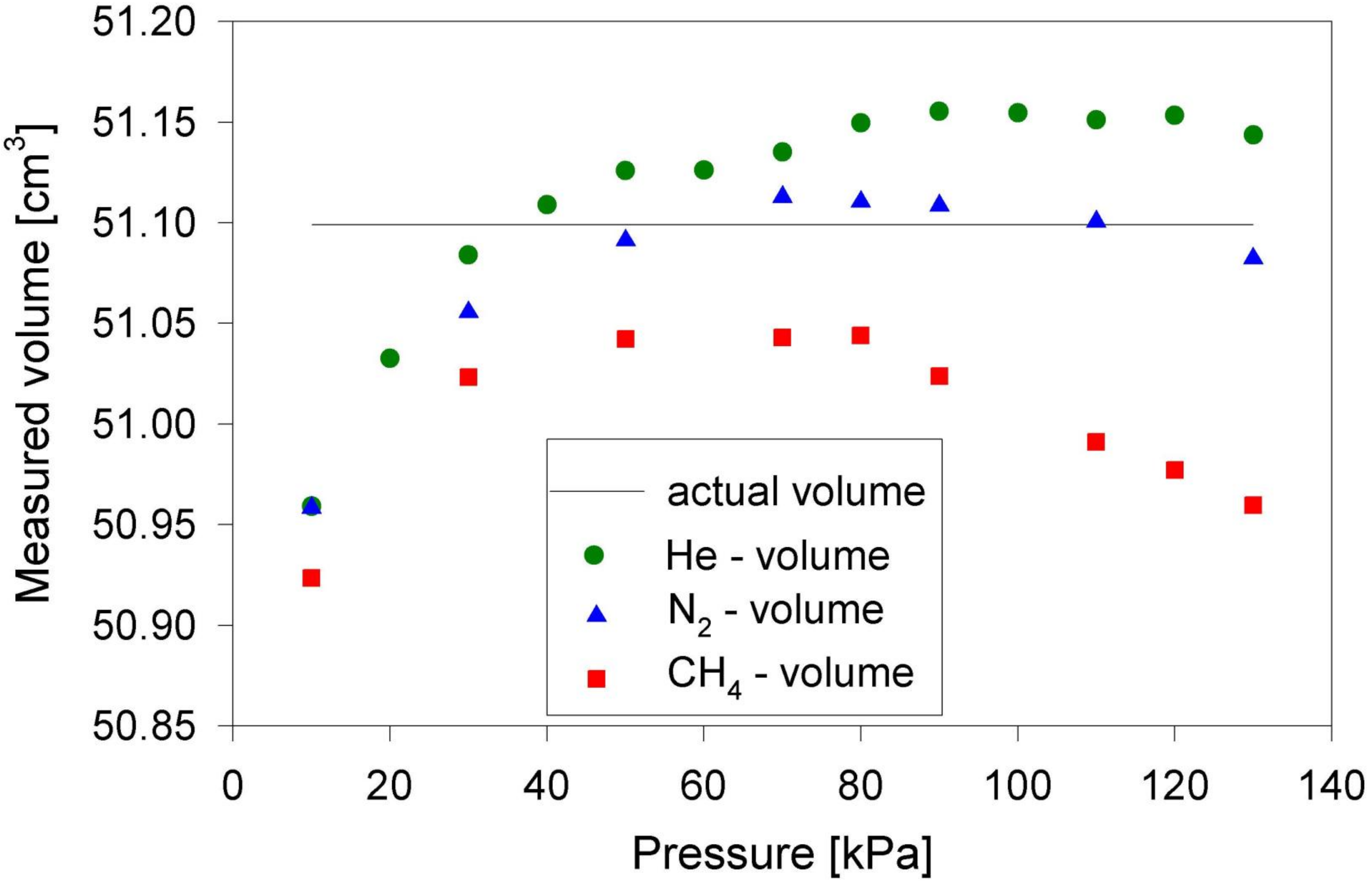
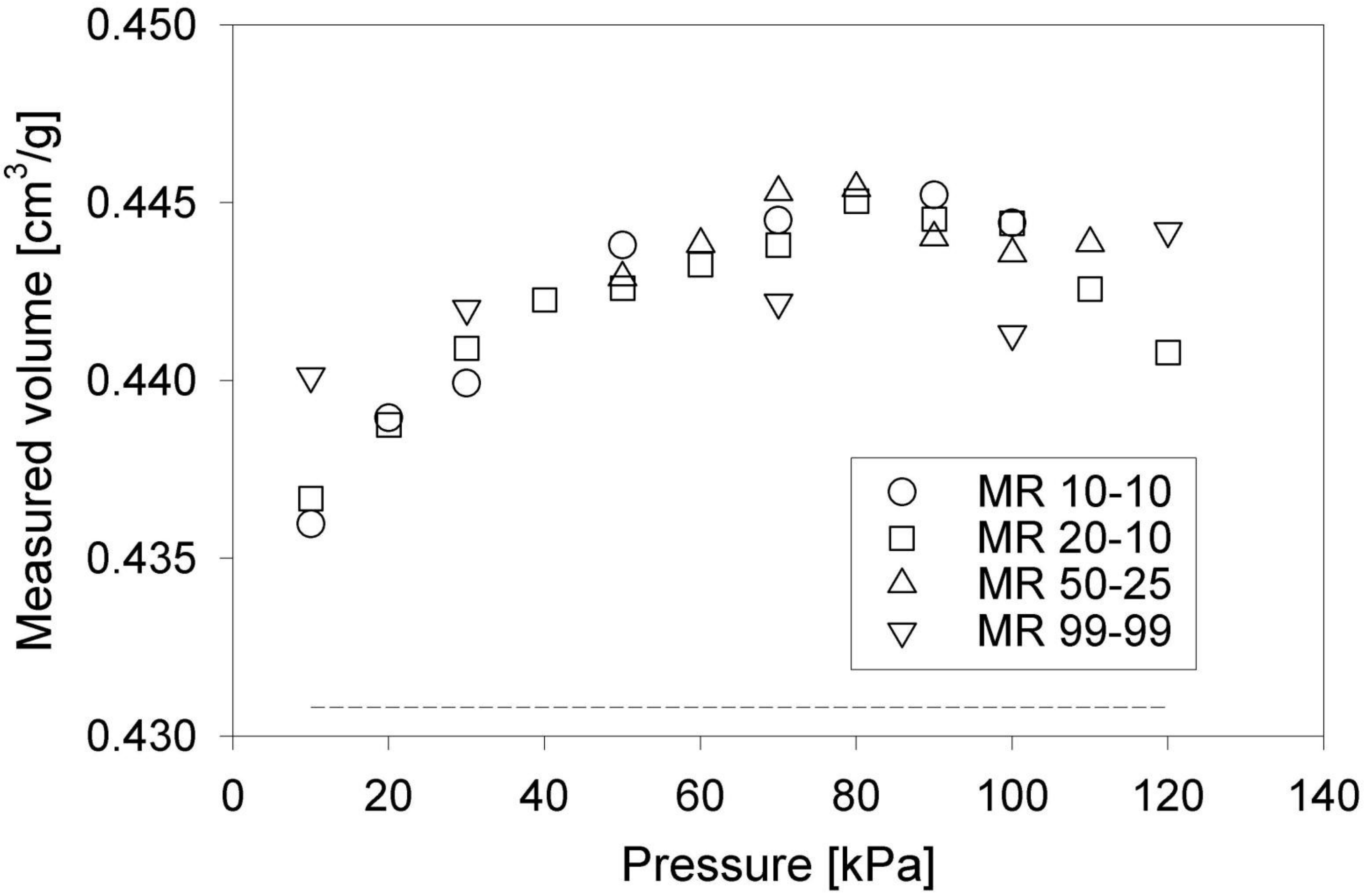
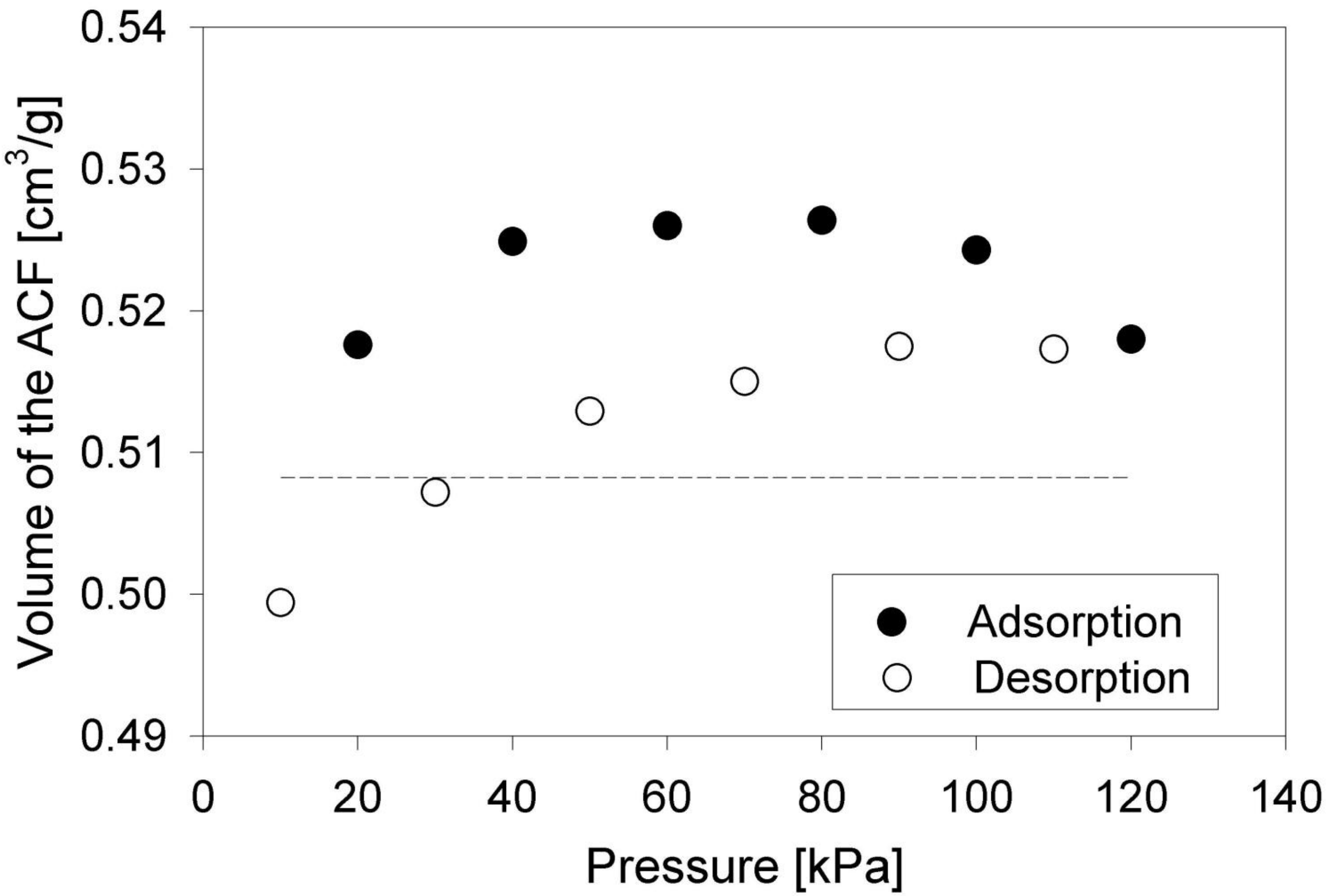


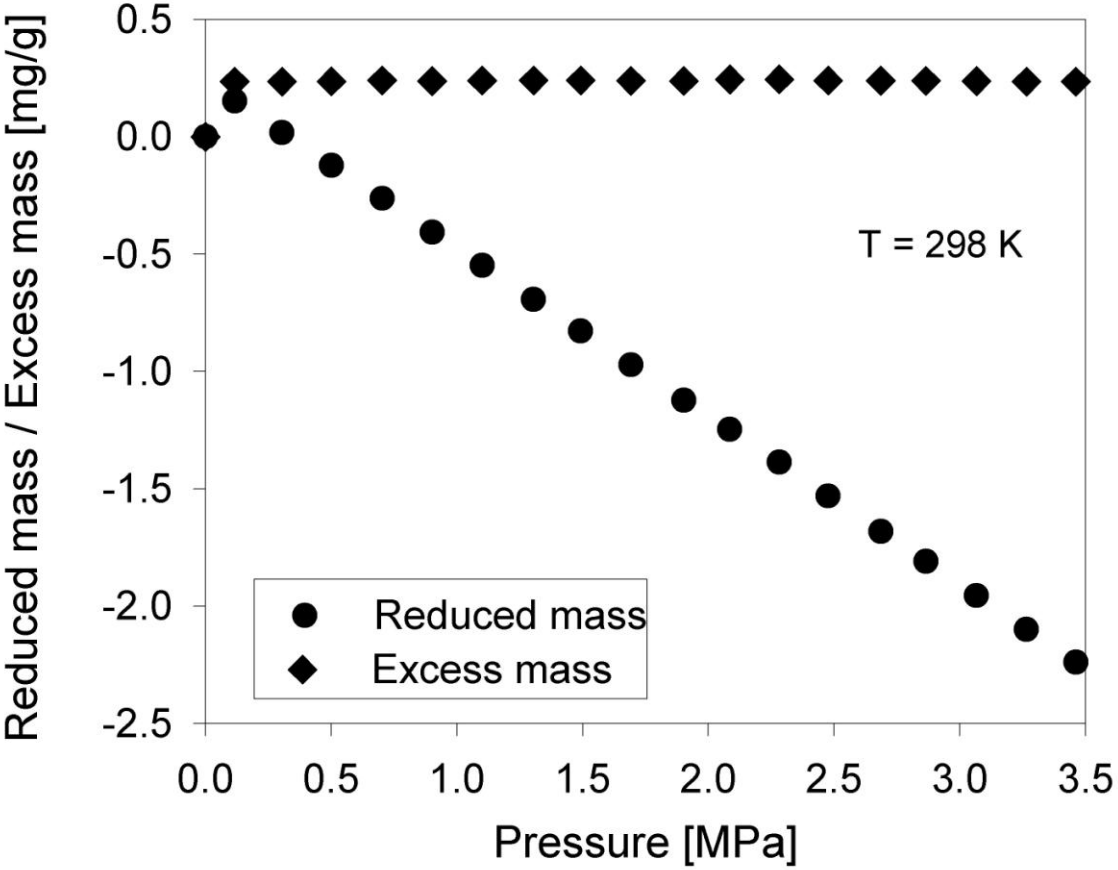
Determination of the (known) volume (51.10 cm^3) of a calibration cylinder by gas expansion experiments using gases He (5.0), N_2 (5.0) and CH_4 (5.5) at 298 K in a commercial gas pycnometer [1].



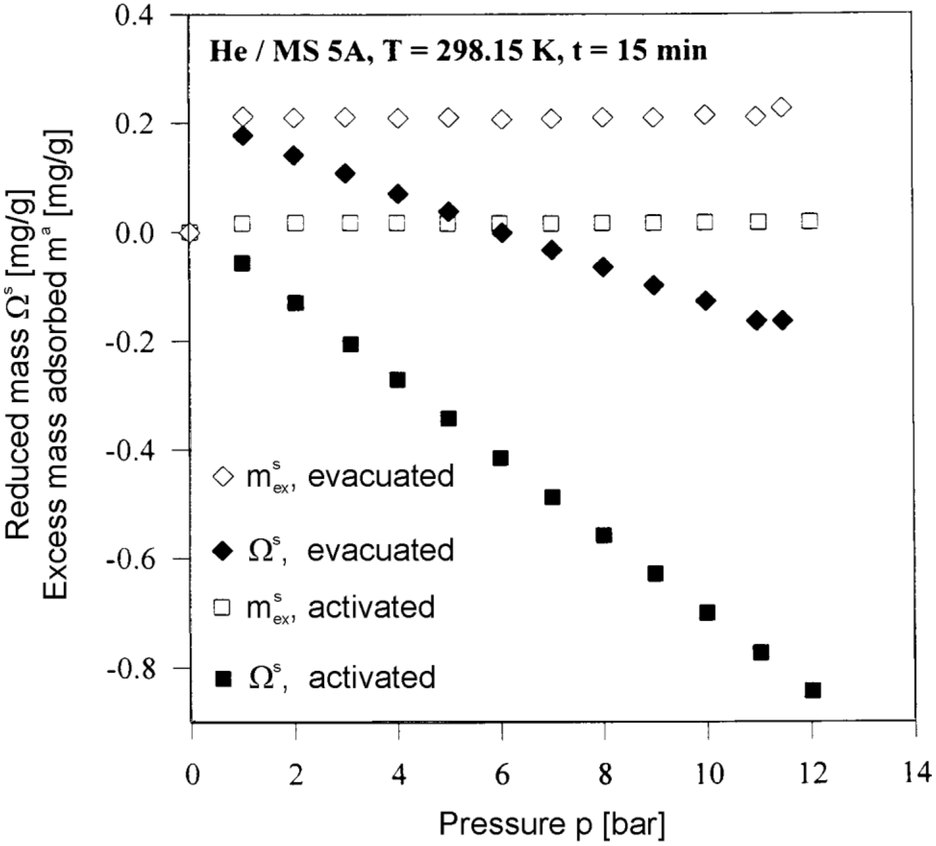
Determination of the volume of activated carbon Norit R1 Extra by helium expansion measurements at 298 K in a commercial gas pycnometer (Micromeritics, Accu Pyc 1330) [1].



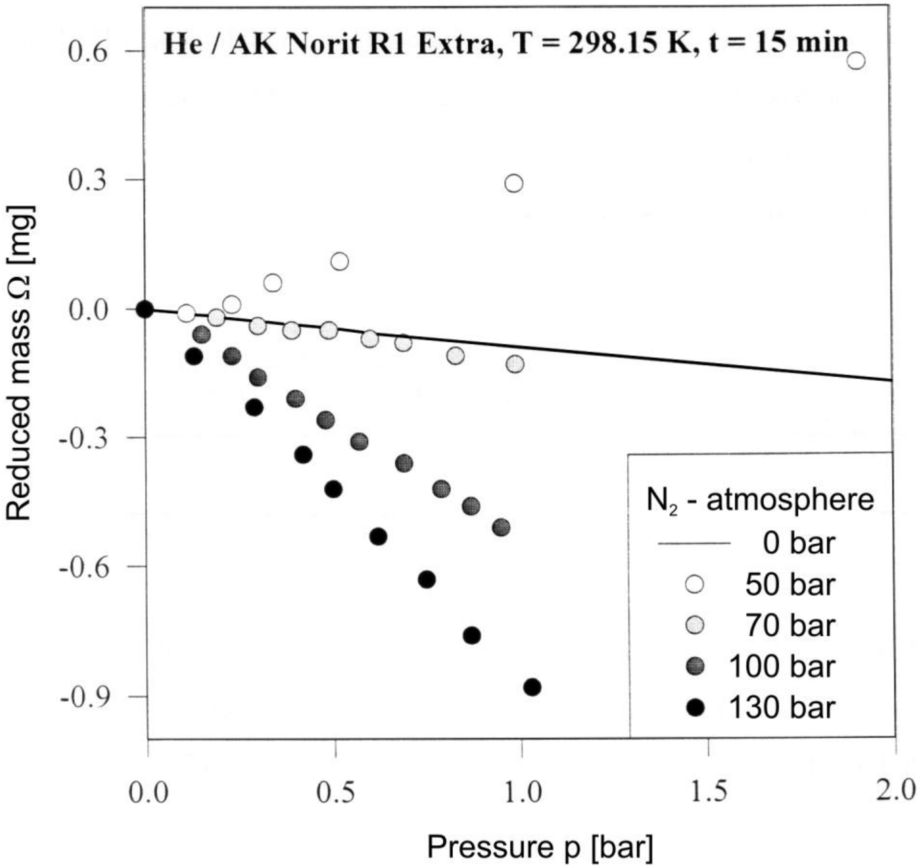
Measurements of the (specific) He-volume of activated carbon fibres (ACF) at 298 K for a set of pressure step up experiments (upper data ●) and respective step down pressures (lower data ○). Measurements were performed in a commercial gas pycnometer using He (5.0) [1].



Adsorption isotherm of helium on activated carbon (AC) Norit R1 Extra at 293 K. Full circles present data of the reduced mass (Ω) defined by Eq. (1.5). As these can be correlated linearly as function of the helium gas density $\rho^f = p/R_{He}T$, the volume of the AC impenetrable to the helium molecules can be calculated from Eq. (1.6). From Eq. (1.5) the mass of helium initially adsorbed at low pressures can be calculated (via Eq. (1.7)) leading to m^a = 0.25 mg/g = const.

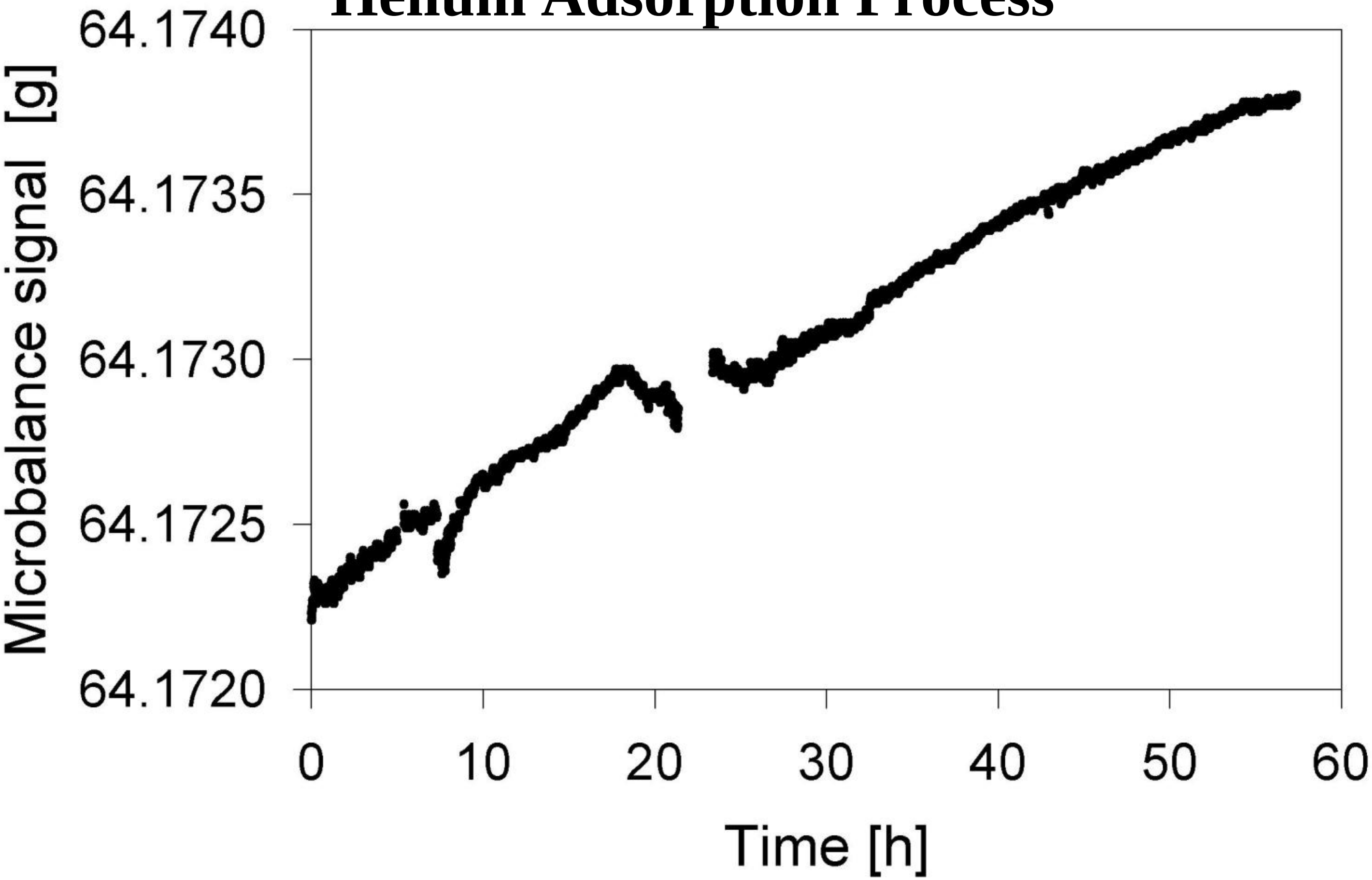


Helium adsorption at T=298.15K on molecular sieves (MS 5A) with different activation procedures. Full symbols (◆, ■) present the measured values of the reduced masses (Ω), cp. Eq. (1.6). Open symbols (◇, □) are masses of helium adsorbed on the samples calculated by Eq. (1.7). Data indicate saturated states of adsorption of helium at increasing pressures for both samples. However, the (specific) volumes (V^{as}) of both samples seen by the helium molecules and calculated by Eq. (1.6) from steepnesses of the linearly correlated Ω-data are quite different [1].



Adsorption of helium added to activated carbon Norit R1 Extra in a nitrogen atmosphere of p^f=0, 5, 7, 10, 13 MPa at T=298.15 K. The reduced mass (Ω), Eq. (1.6), referring to helium gas pressure. Data for p=7, 10, 13 MPa indicate that helium is not adsorbed additionally to nitrogen, but that the volume (V^{as}) of the sorbent sample (s) loaded with increasing amounts of nitrogen (a) as seen by the helium molecules is also increasing monotonously. The p=5MPa-data show adsorption. But this simply may be adsorption of N_2 due to poor mixing of the He- and the N_2-gas immediately after adding helium to the system [1].

Helium Adsorption Process



Adsorption process of helium (He(5.0)) on AC Norit R1 Extra at T=298.17K during 58 hours measured gravimetrically (magnetic suspension balance, Rubotherm). The interruption of measurement data at about 24 h is due to limitations in data storage capacity, i. e. an overflow of data, which made a change of the data storage device necessary.

Theory [1]

Reduced mass to be measured by a helium pycnometer

$$\Omega = m^a - \rho^f V^{as} \qquad (1.5)$$

Volume of adsorbent (s) - Adsorbate (a) system:

(1.5) p→∞:

$$V^{as} = -\left(\frac{\partial \Omega}{\partial \rho^f}\right)_{T,\infty} = -\left(\frac{\partial \Omega}{\partial p}\right)_{T,\infty} R_{He} T \qquad (1.6)$$

Absolute mass adsorbed

(1.5), (1.6):

$$m^a = \Omega - \rho^f \left(\frac{\partial \Omega}{\partial \rho^f}\right)_{T,\infty} \qquad (1.7)$$

ρf … density of helium gas
R_{He} … specific gas constant of helium
T … absolute temperature