



## Measurement of Gas Mixture Adsorption Equilibria of Natural Gas Compounds on Microporous Sorbents\*

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**Abstract.** Physisorption equilibria of multicomponent gases on microporous solids like zeolites or activated carbons are considered. In view of lack of reliable and simple methods to calculate mixture adsorption isotherms from pure component data, experiments are still indispensable. An overview of classical and new methods to measure multicomponent gas adsorption equilibria is given. Some of the basic concepts like the Gibbs excess mass and the absolute mass adsorbed underlying these methods are discussed. Experimental data and a class of new adsorption isotherms for inhomogeneous microporous adsorbents of fractal dimension will be given in another subsequent paper (ADSO 635-98) by the same group of authors.

**Keywords:** coadsorption, gas adsorption equilibria, measurement technique, adsorption isotherm, natural gas

### 1. Introduction

Physisorption phenomena of gas mixtures on inert porous solids like zeolites and activated carbons provide the basis for a variety of gas separation processes including:

- (a) The purification of exhaust air from technical processes including often hazardous compounds like VOCs, FCHCs, HCl, Cl<sub>2</sub> etc. in view of increasing environmental regulations and requirements,
- (b) The separation of air into nitrogen and oxygen enriched components at ambient temperature,
- (c) The purification of natural gas from chemically aggressive or toxic components like H<sub>2</sub>S etc., and
- (d) The regain and/or concentration of valuable components of low BTU-gases like hydrogen from blast-furnace gases or methane from garbage deposit gases (Kast, 1988; Suzuki, 1993; Le Van, 1996).

For design and operation of these processes the so-called adsorption isotherms (AIs) of the multicomponent sorptive gas on the sorbents used are needed among other basic information. Predictions based on pure components' AIs (IAST, RAST) often fail and only seem to be possible for gas mixtures of nearly identical molecules, but even in these cases may be completely misleading.

Various attempts have been undertaken to calculate coadsorption isotherms from first principles (ab initio calculations) most of them based on Statistical Mechanics (Jiang et al., 1994; Maddox and Gubbins, 1996; Sowers and Gubbins, 1995).

Therefore, there is a real need to measure adsorption equilibria of multicomponent gas mixtures on sorbents materials often used today like microporous zeolites, activated carbons and compound materials of these. The resulting formalisms are not known for their simplicity and relevance to technical adsorption processes though there has been progress in this recently (Wang and Do, 1997; Moon, 1993). The main reason for this is that all these formalisms include a variety of model assumptions on the underlying porous structure and

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also on the interaction potential between sorbate and sorbent molecules. This results in introducing several molecular parameters, the numerical values of which only can be provided by experimentally determined coadsorption isotherms.

It is the purpose of this paper to contribute to this field by elucidating classical and new methods to measure coadsorption equilibria and to discuss the advantages and obstacles of each of them.

In the first part of this paper we will discuss some of the basic concepts used today to describe gas-solid adsorption equilibria from an experimental point of view, Section 2. Then in Section 3 we will briefly present four different methods to measure multicomponent gas adsorption equilibria, namely the:

1. Volumetric-chromatographic method,
2. Gravimetric-chromatographic method,
3. Volumetric-gravimetric method,
4. Oscillometric-chromatographic method.

Also combined oscillometric-gravimetric and electrogravimetric measurements will be discussed in brief.

The main advantages and disadvantages of the various methods will be mentioned and basic formulas needed to calculate the masses of all components adsorbed from experimental quantities will be presented. Summarising it can be stated that in all the measurement methods mentioned above additional hypotheses or model assumptions on the void or dead volume of a porous sorbent are needed to calculate masses of (multicomponent) adsorbates from experimental data. Only if oscillometric and gravimetric measurements are combined it seems to be possible under certain conditions to measure the absolute masses adsorbed for a multicomponent system without such a hypothesis.

Experimental results for pure component, binary and ternary gas mixture adsorption equilibria will be presented in another paper (ADSO 635-98) by the same group of authors. There will also be given a generalised version of the well known Langmuir AI for microporous multi-site adsorbents of fractal dimension.

## 2. Remarks on Basic Concepts

In this section we briefly will discuss some of the basic concepts of gasadsorption-systems, namely the absolute mass and the excess mass of an adsorbed phase and related quantities like its volume and density. Working formulae for these quantities will be given. Reference is

made to the respective literature (Gibbs, reprint 1961; Myers, 1984; Sing et al., 1985; Staudt et al., 1993, 1994; Tomalla, 1995; Sircar, 1996; Myers, 1997).

Adsorption equilibria of both, pure gases or gaseous mixtures on microporous solids like activated carbon (AC) or zeolithe today are most often measured by either volumetric or gravimetric methods (Kast, 1988; Le Van, 1996).

However, neither of these procedures actually allows to determine the mass being adsorbed without introducing a model assumption on how the concept of "adsorbed mass" or, likewise the "mass of adsorptive gas" surrounding a solid sorbent/sorbate system is defined, i.e., its boundaries against the other phases are described. On principle this should be done by either a theoretical concept combined with a "gedankenexperiment" or, preferentially, by a measurement procedure.

To elucidate the situation let us consider a closed vessel of volume  $V^*$  including a porous sorbent with mass  $m^s$  and a multicomponent gaseous sorptive with masses  $m_i^f$  of its components  $i = 1, \dots, N$ , Fig. 1. Designating the mass of component  $i$  being adsorbed by  $m_i$ , the mass balance(s) can be formulated as

$$m_i^* = m_i^f + m_i, \quad i = 1, \dots, N \quad (2.1)$$

stating that the total mass of component  $i$  included in the vessel  $m_i^*$ , is equal to the sum of its masses in the sorptive  $m_i^f$  and the sorbate  $m_i$ . To overcome the

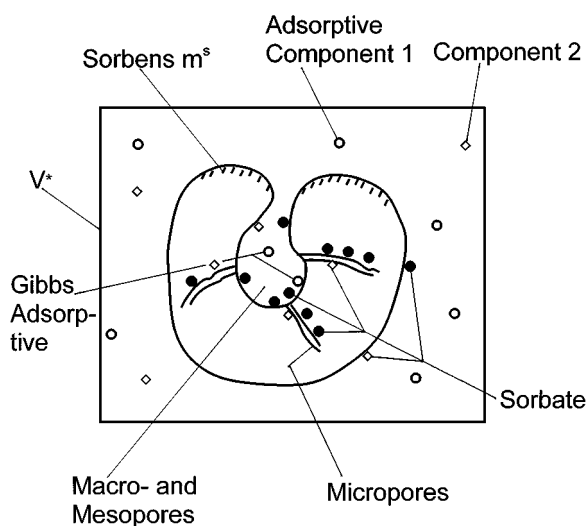


Figure 1. Adsorption vessel of volume  $V^*$  including a porous sorbent mass  $m^s$  and a multicomponent sorptive.

tautological character of the mass balance (2.1) we have to be more specific and to try to define the rhs quantities by experimental procedures!

Following J.W. Gibbs (Gibbs, reprint 1961), we may introduce the concept of the “volume of a porous solid  $V^s$ ” and also assume the single or multicomponent sorptive to fill all the space within the volume  $V^*$  of the vessel except  $V^s$ . Then the mass of component  $i$  of the sorptive can be defined by

$$m_{Gi}^f = \rho_i^f(V^* - V^s), \quad i = 1, \dots, N \quad (2.2)$$

with  $\rho_i^f$  being the partial density of component  $i$  in the adsorptive far away from the sorbent/sorbate system. Let us emphasize that this expression for the so-called Gibbsian adsorptive includes two basic assumptions, namely:

1. The molecules of the adsorptive do not interact with the molecules of the sorbent (gedankenexperiment), that is the spatial extension of any adsorbed phase which may or may not exist on the outer or inner surface of the sorbent is not taken into account, and
2. The volume  $V^s$  inaccessible to sorptive/s molecules does not depend on their size, i.e., is the same for all components  $i = 1, \dots, N$ .

Introducing auxiliary partial densities  $\rho_i^*$  by the relations

$$m_i^* = \rho_i^*(V^* - V^s), \quad i = 1, \dots, N \quad (2.3)$$

and combining Eqs. (2.1)–(2.3) we can express the mass of component  $i$  being adsorbed as

$$m_{Gi} = (\rho_i^* - \rho_i^f)(V^* - V^s), \quad i = 1, \dots, N \quad (2.4)$$

These are the so-called Gibbs excess masses of the adsorbed phase. Though these quantities today are widely used and have proved to be useful concepts for engineering purposes, it must be emphasized that on principle Eq. (2.4) lacks relevance in that the “volume of a porous solid  $V^s$ ” hardly can be measured without a strong coupling to the measurement procedure!

Moreover it may be debated whether  $V^s$  exists at all in a strict sense. (Compare for example the positivistic statements of the International Organisation for Standardisation, ISO, Geneva, on the concept of the “true value” of a measurable quantity (ISO, 1993, 1995)).

Therefore now, one may well introduce other assumptions on the extension of the sorptive gas surrounding a sorbent/sorbate system than (2.2). For example one may assume the latter to have a volume  $V^{as}$  being inaccessible to sorptive’s molecules, which is quite different from  $V^s$ .

Then we have for the mass of component  $i$  of the sorptive

$$m_i^f = \rho_i^f(V^* - V^{as}). \quad (2.5)$$

Using the mass balance (2.1) and Eqs. (2.3) and (2.4) we get for the “absolute mass adsorbed”

$$\begin{aligned} m_i &= m_i^* - m_i^f \\ &= \rho_i^*(V^* - V^s) - \rho_i^f(V^* - V^{as}) \\ &= m_{iG} + \rho_i^f(V^{as} - V^s) \geq m_{iG} \end{aligned} \quad (2.6)$$

Introducing formally the “volume of the adsorbed phase” by

$$V^a = V^{as} - V^s, \quad (2.7)$$

Equation (2.6) may be rewritten as

$$m_i = m_{iG} + \rho_i^f V^a, \quad i = 1, \dots, N. \quad (2.8)$$

The difference between the absolute mass adsorbed  $m_i$  and the Gibbsian excess mass  $m_{iG}$ , namely  $\rho_i^f V^a$  may be negligible, especially for low gas pressure i.e., low values of  $\rho_i^f \rightarrow 0$ ,  $V^a \cong m_i \rightarrow 0$ .

However, it may become comparable to  $m_{Gi}$  itself if for example the saturation pressure of the sorptive is approached and condensation occurs, i.e., if  $\rho_i^f \rightarrow \rho_{i,s}^f$  and  $V^a \cong \rightarrow \infty$ !

The quantity most often used today to approximate the volume  $V^s$  of a porous solid is the so-called helium volume  $V_{He}$  (Sing, 1985; Sircar, 1985). It is simply measured by exerting the (activated) sorbent to a helium atmosphere at known pressure and temperature. Assuming helium neither to be adsorbed nor absorbed in the sorbent, i.e.,  $m_{GHe} = m_{He} = 0$ , we get from the mass balance (2.1) and Eq. (2.2) the “helium volume” of the sorbent

$$V_{He}^s = V^* - \frac{m_{He}^*}{\rho_{He}^f(p, T)} \quad (2.9)$$

Here  $m_{He}^*$  is the total mass of helium prepared in the installation and  $\rho_{He}^f$  the density of helium gas as either

measured (by buoyancy effect in a float-type densitometer) or calculated from measured values of pressure  $p$  and temperature  $T$  via the helium thermal equation of state (IUPAC, 1975). Unfortunately, helium is adsorbed and probably also absorbed in small amounts even at ambient temperature and low pressures ( $\approx 1$  bar) by most microporous sorbents and not only by supermicroporous ones (Staudt et al., 1997).

This seems to be the main reason for getting ambiguous, but reproducible results in density measurements of highly porous materials with commercial helium-pycnometers, as shown in Fig. 2. Here the specific volume of AC Norit R 1 Extra (Norit Company, Amersfoort, NL) has been measured at ambient temperature ( $T = 293$  K) and varying helium gas pressure  $10 \text{ kPa} \leq p \leq 120 \text{ kPa}$  and measurement modes (MR), (Staudt et al., 1997; Bohn, 1996). As can be seen there are small, but systematic variations in the specific volume of about 2% depending on the gas pressure applied!

Moreover, long term experiments in our laboratory have shown that helium penetrates at a nearly constant rate many sorbents materials, especially activated carbon! Consequently, equilibrium may not be reached even after a period of several weeks (Staudt et al., 1997). In view of this experimental evidence we recommend to use argon as a test gas instead of helium! The kinetics of argon adsorption processes seems to be much faster, i.e., equilibrium is attained much more rapidly than for helium. Also, the amount of argon adsorbed at room temperature is for many materials roughly speaking only half of that of nitrogen!

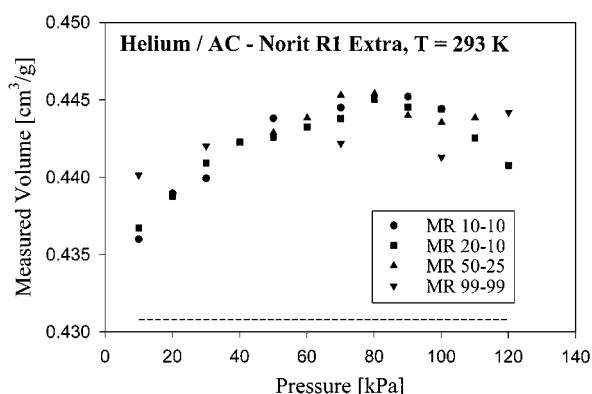


Figure 2. Specific volume of AC Norit R 1 Extra at 293 K as measured with a commercial helium pycnometer at various gas pressures and modes (MR).

The volume of the sorbent/sorbate system can be approximated by the working formula

$$V^{\text{as}} = V_{\text{He}}^{\text{s}} + \sum_i^N \frac{m_i}{\rho_{io}^{\text{L}}} \quad (2.10)$$

Equivalently, we have in view of Eq. (2.7) for the volume of the adsorbed phase

$$V^{\text{a}} = \sum_i^N \frac{m_i}{\rho_{io}^{\text{L}}} \quad (2.11)$$

Here  $m_i$  is the absolute mass of component  $i$  adsorbed and  $\rho_{io}^{\text{L}}$  is the density of pure component  $i$  in a liquid reference state, i.e., the liquid triple point state or—if it exists—the liquid saturated state at ambient temperature or pressure. In view of (2.11) a density  $\rho$  of the adsorbed phase formally can be introduced by

$$\frac{1}{\rho} = \sum_i^N \frac{w_i}{\rho_{io}^{\text{L}}} \quad (2.12)$$

with  $w_i = m_i / \sum_k m_k$  being the mass fraction of component  $i$  in the adsorbate.

Obviously, in Eqs. (2.10)–(2.12), the adsorbed phase has been assumed to be ideal, i.e., the excess volume due to components' interactions has been neglected.

Finally we would like to mention that statistical molecular models of adsorbed phases generally will lead to the absolute mass adsorbed and not to the Gibbs excess mass. Experimentally the absolute mass adsorbed up to now only can be determined under special conditions by oscillometric methods (Keller, 1995), Section 3.4. Both the volumetric and the gravimetric method only lead to the so-called reduced mass of the (single or multicomponent) adsorbate

$$\Omega_i = m_i - \rho_i^{\text{f}} V^{\text{as}}, \quad (2.13)$$

$$= m_{\text{Gi}} - \rho_i^{\text{f}} V^{\text{s}}. \quad (2.14)$$

From these relations either the total mass of component  $i$  adsorbed  $m_i$ , or the Gibbs excess mass  $m_{\text{Gi}}$  may be obtained if a model for either of the volumes  $V^{\text{as}}$  or  $V^{\text{s}}$ , i.e., for example Eqs. (2.10) or (2.9) is introduced. Details are given in the following sections.

### 3. Experimental Methods

In this section we present in brief three different methods to measure multicomponent gas adsorption equilibria. These are the volumetric, the gravimetric and

the oscillometric method. The physical properties of matter underlying these methods are its extensivity in space, gravity and inertia. Some of the possible combinations of these methods will also be considered, in particular the volumetric-gravimetric method for binary mixture adsorption. All these measurement methods can be used likewise for scientific, laboratory and industrial measurements. In discussing these methods emphasis lies on model assumptions needed to actually calculate the masses adsorbed from experimental data.

### 3.1. Volumetric-Chromatographic Method

In this measurement procedure a well known amount of a gas mixture with masses  $m_i^*$ ,  $i = 1, \dots, N$ , prepared in a storage vessel of volume  $V_{ST}$  is expanded into an adsorption chamber of volume  $V_{AC}$  and partly adsorbed in a sorbent of mass  $m^s$ , Fig. 3. After equilibrium has reached, i.e., constant values of pressure  $p$  and temperature  $T$  in the system have been attained, the molar concentrations

$$y_i = \frac{n_i^f}{\sum_{k=1}^N n_k^f}, \quad i = 1, \dots, N, \quad (3.1)$$

or likewise the mass concentrations

$$w_i^f = \frac{m_i^f}{\sum_k m_k^f} = \frac{M_i y_i}{\sum_k M_k y_k} \quad (3.2)$$

of all components  $i$  of the remaining adsorptive are measured by taking a sample and send it (augmented

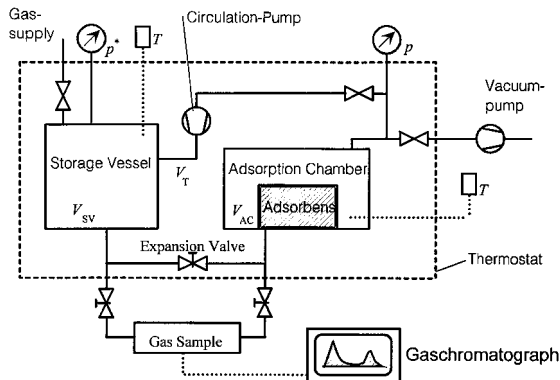


Figure 3. Schematic diagram for volumetric-chromatographic measurements of multicomponent gas adsorption equilibria.

by a carrier gas) to a gas chromatograph (GC) or mass spectrometer.

The total mass of the sorptive is

$$m^f = \rho^f (V^* - V^v). \quad (3.3)$$

Here the density is given by the thermal equation of state (EOS)

$$\rho^f = \frac{pM^f}{ZRT} \quad (3.4)$$

as function of pressure  $p$ , Temperature  $T$ , with  $M^f = \sum_i M_i y_i$  being sorptive's molar mass,  $R$  the universal gas constant and

$$Z = Z(p, T, y, \dots, y_N) \quad (3.5)$$

the compressibility function of the sorptive gas mixture. It must be included in (3.4) in order to take real gas properties into account. (For a mixture of ideal gases  $Z \equiv 1$ .) Reliable and accurate values of  $Z$  are essential to get reliable and accurate adsorption data, especially at higher pressures ( $p \geq 1$  MPa).

If no high precision data for  $Z$  are available (Reid et al., 1977) it is recommended to determine  $Z$  on line by simultaneous measurements of sorptive's density  $\rho^f$  and to calculate its value via Eq. (3.4). Measurements of this type have been performed in our laboratory using a magnetic suspension balance with two different loads. They will be reported in a separate paper (Keller et al., 1998).

The volume  $V^*$  in Eq. (3.3) is the total volume of the experimental installation, Fig. 3, consisting of the storage vessel ( $V_{sv}$ ), the adsorption chamber ( $V_{ac}$ ) and a gas circulation loop including tubes and a circulation pump ( $V_T$ ):

$$V^* = V_{sv} + V_{ac} + V_T. \quad (3.6)$$

$V^v$  indicates the void volume inaccessible to sorptive molecules, i.e., either the volume of the sorbent mass  $m^s$  located in the adsorption chamber or the volume of the combined sorbent/sorbate system, cp. Section 2.

Multiplying (3.3) with the mass concentration  $w_i^f$  of the sorptive and inserting this equation in the mass balance (2.1), we get a formal expression for the mass of component  $i$  adsorbed:

$$m_i = \Omega_i + \rho_i^f V^v. \quad (3.7)$$

Here all measurable or otherwise known quantities have been collected in an auxiliary quantity

$$\Omega_i = m_i^* - \rho_i^f V^*, \quad (3.8)$$

with sorptive's partial densities

$$\rho_i^f = \rho^f w_i^f = \frac{p M^f}{Z R T} w_i^f, \quad i = 1, \dots, N, \quad (3.9)$$

According to (3.7)  $\Omega_i$  may be interpreted as reduced mass adsorbed of component  $i$

$$\Omega_i = m_i - \rho_i^f V^V, \quad (3.7a)$$

the reduction being due to the void volume  $V^V$ , i.e., spatial extension of the sorbent/sorbate system.

To calculate  $m_i$  from Eq. (3.7) we have to introduce a model for the void volume  $V^V$  of the sorbent which basically is an unknown quantity, cp. Section 2. We here confine to two special cases:

- (a) The void volume  $V^V$  is identified with the sorbent volume  $V^s$  approximated by either the helium volume or the argon volume (cp. (2.9)),

$$V^V = V^s \cong \begin{cases} V_{\text{He}}^s \\ V_{\text{Ar}}^s \\ \dots \end{cases} \quad (3.10)$$

Then Eqs. (3.7) and (3.10) yield the (helium related) Gibbs excess mass of component  $i$

$$m_{\text{Gi}} = \Omega_i + \rho_i^f V_{\text{He}}^s, \quad i = 1, \dots, N, \quad (3.11)$$

which numerically can be calculated by taking Eq. (3.8) into account.

- (b) The void volume  $V^V$  can be identified with the volume of the combined sorbent/sorbate system  $V^{\text{as}}$  approximated by (2.10):

$$V^V = V^{\text{as}} \cong V_{\text{He}}^s + \sum_i^N \frac{m_i}{\rho_{i0}^L}. \quad (3.12)$$

Then Eqs. (3.7) and (3.12) deliver  $N$  linear equations for the absolute masses of all components  $m_i$  being adsorbed

$$m_i = \Omega_i + \rho_i^f \left( V_{\text{He}}^s + \sum_k^N \frac{m_k}{\rho_{k0}^L} \right), \quad i = 1, \dots, N. \quad (3.13)$$

From these equations the masses  $m_i$  can be determined by (direct or iterative) algebraic calculations.

Accuracy of the gas chromatograph/mass spectrometer system for determining sorptive's concentrations and of the EOS (3.4) is vital to the applicability and reliability of the volumetric-chromatographic method. Needless to say that prior to taking gas samples for concentration measurements circulation of the sorptive in the installation is recommended in order to avoid local concentration differences and to enhance equilibrium. To reduce adsorption on walls of vessels and tubes, use of high quality stainless steel, electro-polishing of surfaces and passivation by "zero-experiments" are recommended. Thermostatization of all vessels and tubes of the gas loop with uncertainties in temperature smaller than 0.1 K is mandatory in order to get reproducible and reliable results.

The volume-chromatographic method is the one which is most often used today for multicomponent gas adsorption measurements (Brüggendick and Jüntgen, 1985; Calleja et al., 1996; Münstermann and Mersmann, 1984; Schütz, 1988; Rao et al., 1994 etc.). There is a variety of commercial instruments available (Micromeritics, Quantachrome, Porotec etc.) normally offering high standard measurement techniques, but not always satisfying data processing!

### 3.2. Gravimetric-Chromatographic Method

Alternatively to the volumetric-chromatographic method (Section 3.1), multicomponent adsorption equilibria can also be measured by the so-called gravimetric-chromatographic method. A schematic diagram of the installation is given in Fig. 4. It mainly consists of a microbalance holding a sample sorbent of mass  $m^s$  and a kentlage within an adsorption chamber of volume  $V_{\text{AC}}$ , a gas circulation pump and a gas chromatograph or mass spectrometer. A gas mixture of known molar concentrations  $y_i^*$ ,  $i = 1, \dots, N$ , and mass concentrations  $w_i^*$ ,  $i = 1, \dots, N$ , provided by a gas supply system is expanded in the sorption vessel where it is partly adsorbed. After equilibrium is reached, i.e., constant values of the temperature  $T$ , pressure  $p$  and balance display have been attained, a sample of the sorptive is analysed in the GC to give its molar concentrations  $y_i$  or, equivalently, mass concentrations  $w_i$ ,  $i = 1, \dots, N$ , cp. (3.1) and (3.2).

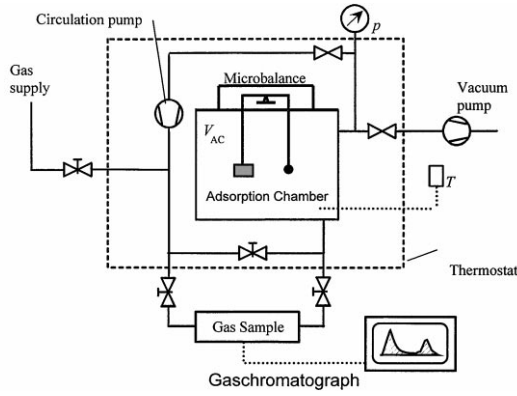


Figure 4. Schematic diagram for gravimetric-chromatographic measurements of multicomponent gas adsorption equilibria.

In order to calculate masses adsorbed  $m_i$  from the mass balance Eq. (2.1), we have to determine adsorptive's mass  $m^f$  and the total mass  $m^*$  given from the gas supply to the installation.

The total mass of the sorptive is

$$m^f = \rho^f(V^* - V^V). \quad (3.14)$$

Here sorptive's density  $\rho^f$  again is given by the thermal EOS (3.4). The volume

$$V^* = V_{AC} + V_T + V_{MB} \quad (3.15)$$

is the total net volume of the experimental setup, namely the sum of the volume of the adsorption chamber ( $V_{AC}$ ), tubes and gas circulator ( $V_T$ ) and the internal volume of the microbalance ( $V_{MB}$ ).  $V^V$  is the void volume inaccessible to sorptive's molecules which will be specified later on.

From microbalance measurements one can obtain a reduced mass adsorbed in the sorbent, namely the quantity

$$\Omega_{MB} = m - \rho^f V^V. \quad (3.16)$$

Here we already have identified the void volume of the sorbent/sorbate system causing buoyancy in the sorptive of density  $\rho^f$  with the void volume  $V^V$  inaccessible to sorptive's molecules in volumetric experiments as has been introduced in Section 3.1. This seems to be justified since extensivity of mass—which is used in volumetry—is proportional to its gravity—which is used in microbalance measurements.

The quantity

$$m = \sum_i^N m_i \quad (3.17)$$

is the sum of all masses  $m_i$  of component  $i = 1, \dots, N$  adsorbed on the surface of the sorbent. It can only be described in more detail after specification of the concept of “void volume”  $V^V$ .

The quantity  $\Omega_{MB}$  can be derived from microbalance measurements. In case of a two-sided balance (Kahn, Sartorius) four different measurements are necessary (Tomalla, 1994), namely:

- The empty balance, i.e., the balance without a sorbent and a kentlage in vacuum ( $p < 10^{-4}$  mbar),
- The empty balance exerted to the sorptive at pressure  $p$ , temperature  $T$ ,
- The balance loaded with sorbent and kentlage in vacuum,
- The loaded balance in the gaseous sorptive.

For one-sided or single beam balances (Mettler, etc.) normally only measurements (b)–(d) are necessary.

To calculate the total mass of gas supplied to the system we consider the overall mass balance

$$m^* = m^f + m \quad (3.18)$$

resulting from Eqs. (2.1) by adding to all components  $i = 1, \dots, N$ .

Introducing in (3.18) for  $m^f$  expression (3.14) and for  $m$  Eq. (3.16) we get

$$m^* = \rho^f V^* + \Omega_{MB} \quad (3.19)$$

That is the total mass of gas supplied to the adsorption installation can be determined from density and microbalance adsorption measurements! Multiplying (3.19) with the initial mass concentration  $w_i^*$  of the sorptive gas and also Eq. (3.14) with  $w_i$ , we get from the mass balance of component  $i$ , Eq. (2.1) the expression

$$m_i = \Omega_{MBi} + \rho_i^f V^V, \quad i = 1, \dots, N \quad (3.20)$$

with the auxiliary quantity

$$\Omega_{MBi} = (w_i^* - w_i) \rho_i^f V^* + w_i^* \Omega_{MB} \quad (3.21)$$

and

$$\rho_i^f = \rho^f w_i = \frac{pM^f}{ZRT} w_i \quad (3.22)$$

as partial density of component  $i$  in the sorptive.

From Eqs. (3.20) and (3.21) the masses adsorbed  $m_i$  can be calculated if model assumptions for the void volume  $V^V$  are introduced.

(a) Assuming

$$V^V \cong V_{\text{He}}^s \cong V_{\text{Ar}}^s$$

we get similarly to Section 3.1 for the Gibbs excess mass of component  $i$

$$m_{\text{Gi}} = \Omega_{\text{MB}i} + \rho_i^f V_{\text{He}}^s. \quad (3.23)$$

(b) If  $V^V$  is identified with the volume of the sorbent/sorbate system and approximated by (3.12), i.e.,

$$V^V = V^{\text{as}} \cong V_{\text{He}}^s + \sum_i^N \frac{m_i}{\rho_{io}^L},$$

we get from (3.20)  $N$  linear equations

$$m_i = \Omega_{\text{MB}i} + \rho_i^f \left( V_{\text{He}}^s + \sum_k^N \frac{m_k}{\rho_{ko}^L} \right) \quad (3.24)$$

which allow to determine the absolute masses adsorbed  $m_i$  by (direct or iterative) algebraic calculation since all other parameters either have been measured ( $w_i^*$ ,  $w_i^f$ ,  $p$ ,  $T$ ,  $\Omega_{\text{MB}}$ ) or are known as system's parameters ( $V^*$ ,  $Z$ ,  $M^f$ ,  $\rho^f$ ,  $\rho_{ko}^L$ ).

The main advantage of the gravimetric-chromatographic method compared to the volumetric-chromatographic method is that it only needs small amounts of sorbent material, typically 1 g, a high sensitive microbalance provided. Disadvantage is that most balances can not be used in corrosive gas atmospheres like  $\text{H}_2\text{S}$ ,  $\text{SO}_2$  etc. In this case use of a magnetic suspension balance (Rubotherm, Bochum) is recommended, cp. Figs. 7 and 8 (Dreisbach et al., 1996; Dreisbach, 1998).

### 3.3. Gravimetric-Volumetric Measurements

Methods described in Sections 3.1 and 3.2 may be combined to allow volumetric-gravimetric-chromatographic measurements.

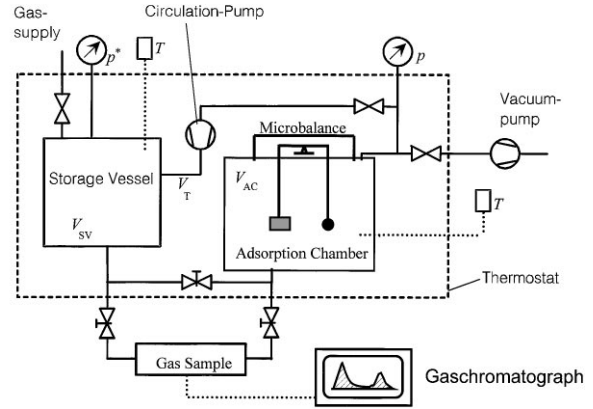


Figure 5. Experimental setup for volumetric-gravimetric-chromatographic measurements of multicomponent gas adsorption equilibria.

The scheme of an installation of this type is displayed in Fig. 5. It consists of a storage vessel ( $V_{\text{SV}}$ ), an adsorption chamber ( $V_{\text{AC}}$ ), a gas circulation loop including a pump ( $V_{\text{T}}$ ), microbalance ( $V_{\text{MB}}$ ), gaschromatograph, thermostat, gas supply, vacuum pump, valves, thermocouples and manometers to take measurements of temperatures and pressures. Such a device has been designed and built in our laboratory (Fig. 6). It allows to do simultaneously or alternatively volumetric-chromatographic, gravimetric-chromatographic or volumetric-gravimetric measurements as will be discussed later.

It may be argued that by combining volumetric and gravimetric measurements of coadsorption equilibria not only the masses of all components adsorbed but also the “void volume”  $V^V$  experimentally can be determined without introducing any of the hypotheses (3.10) or (3.12). Unfortunately, this is not the case. This can easily be recognised from Fig. 5 and Section 3.2: all the basic equations given there for gravimetric-chromatographic measurements also hold for volumetric-gravimetric-chromatographic measurements except that the volume of the gas filled installation is not given by (3.15) but is

$$V^* = V_{\text{AC}} + V_{\text{SV}} + V_{\text{T}} + V_{\text{MB}}. \quad (3.25)$$

Hence, for calculating the masses  $m_i$  of all components adsorbed we again end up with Eqs. (3.20) and (3.21) including the unknown void volume  $V^V$ , whereas Eq. (3.19) turns out to be a consistency relation for measured quantities ( $m^*$ ,  $V^*$ ,  $\rho^f$ ,  $\Omega_{\text{MB}}$ ). Thus the so-called “volume problem of adsorption”,



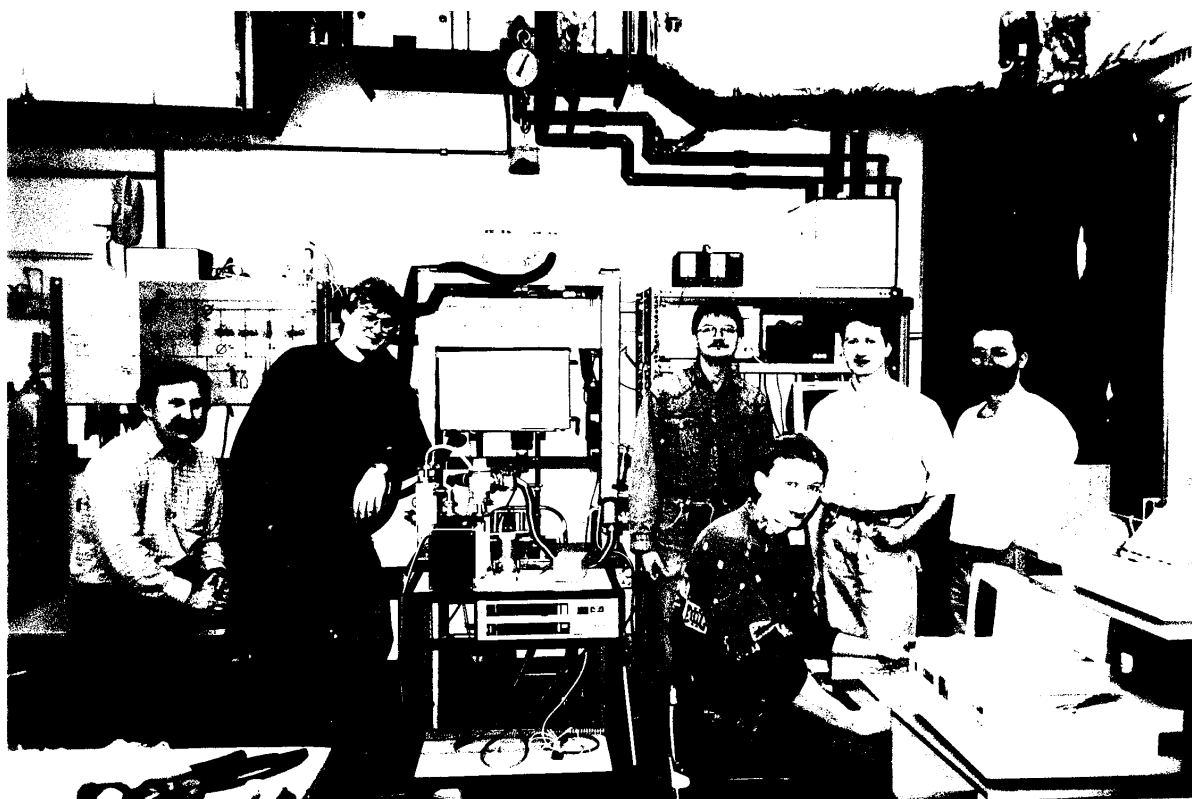


Figure 6. Installation for volumetric-gravimetric-chromatographic measurements of multicomponent gas adsorption equilibria.

i.e., the necessity to introduce model assumptions for the void volume  $V^V$  in Eqs. (3.7) and (3.20) can not be solved by combining volumetric and gravimetric measurements.

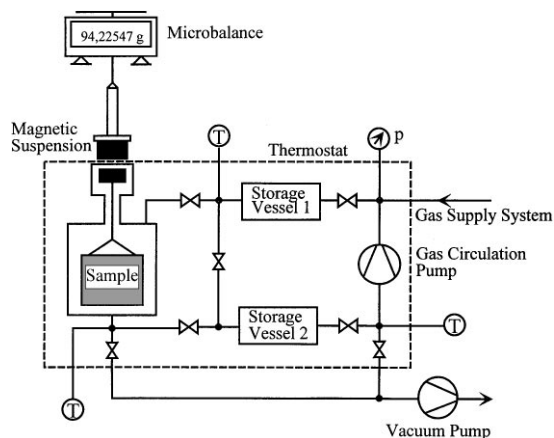


Figure 7. Schematic diagram for volumetric-gravimetric measurements of binary coadsorption equilibria including a magnetic suspension balance.

However, this type of measurements proves to be useful to determine co-adsorption equilibria of binary gas mixtures including non-isomeric components without analysing the sorptive phase, i.e., without using a gas chromatograph or mass spectrometer (Keller, 1992).

An example for an installation in which volumetric-gravimetric measurements can be done is depicted in Fig. 7. It includes a magnetic suspension decoupling the gas filled adsorption chamber from the micro-balance thus allowing measurements with corrosive gases ( $\text{H}_2\text{S}$ ,  $\text{SO}_2$ ,  $\text{Cl}_2$  etc.). The gas mixture accurately can be prepared by supplying pure components with masses  $m_1^*$ ,  $m_2^*$  to two separate storage vessels with volumes  $V_{\text{SV}1}$ ,  $V_{\text{SV}2}$ . After mixing the pure components by use of a gas circulation loop including a pump (volume  $V_T$ ) the mixture is expanded to a sorption chamber ( $V_{\text{AC}}$ ). After equilibrium has been maintained, the masses of both components adsorbed  $m_1$ ,  $m_2$  and those of the sorptive's components  $m_1^f$ ,  $m_2^f$  can be calculated from four resulting equations:

Mass balances (2.1):

$$m_i^* = m_i^f + m_i, \quad i = 1, 2. \quad (3.26)$$



Figure 8. Apparatus for volumetric-gravimetric measurements of binary coadsorption equilibria including a magnetic suspension balance.

Microbalance measurements (Eqs. (3.16) and (3.3)):

$$\Omega_{\text{MB}} = m_1 + m_2 - \frac{m_1^f + m_2^f}{V^* - V^V} V^V \quad (3.27)$$

Adsorptive's thermal equation of state (Eqs. (3.3) and (3.4)):

$$\frac{m_1^f}{M_1} + \frac{m_2^f}{M_2} = \frac{p(V^* - V^V)}{ZRT}. \quad (3.28)$$

Here the total internal volume of the installation has been indicated by

$$V^* = V_{\text{SV1}} + V_{\text{SV2}} + V_{\text{AC}} + V_{\text{T}} \quad (3.29)$$

and  $V^V$  again is the void (or dead) volume of the sorbent/sorbate system to be specified by either of the models (3.10) or (3.12).

Numerical treatment of Eqs. (3.26)–(3.28) can be cumbersome, especially if the compressibility  $Z$  is a sophisticated function of the gas concentrations  $y_i$ ,  $w_i^f$  as it may be for polar components at elevated pressures (Tomalla, 1995).

Let us emphasise that for this method no GC or mass-spectrometer is needed! However, it should be pointed out that this method can not be applied to mixtures with isomeric components ( $M_1 = M_2$ ) such as ( $\text{N}_2$ ,  $\text{CO}$ ), since then Eq. (3.28) becomes linearly dependent on Eqs. (3.26) and (3.27). Also the method may pose some accuracy problems for highly diluted mixtures, i.e., if the initial concentration of any of its components is nearly 0 or 1 (Dreisbach, 1998).

### 3.4. Oscillometric-Chromatographic Measurements

The total mass of a gas mixture adsorbed on the surface of a porous solid on principle can be determined by observing the frequency of oscillations of the sorbent/sorbate system thus using another basic property of matter, namely its inertia.

Experiments with high frequency systems such as piezoelectric oscillations of combined quartz/sorbent systems (Ward and Buttry, 1990) have not been successful. Among the various problems still to be solved are those of fixing the sorbent to the quartz without using a glue, which normally could change sorbent's properties, and the gas flow around the oscillating system which due to sorptive's viscosity will cause additional damping. This on principle can be calculated by solving Navier-Stokes-equations (NSE) for the gas flow initiated by the motion of the oscillating system. However, for linear high frequency oscillations the boundary conditions are so complicated, that solutions of this problem in analytic form even for the approximated NSE have not been achieved up to now. The situation is much more favourable if low frequency, i.e., slow oscillations of a rotational pendulum (Keller, 1995), or the relaxation of a floating rotator (Docter et al., 1997; Keller, 1998) are considered. Since the oscillating or rotating system during motion is basically always transformed in itself, the boundary conditions become rotationally symmetric allowing thus analytic solutions of the approximated NSE.

We here confine to present results for a rotationally symmetric sorbent/sorbate system, i.e., a disk, oscillating slowly in a gaseous sorptive, Fig. 9 (Keller, 1995). The instrument consists of a flat sample disk fixed to a torsional wire and complemented by a stem

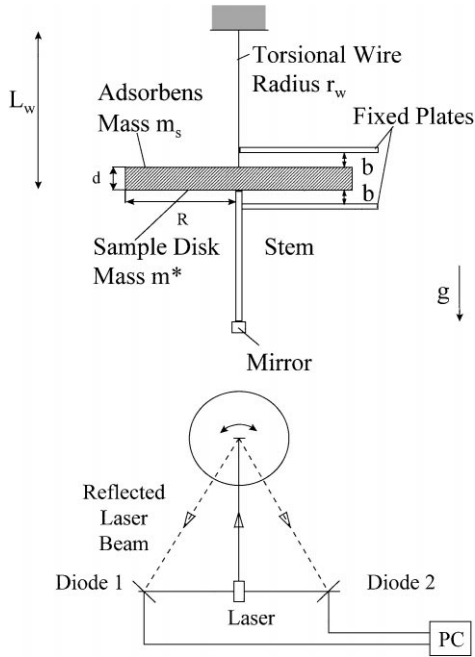


Figure 9. Scheme of a rotational pendulum bearing a sorbens disk.

bearing a small mirror to reflect a laser beam to observe pendulum's rotational oscillations. Figure 10 shows an experimental installation designed and built in our laboratory, made of stainless steel and operable at ambient temperature 293 K at pressures up to 5 MPa.

The ratio of the total mass adsorbed ( $m$ ), to the mass of the sorbent ( $m^s$ ) can be determined from the angular frequency ( $\omega$ ) and the logarithmic decrement ( $\Delta$ ) of damped harmonic oscillations of the pendulum taken for:

- The empty pendulum (mass  $m_p^*$ ), i.e., pendulum without sorbent in vacuum ( $\omega^*$ ,  $\Delta^*$ ),
- The pendulum (mass  $m_p^*$ ) loaded with sorbent ( $m^s$ ) in vacuum ( $\omega_o$ ,  $\Delta_o$ ),
- The pendulum (mass  $m_p^*$ ) loaded with sorbent ( $m^s$ ) and sorbate ( $m = \sum_i m_i$ ), in gaseous sorptive ( $\omega_E$ ,  $\Delta_E$ ),

by the formula

$$\frac{m}{m^s} = \left( \frac{1 + \Delta_o^2}{1 + \Delta_E^2} \left( \frac{\omega_o}{\omega_E} \right)^2 - 1 \right) \left( 1 - \frac{\Delta_o \omega_o}{\Delta^* \omega^*} \right)^{-1} \equiv f(\omega_E, \Delta_E) \quad (3.30)$$

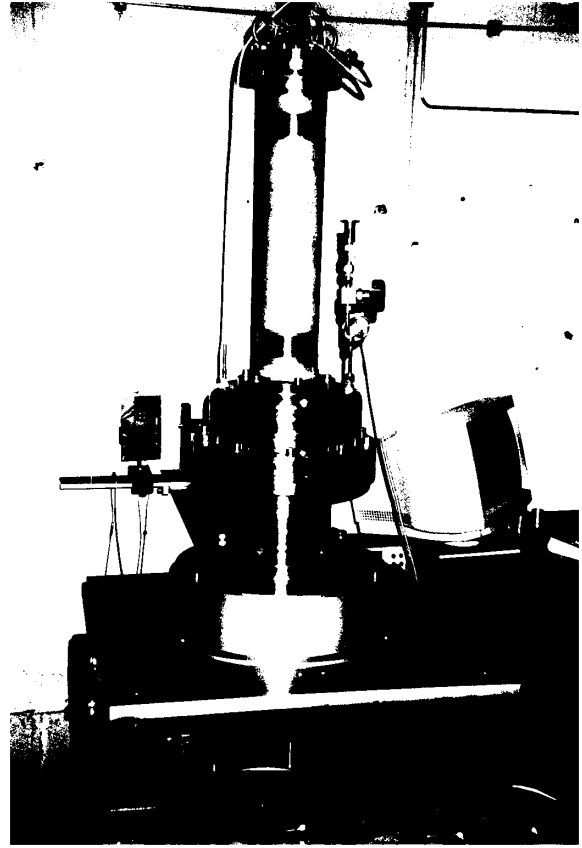


Figure 10. Rotational pendulum for oscillometric measurements of gas adsorption equilibria.

To derive this formula from the equation of motion of the pendulum and the NSEs, no assumption on the "volume" of the sorbent/sorbate system is needed but only on its existence and its rotational symmetry around pendulum's wire. Hence, Eq. (3.30) holds valid even for sorbent systems with surfaces of fractal dimension the area of which may tend to infinity! (Mandelbrot, 1983; Bunde et al., 1991).

Assuming local inhomogeneities at the surface of the quasi-homogeneous porous disk, i.e., open macropores with characteristic diameter  $r_m$ , to be 3–4 orders of magnitude smaller than its macroscopic dimensions ( $R \cong 10$  cm), i.e.,

$$r_m \ll R, \quad (3.31)$$

the local Reynolds number

$$Re_m = \frac{r_m u}{\nu}$$

always is very small compared to the Reynolds number

$$Re = \frac{Ru}{\nu}$$

of sorptive's flow around the disk. Lets also assume  $Re$  itself not to exceed an approximate value of 100 to maintain laminarity of the flow and to neglect secondary flows. Then the inequalities hold

$$Re_m \ll Re \leq 100. \quad (3.32)$$

Under these conditions, i.e., not too low gas pressures and a smooth disk surface, we consider the mass ( $m$ ) in (3.30) to be the absolute mass adsorbed in the porous disk, since not only adsorbed molecules on its external or internal surfaces but also microsorptive molecules which may be present in internal meso- or macropores add to the disk's (moment of) inertia which actually is measured in (3.30).

A rotational pendulum for oscillometric adsorption measurements can be integrated in installations for either volumetric or gravimetric measurements to allow simultaneously oscillometric-volumetric and/or oscillometric-gravimetric measurements. Schemes for such installations are sketched in Figs. 11 and 12. Measurements of this type would allow on principle to measure both the mass adsorbed and the void volume of a given amount of sorbents (Keller, 1995).

Indeed, combining oscillometric measurements with microbalance measurements of the same sorbents at the same sorptive conditions, we get additionally to (3.30) the microbalance equation (cp. (3.16)),

$$\Omega_{MB} = m - \rho^f V^{as} \quad (3.33)$$

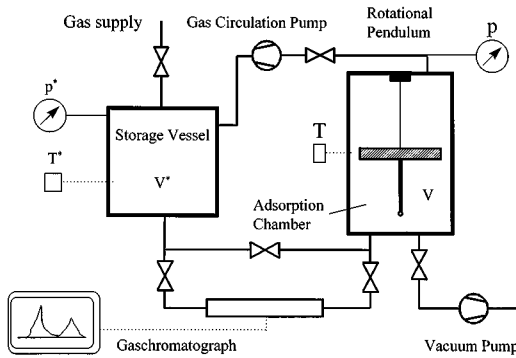


Figure 11. Experimental setup for oscillometric-volumetric measurements of gas adsorption equilibria.

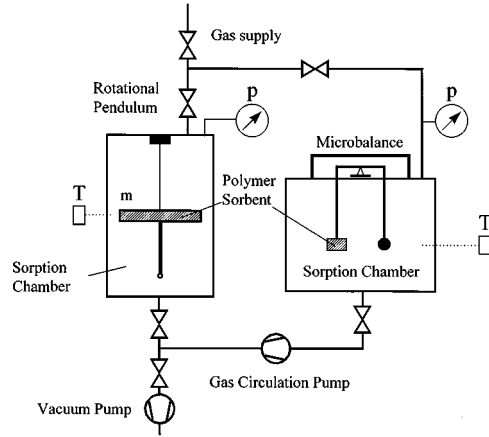


Figure 12. Experimental setup for oscillometric-gravimetric measurements of gas adsorption equilibria.

where  $\rho^f$  indicates sorptive's density and  $V^{as}$  the volume of the combined sorbent/sorbate system.

Combining (3.30) and (3.33) we get an expression for this quantity, namely

$$V^{as} = \frac{1}{\rho^f} (f(\omega_E, \Delta_E) m^s - \Omega_{MB}), \quad (3.34)$$

which, therefore, can be measured by simultaneous oscillometric and gravimetric measurements! Preliminary experimental results of adsorption measurements of  $N_2$  and  $CH_4$  on AC Norit R1 indicate that numerical values resulting from (3.34) coincide fairly well with those gained from the model assumption (2.10).

To calculate masses of components  $m_i$  adsorbed we have to combine (3.30) with the mass balance equations

$$m_i^* = m_i^f + m_i, \quad i = 1, \dots, N, \quad (3.35)$$

the overall mass balance

$$m^* = m^f + m, \quad (3.36)$$

with sorptive's mass

$$m^f = \rho^f (V^* - V^{as}) \quad (3.37)$$

and the EOS

$$\rho^f = \frac{pM^f}{ZRT}. \quad (3.38)$$

From (3.35) we get with (3.30), (3.36)–(3.38)

$$m_i = (w_i^{\text{f}*} - w_i^{\text{f}})(\rho^{\text{f}}V^* + \Omega_{\text{MB}}) + w_i^{\text{f}}f(\omega_R, \Delta_E)m^{\text{s}},$$

$$i = 1, \dots, N. \quad (3.39)$$

Here  $w_i^{\text{f}*}$ ,  $w_i^{\text{f}}$  are the mass concentrations of component  $i$  in the sorptive prior to adsorption and after adsorption equilibrium in the pendulum has been attained. The quantity  $V^*$  indicates the total volume of the case covering the pendulum. It can be measured by either nitrogen or helium gas expansion experiments with the empty pendulum, i.e., the pendulum without a sorbent disk!  $\Omega_{\text{MB}}$  results from microbalance measurements, cp. Section 3.2,  $f(\omega_E, \Delta_E)$  is given by (3.30) and  $m^{\text{s}}$  is the mass of the sorbent disk measured in vacuum by either using a balance or the rotational pendulum itself!

It should be noted that according to (3.39) in a multi-component gas adsorption system the absolute masses adsorbed on principle can be measured by combining oscillometric and gravimetric measurements condition (3.32) provided!

Several other methods to measure multicomponent gas mixture adsorption equilibria are presently discussed in literature. We here mention only the electro-gravimetric and the magneto-gravimetric methods where dielectric and magnetic properties of sorbent/sorbate systems are measured which under certain conditions can be related to the absolute masses of the components adsorbed (Staudt et al., 1994). However, these methods can only be applied under special circumstances and today may be considered as premature.

## Nomenclature

$M_i$	molar mass of component $i$ of a multicomponent system	g/mol
$m = \sum_i^N m_i$	total mass adsorbed on a solid sorbent of mass $m^{\text{s}}$	g, kg
$m_i$	mass of component $i = 1, \dots, N$ being adsorbed on the surface of a solid sorbent of mass $m^{\text{s}}$	g, kg
$m^{\text{f}} = \sum_i^N m_i^{\text{f}}$	total mass of sorptive	g, kg

$m_i^{\text{f}}$	mass of component $i = 1, \dots, N$ of the fluid (f) sorptive	g, kg
$m^* = \sum_i^N m_i$	total mass of fluid included in an adsorption chamber	g, kg
$m_i^*$	total mass of component $i$ of a fluid included in an adsorption chamber	g, kg
$m_{\text{Gi}}$	Gibbs excess mass of component $i$ adsorbed	kg
$m_{\text{p}}^*$	mass of a rotational pendulum	kg
$m^{\text{s}}$	mass of a porous solid (sorbent)	g, kg
$N$	total number of components of adsorptive or adsorbate	—
$n_i^{\text{f}}$	mol number of component $i = 1, \dots, N$ of the fluid (f) adsorptive	mol
$p$	pressure	Pa, MPa
$R$	radius of a rotational pendulum; also used for absolute gas constant	cm, J/g mol
$Re = (Ru/v)$	reynolds number	1
$T$	temperature	K
$u$	velocity of sorptive's flow around a rotational pendulum	$\text{ms}^{-1}$
$V^*$	volume of an isolated adsorption chamber partly filled with sorbens	$\text{m}^3$
$V^{\text{a}}$	volume of an adsorbed phase (cp. (2.7))	$\text{m}^3$
$V^{\text{as}}$	volume of the combined sorbent/sorbate system inaccessible to molecules of a gaseous sorptive (related to absolute mass adsorbed)	$\text{m}^3$

$V_{AC}$	volume of adsorption chamber being part of an experimental installation for sorption measurements	$m^3$	$\rho^f$	density of fluid, i.e., liquid or gaseous adsorptive	$kg/m^3$
			$\rho_{He}^f$	density of helium gas	$kg/m^3$
			$\rho_i^f$	partial density of component $i$ of sorptive	$kg/m^3$
$V^s$	volume of a porous sorbent (related to Gibbs excess mass)	$m^3$	$\rho_i^*$	fictitious partial density of component $i$ of a gaseous adsorptive prior to adsorption on a solid sorbent	$kg/m^3$
$V_{He}^s$	volume of a porous sorbent measured with a helium pycnometer	$m^3$		cp. Eq. (2.3)	
$V_{MB}$	internal volume of a microbalance filled with sorptive gas	$m^3$	$\rho_{ko}^L$	density of adsorptive's pure component $k$ in a liquid reference state	$kg/m^3$
$V_{SV}$	volume of a gas storage vessel being part of an installation for adsorption measurements	$m^3$	$\omega$	angular frequency of harmonic rotational oscillations	$s^{-1}$
$V_T$	volume of tubes and valves connecting vessels in an installation	$m^3$	$\Omega_i$	reduced adsorbed mass of component $i$ measured in volumetric gas expansion experiments, Eqs. (3.7) and (3.8)	$kg$
$V^v$	void volume of a sorbent/sorbate system	$m^3$			
$w_i^f$	mass concentration of component $i$ in the sorptive	$kg/m^3$	$\Omega_{MB}$	reduced mass measured in microbalance experiments	$g$
$w_i^*$	mass concentration of component $i$ in a gas mixture prior to adsorption	$kg/m^3$			
$y_i$	molar concentration of component $i$ in the sorptive	$kg/m^3$			
$Z$	compressibility or real gas factor of the sorptive gas	1			
$\Delta$	logarithmic decrement of damped harmonic oscillations	1			
$\nu(p, T, y, \dots, y_N)$	kinematic viscosity of a multicomponent fluid sorptive				

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