

Chapter 2

VOLUMETRY / MANOMETRY

Abstract The physical principles and experimental techniques of pure gas- and multi-component gas adsorption measurements by the volumetric (or manometric) method are outlined. Examples are given. Thermovolumetric and combined volumetric–calorimetric measurements are presented. Pros and cons of the method are discussed. References. List of Symbols.

1. INTRODUCTION

Volumetry or, preferably “Manometry”, cp. Sect. 2.1, is the oldest method to investigate sorption of gases in solids. Early experiments had already been performed by C. W. Scheele (1777), Chappuis (1881), W. Ostwald (1905) and J. Langmuir (1912), [1.1]. Some of these experiments were designed to determine the volume of geometrically complicated objects like cauliflower or sea-urchins. A special instrument for this purpose was designed by R. W. Pohl about 1940 and was called a “volumimeter” [2.1]. It served as a prototype of many of today’s volumetric instruments.

The physics of volumetric gas adsorption experiments is simple: a given amount of sorptive gas is expanded into a vessel which includes a sorbent sample and which initially has been evacuated. Upon expansion the sorptive gas is partly adsorbed on the (external and internal) surface of the sorbent material, partly remaining as gas phase around the sorbent. By a mass balance, the amount of gas being adsorbed can be calculated if the void volume of the sorbent, i. e. the volume which can not be penetrated by the sorptive gas molecules is known – at least approximately.

The adsorbed mass per unit mass of sorbent is a characteristic quantity for a porous solid. Assuming a characteristic area per single molecule adsorbed on the surface of a solid – for N₂ at 77 K this area is 0.162 nm², for Kr at 87 K it is 0.152 nm² [2.2, p. 173] – the surface area of the solid can be calculated and from this the porous solid can be “characterized”. Actually, many

different types of instruments, normally operating around or below ambient pressure, have been designed for this purpose including static, gas flow and differential gas flow instruments. An overview is given in [2.2]; a list of commercial suppliers which in no way is meant to be exclusive or complete is given in Table 2.1 below, cp. also [2.3, 2.4, 3.7].

Table 2.1 Manufacturer of volumetric and carrier gas sorption measuring instruments and of gas pycnometers.

Manufacturer	A	P	C	D
Beckman Coulter UK Ltd., Oakley Court, Kingsmead Business Park, London Rd. High Wycombe Bucks. HP11 1JU, U.K. (including Omicron), Tel.: +44-149444-1181, Fax: -7558 beckmancoulter_uk@beckman.com, www.beckmancoulter.com	•	•	•	•
Thermo Finnigan, Thermoquest Italia, Strada Rivoltana, s.n., I-20090 Rodano, Milano, Italy, Tel.: +39-02950592-66, Fax: -56, woodwardc@finnigan.co.uk, www.thermo.com, www.porotec.de, info@porotec.de	•	•	•	•
Jouan Robotics - Gira, Rue des Bruyères, Z.I. Berlanne, F - 64160 Morlaas, France, Tel: +33-559-308-38-3, Fax: -4, g.chancel@gira-france.com, www.gira.fr	•	•	•	
Micromeritics, 1 Micromeritics Drive, Norcross, GA 30093-1877, USA, Tel.: +1-770-662-36-60, Fax: -96 international@micromeritics.com, www.micromeritics.com	•	•	•	•
Porous Materials, Inc., Cornell University Research and Technology Park, 83 Brown Road, Bldg. 4, Ithaca, NY 14850, USA, Tel.: +1-607-257-554, Fax: -5639, www.pmiapp.com, info@pmiapp.com	•	•	•	•
Quantachrome Corp., 1900 Corporate Drive, Boynton Beach, Florida 33426 USA, Tel.: +1-561-731-4999 Fax: -732-9888, www.quantachrome.com, webmaster@quantachrome.com	•	•	•	•
Zeton Altamira, 149 Delta drive, Suite 200 Pittsburgh, PA 15238, USA Tel: +1-412-9636-385, Fax: -485, www.zetonaltamira.com, altamira@compuserve.com	•			

A = specific surface area, P = pore size distribution, C = chemisorption,
D = density

As we here are mainly interested in adsorption measurement techniques for industrial purposes, i. e. at elevated pressures (and temperatures), we restrict this chapter to volumetric instruments which on principle can do this for pure sorptive gases ($N = 1$), Sect. 2. Thermovolumetric measurements, i. e. volumetric/manometric measurements at high temperatures (300 K - 700 K) are considered in Sect. 3. In Section 4 volumetric-chromatographic measurements for multi-component gases ($N > 1$), are considered as mixture gas adsorption is becoming more and more important for a growing number of industrial gas separation processes. In Section 5 we discuss combined volumetric-calorimetric measurements performed in a gas sensor calorimeter (GSC). Finally pros and cons of volumetry/manometry will be discussed in Sect. 6, and a list of symbols, Sect. 7, and references will be given at the end of the chapter.

2. VOLUMETRIC MEASUREMENT OF PURE GAS ADSORPTION EQUILIBRIA ($N = 1$)

2.1 Experimental

An instrument for volumetric measurements of pure gas adsorption basically consists of a gas storage vessel (volume V_{SV}) and an adsorption chamber (V_{AC}) being connected by a tube bearing a valve. Both vessels should completely be placed within a thermostat (water, oil, air etc.) and provided with tubes for gas supply and evacuation as well as with thermometers and manometers to measure the temperature (T) and pressure (p) inside the vessels, cp. Figure 2.1.

For pressures above ambient all vessels and tubes should be manufactured of stainless steel, inside surfaces should be electropolished or, preferably gilded. For pressures below ambient, i. e. vacuum systems glass should be preferred. Sealing materials should be chosen according to the sorptive gases to be used and the ranges of temperature and pressure of operation. For corrosive gases and high pressures the use of metallic sealings (silver, steel) always is recommended. The adsorption chamber includes a sample of sorbent material of mass (m^s), which prior to measurement should have been “activated” at higher temperature and in vacuum for several hours to reduce the amount of pre-adsorbed molecules. Standard procedures for activation have been described in [2.2, 2.5 – 2.7].

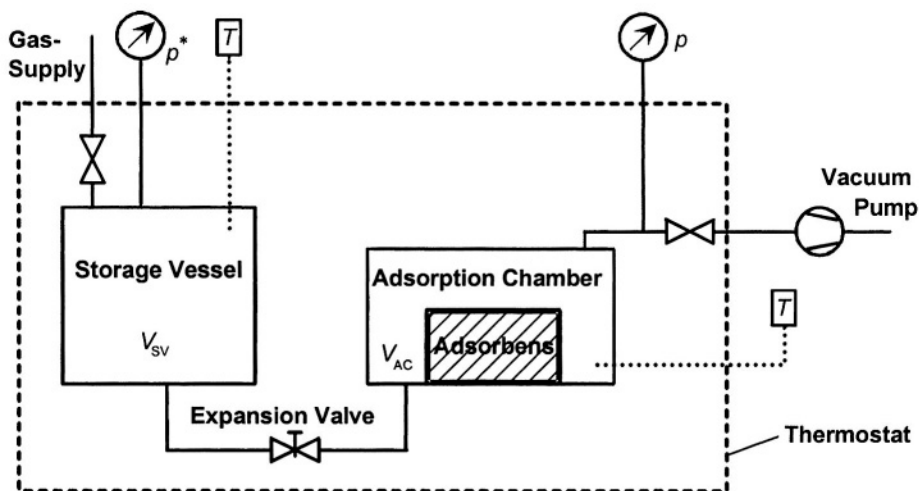


Figure 2.1. Experimental setup for (static) volumetric measurements of pure gas adsorption equilibria.

To measure adsorption a certain amount of gas of mass (m^*) is prepared in the storage vessel and the adsorption chamber is evacuated. Upon opening the expansion valve, the gas expands to the adsorption chamber where it is partly adsorbed on the (external and internal) surface of the sorbent material. This process may last milliseconds, minutes, hours or even several days – as in case of helium on activated carbon (Norit R1) [2.8]. After thermodynamic equilibrium, i. e. constancy of pressure (p) and temperature (T) inside the vessels has been realized, these data can be taken as a basis to calculate the mass of the gas adsorbed on the sorbent (m^S). That is, volumetric adsorption experiments mainly result in pressure measurements. Hence the name “Manometry” for this method should be used [2.2].

2.2 Theory

To determine the mass (m^a) adsorbed in a volumetric experiment we consider the mass balance of the sorptive gas:

$$m^* = m^f + m^a \quad 2.1$$

Here $m^* = m^*(p^*, T, V_{sv})$ is the mass of gas initially prepared in the storage vessel, m^f is the mass of the sorptive gas in the adsorption equilibrium state considered. It also can be calculated from its thermal equation of state (EOS)

$$pV^f = \frac{m^f}{M}RTZ(p, T) \quad 2.2$$

In this equation M is the molar mass of the sorptive gas, $R = 8.314 \text{ J/molK}$ the universal gas constant and $Z = Z(p, T)$ the compressibility factor or real gas factor of the gas which can be determined from p , V , T -measurements. Analytic expressions for Z are given for example in [2.9, 2.10], numerical values for a variety of technical gases over a considerable range of pressure and temperature can be found in [2.11 – 2.15]. For an ideal gas we have $Z = 1$ for any value of p , T . The volume (V^f) of the sorptive gas in Eq. (2.2) can be calculated from the relation

$$V^f = V_{SV} + V_{AC} - V^{as} \quad 2.3$$

where V^{as} indicates the so-called void volume of the sorbent material and the sorbate phase which can not be penetrated by the sorptive's gas molecules. Equations (2.1-2.3) can be combined to present the result of volumetric measurements:

$$\Omega_V = m^a - \rho^f V^{as} \quad 2.4$$

Here Ω_V has been introduced as an abbreviation being defined by

$$\Omega_V \equiv m^* - \rho^f(V_{SV} + V_{AC}) \quad 2.5$$

with the sorptive gas density, cp. (2.2),

$$\rho^f = \frac{m^f}{V^f} = \frac{pM}{RTZ(p, T)} \quad 2.6$$

It should be emphasized that the auxiliary quantity (Ω_V) only includes measurable quantities. Hence its numerical value is known from the gas expansion experiment. According to Eq. (2.4), Ω_V can be called “reduced mass” of the adsorbed phase as it is the difference between the mass of the adsorbed phase (m^a) and the mass of the sorptive gas that would be included in the void volume of both the sorbent and the sorbate phase (V^{as}) [2.3, 2.7]. As this quantity also is unknown, some model assumptions for it have to be introduced to calculate the adsorbed mass (m^a) from Eq. (2.4).

As outlined in Chapter 1, V^{as} is often approximated by the so-called helium volume,

$$V^{as} \cong V_{He}^s \quad 2.7$$

that is the volume of the sorbent without that of the sorbate phase as “seen” by helium molecules which are assumed not to be adsorbed at all on the surface of the sorbent. Indeed under these conditions V_{He}^s can be determined from volumetric experiments performed with helium – preferably at room temperature or even at higher temperatures – leading via (2.1 - 2.3) with $m_{He}^a = 0$ to

$$V_{He}^s = V_{sv} + V_{AC} - V_{He}^f, \quad 2.3a$$

with

$$V_{He}^f = \frac{m_{He}^*}{p_{He} M_{He}} RT Z_{He}(p_{He}, T) \quad 2.2a$$

Here V_{He}^f is the volume of the helium gas of mass m_{He}^* at pressure p_{He} , temperature T and Z_{He} is the compressibility or real gas factor of helium [2.11, 2.12]. In view of the approximation (2.7), the sorbate mass m^a in Eq. (2.4) is the Gibbs surface excess mass (GSE) (m_{GE}^a) cp. Chap. 1. Inserting Eqs. (2.5 - 2.7) in (2.4) this mass can be represented as

$$m_{GE}^a = m^* - \frac{pM}{RTZ(p, T)} (V_{sv} + V_{AC} - V_{He}^s) \quad 2.8$$

If the void volume (V^{as}) in (2.4) is approximated by

$$V^{as} = V_{He}^s + \frac{m^a}{\rho_0^L}, \quad 2.9$$

cp. Chapter 1, m^a in Eq. (2.4) is the absolute or total mass adsorbed which equivalently to (2.8) via Eqs. (2.4 – 2.5, 2.8, 2.9) can be represented as

$$m^a = \frac{m_{GE}^a}{1 - (\rho^f / \rho_0^L)} \quad 2.10$$

with m_{GE}^a as given by (2.8) and ρ^f by (2.6).

It should be noted that for $\rho^f \rightarrow 0$, $m^a \cong m_{GE}^a$, and for $\rho^f \rightarrow \rho_0^L$, $m^a \rightarrow \infty$, which reflects the occurrence of a liquid phase outside the sorbent material, i. e. a vapor-liquid-state of the sorptive fluid.

Auxiliary remarks:

1. The quantity m^a in Eq. (2.1) on principle also includes the mass of gas adsorbed on the walls of the adsorption chamber and possibly desorbed from the walls of the storage vessel upon gas expansion (Δm_{wall}^a). These quantities should be determined by calibration experiments without using a sorbent sample, i. e. $m^s = 0$, cp. Chapter 4. If the surface of the walls of the adsorption chamber and the storage vessel is small compared to the BET surface of the sorbent sample, one may assume $(\Delta m_{wall}^a) \ll m^a$, i. e. neglect (Δm_{wall}^a) compared to (m^a) .
2. The volumes V_{AC} , V_{SV} should be determined experimentally by using a sample, preferably a cylinder of calibrated volume (V_0) made of dense material (Ti, Au) and performing gas expansion experiments as described above. The amount of gas adsorbed on the surface of the sample normally can be neglected.**
3. Waiting times for thermodynamic equilibrium in the gas adsorption system are based on experimental experience which comes from gravimetric measurements, cp. Chap. 3. No general rules for these times are available today.

2.3 Uncertainties or Errors of Measurements

An important part of any kind of experimental work is to consider errors or uncertainties of measurements [2.16 – 2.18]. To keep these down, it is always recommended to repeat measurements of any experimental quantity at

** Suppose the sample (V_0) is placed in the adsorption chamber and a certain amount of nearly not adsorbing gas (He, Ar at $\simeq 300$ K) has been prepared at pressure (p^*) in the storage vessel (V_{SV}). If after expansion to the adsorption chamber the gas is at pressure (p), the volume V_{AC} can be calculated via Eq. (2.2) by

$$V_{AC} = \left(\frac{p^* Z(T, p)}{p Z(T, p^*)} - 1 \right) V_{SV} + V_0 \quad (2.11)$$

least three times to guarantee reproducibility of data and reduce the uncertainty by a factor (1 / 3). To be more explicit let us consider briefly an arbitrary quantity (x) which has been measured $N \geq 3$ times, the result of the i -th measurement being

$$x_i \pm \Delta x_i \quad 2.12$$

with the uncertainty or error $\Delta x_i > 0$. Then the statistical mean value of all measurements

$$\bar{x} = \frac{1}{N} \sum_{i=1}^N x_i \quad 2.13$$

has, according to Gauss' law of propagation of error a dispersion (or variance or mean square deviation, MSD) of

$$\sigma^2(\bar{x}) = \sum_{i=1}^N \left(\frac{\partial \bar{x}}{\partial x_i} \right)^2 (\Delta x_i)^2 = \frac{1}{N} (\Delta x)^2 \quad 2.14$$

We consider this quantity as uncertainty of the representative value \bar{x} of the quantity x . In (2.14) it has been assumed that the uncertainties of all single measurements are equal ($\Delta x_i \equiv \Delta x$, $i = 1 \dots N$), and that measurements themselves are statistically independent [2.16].

In view of space limitations we here consider only the uncertainty of the Gibbs surface excess mass adsorbed according to Eq. (2.8). The Gauss law of error propagation immediately leads to the expressions

$$\sigma_{mGE}^2 = \sigma_{m*}^2 + \sigma_{mf}^2 \quad 2.15$$

$$\begin{aligned} \sigma_{mf}^2 = & \left(1 - \frac{p}{Z} \left(\frac{\partial Z}{\partial p} \right)_T \right)^2 \left(\frac{M}{RTZ} \right)^2 (V_{SV} + V_{AC} - V_{He}^s)^2 \sigma_p^2 \\ & + \left(1 + \frac{T}{Z} \left(\frac{\partial Z}{\partial T} \right)_p \right)^2 \left(\frac{pM}{T^2 RZ} \right)^2 (V_{SV} + V_{AC} - V_{He})^2 \sigma_T^2 \\ & + \left(\frac{pM}{RTZ} \right)^2 (\sigma_{VSV}^2 + \sigma_{VAC}^2 + \sigma_{sHe}^2), \end{aligned} \quad 2.16f$$

$$\begin{aligned} \sigma_{m^*}^2 = & \left(1 - \frac{p^*}{Z^*} \left(\frac{\partial Z^*}{\partial p^*}\right)_T\right)^2 \left(\frac{V_{SV} M}{RTZ^*}\right)^2 \sigma_{p^*}^2 + \\ & + \left(1 + \frac{T}{Z^*} \left(\frac{\partial Z^*}{\partial T}\right)_{p^*}\right)^2 \cdot \frac{\sigma_T^2}{(T^2 Z^*)^2} + \left(\frac{p^* M}{RTZ^*}\right)^2 \sigma_{VSV}^2 \end{aligned} \quad 2.16^*$$

Analysis of numerical data shows that measurements of pressures (p , p^*), i. e. values of $(\sigma_p^2, \sigma_{p^*}^2)$ are the most crucial for accurate measurements of m_{GE}^a followed of course by temperature measurements (σ_T^2) and those for basic data of the equipment ($\sigma_{VSV}^2, \sigma_{VAC}^2$) and of the sorbing material (σ_{stHe}^2). To achieve useful results, i. e. $(\sigma_{mGE} / m_{GE}^a) < 5\%$, limiting values of variances should hold as follows [2.7]: $\sigma_p < 10^{-4} p, \sigma_T < 10^{-3} T$, $\sigma_{VSV} \approx \sigma_{VAC} < 10^{-6} (V_{SV} + V_{AC})$.

2.4 Example

In Figure 2.2 equilibrium adsorption data for carbon dioxide (CO_2) on zeolite Na 13X (Linde, UOP) are presented for temperatures 298 K and 303 K. The mol numbers of the Gibbs surface excess amounts per unit mass of sorbent are depicted as function of the sorptive gas pressure and temperature. Relative uncertainties of measurements are about $(\sigma_{mGE} / m_{GE}^a) \leq 2\%$. The subcritical isotherms are in the range of pressure measured of Type I – IUPAC classification [2.20].

However, the adsorption isotherms exhibit Type II structure if the saturation pressure ($p_0(T)$) is approached, cp. Chapter 3. Prior to adsorption, the zeolite has been “activated” at 623 K for 3 hours under vacuum conditions ($p < 15$ Pa). Some characteristic data of the zeolite also have been measured in our laboratory [2.19], namely the BET surface at 77 K being $577 \text{ m}^2 / \text{g}$ (UOP-date: $572.5 \text{ m}^2 / \text{g}$), the total pore volume being $420 \text{ cm}^3 / \text{kg}$, the He-expansion density being $2.51 \text{ g} / \text{cm}^3$.

Equilibration times varied from 15 minutes at low pressures up to (nearly) 1 hour at the higher pressures considered, i. e. $p \approx 0,03 p_0(T)$. This information was gained from time dependent temperature signals produced by the sorbent sample and gained simultaneously with adsorption equilibria measurements [2.23], cp. Sect. 5.

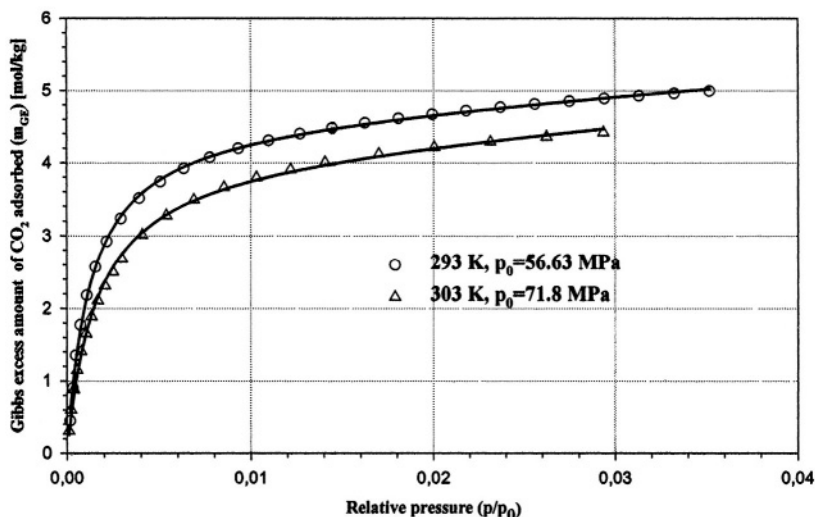


Figure 2.2. Adsorption equilibria of CO_2 on zeolite Na13X (Linde, UOP) at 293 K and 303 K for pressures up to 0.2 MPa. Lines indicate correlation of data by a generalized Langmuir type adsorption isotherm, cp. Chap. 7.

3. THERMOVOLUMETRY

Sorption of gases in highly porous and thermally stable materials like zeolites at high temperatures are becoming important in view of an increasing number of technical applications with considerable economic potential. Two examples of these are

- i) Sorption enhanced chemical reactions [2.21]
- ii) Volumetric receivers of solar radiation in solar-thermal energy converters [2.22].

In view of some inherent problems of traditional thermogravimetric measurements, cp. Chapter 3, it seems to be worthwhile to consider also volumetric / manometric measurements of gas adsorption equilibria at higher temperatures ($T > 400$ K). An instrument of this type has been designed and built in the labs of the authors, the scheme of it being presented in Figure 2.3. A photo showing mainly the high temperature thermostat and auxiliary equipment is given below.

Adsorption and desorption experiments of nitrogen (N_2 (5.0)) on zeolite KE-H 555 (UOP) have been performed in the temperature range

$293\text{ K} < T < 673\text{ K}$ and for pressures up to 5.5 MPa. Data are given in Figure 2.5 that show clearly that nitrogen is adsorbed even at high temperatures.

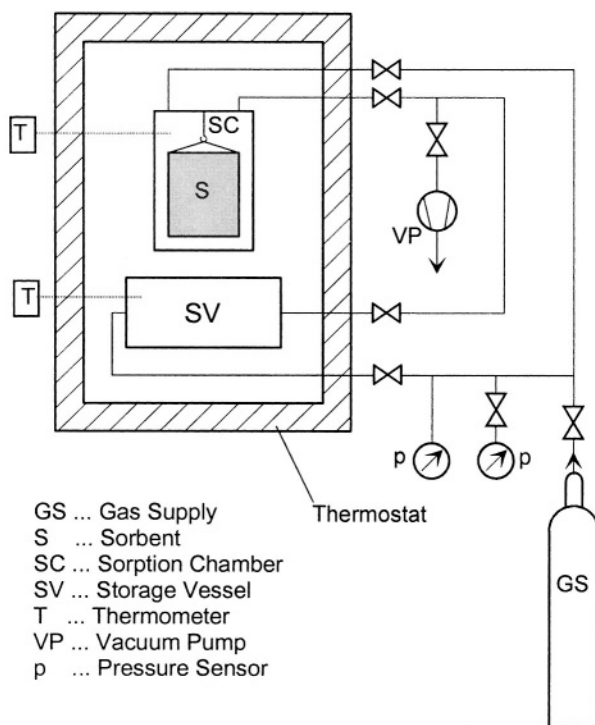


Figure 2.3.
Experimental set-up for
volumetric high temperature
adsorption / desorption
experiments.

In calculating the adsorbed masses of nitrogen, the thermal expansion of the storage and of the adsorption vessel at higher temperatures must be taken into account. Also slight changes in the so-called helium-volume of the zeolite (V_{He}^s) depending also on temperature should be considered.

No coadsorption measurements at high temperatures using the volumetric / manometric method seem to have been performed yet. Some experiments with humid nitrogen, i. e. $\text{N}_2 / \text{H}_2\text{O}$ mixtures are presently (2003) under way at the author's institute. Data will be reported in the homepage of IFT, cp. [4.15].

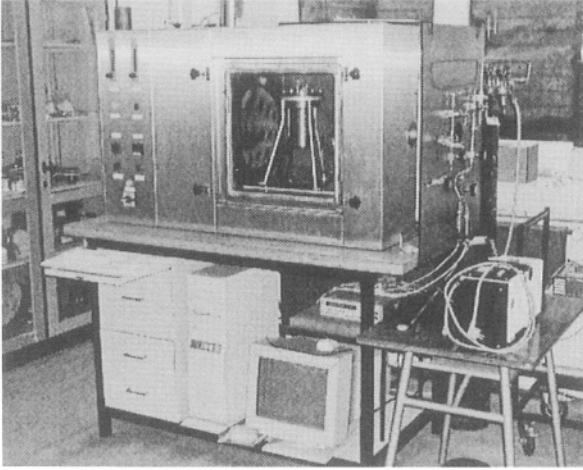


Figure 2.4.
Volumetric high
temperature sorption
system
($293\text{ K} < T < 673\text{ K}$,
 $p < 10\text{ MPa}$)
© IFT, University
of Siegen, 2000.

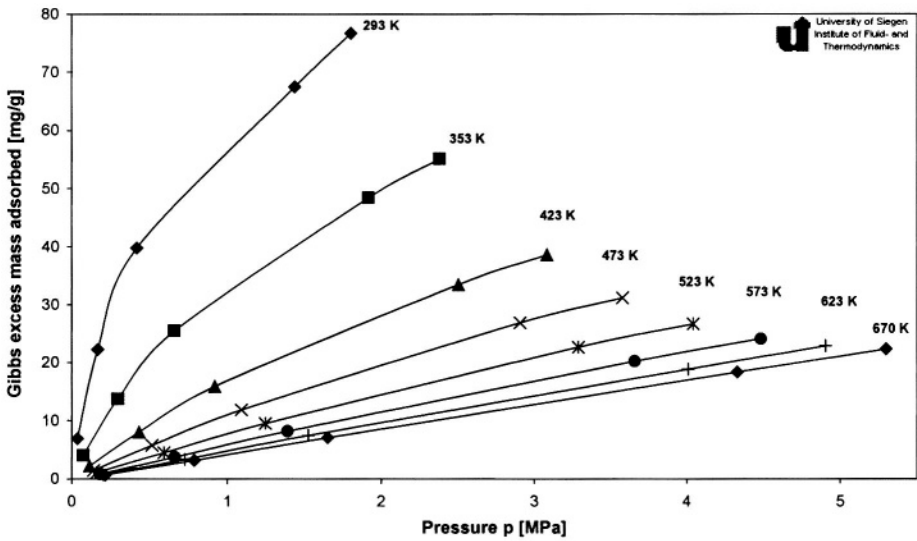


Figure 2.5. Adsorption isotherms of N_2 on zeolite KE-H 555 (UOP) at different temperatures ($293\text{ K} - 673\text{ K}$); helium volume $V_{\text{He}}^s = 0.45\text{ cm}^3/\text{g}$.

4. VOLUMETRIC MEASUREMENT OF MULTICOMPONENT GAS ADSORPTION EQUILIBRIA ($N > 1$)

4.1 Experimental

Coadsorption equilibria of multi-component gases on porous materials today most often are measured by using volumetric / manometric instruments. The flow diagram of such a device is sketched in Fig. 2.6. It basically has the same structure as the instrument for pure gas adsorption measurements, Fig. 2.1. However, one now has to provide a gas circulation loop including a pump between the storage vessel and the adsorption chamber in order to maintain equal and constant sorptive gas concentrations everywhere in the system. Also a sample loop has to be added which may be outside the thermostat but in any case has to be connected to a gas chromatograph or mass spectrometer. No commercial suppliers of volumetric multi-component gas adsorption instruments are known to the authors, cp. [2.3, 2.4]. However, an instrument which easily can be used as such, after having been equipped with a standard gas chromatograph, is offered by BEL Japan, cp. Chapter 4. Materials of vessels and tubes should be chosen according to the recommendations given in Section 2.1. For the analysis of a sorptive gas sample in a gas chromatograph, helium at elevated temperatures (373 K – 473 K) should be used as a carrier gas. More information for design of a multicomponent volumetric gas adsorption instrument is given in [2.20].

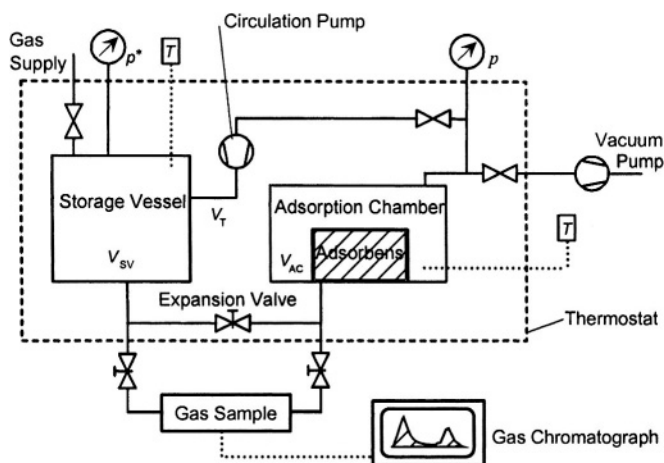


Figure 2.6. Experimental set-up for (static) volumetric / manometric measurements of multicomponent gas adsorption equilibria.

4.2 Theory

Let us assume a certain amount of gas mixture with known mass concentrations w_i^* , and molar concentrations y_i^* , $i = 1 \dots N$ is in the storage vessel (V_{sv}) of the instrument, Fig. 2.6. The adsorption chamber (V_{ac}) including the sorbent mass (m^s) has been evacuated. Upon opening the valve connecting both vessels, adsorption occurs. Recirculating the gas in the system will enhance equilibrium between the gas and the sorbate phase. If this is attained, a gas sample may be taken to determine its molar concentrations (y_i^f , $i = 1 \dots N$). From this information the masses (m_i^a) of components $i = 1 \dots N$ of the adsorbate can be determined as follows: First we note the mass balances of all components

$$m_i^* = m_i^a + m_i^f, \quad i = 1 \dots N \quad 2.20$$

Here m_i^* is the mass of component i of the sorptive gas filled to the storage vessel (V_{sv}). It can be calculated from the relation

$$m_i^* = \rho_i^* V_{sv} = M_i y_i^* n^*, \quad i = 1 \dots N \quad 2.21$$

with the total number of mols (n^*) of the gas originally supplied being given by the thermal equation of state (EOS)

$$n^* = \sum_i \frac{m_i^*}{M_i} = \frac{p^* V_{sv}}{RTZ^*} \quad 2.22$$

Here

$$Z^* = Z(p^*, T, y_1^* \dots y_n^*) \quad 2.23$$

is the compressibility or real gas factor of the gas mixture. Its numerical value can be calculated from an analytical EOS, [2.9-2.25] measured values from pressure (p^*) and Temperature (T) and known molar concentrations ($y_1^* \dots y_N^*$) of the gas.

Similarly to (2.21-2.23) we have for the mass of component i in the sorptive gas

$$m_i^f = \rho_i^f V^f = M_i y_i^f n^f, \quad i = 1 \dots N \quad 2.24$$

with the total mol number (n^f) again being obtained from the EOS

$$n^f = \sum_i^N \frac{m_i^f}{M_i} = \frac{p V^f}{RT Z^f} \quad 2.25$$

including the compressibility factor

$$Z^f = Z(p, T, y_1^f \dots y_N^f) \quad 2.26$$

Inserting Eqs. (2.21-2.25) into the mass balance (2.20) and taking Eq. (2.3) into account we get the equations

$$\Omega_{Vi} = m_i^a - \rho_i^f V^{as}, \quad i = 1 \dots N \quad 2.27$$

with

$$\Omega_{Vi} \equiv m_i^* - \rho_i^f (V_{SV} + V_{AC}), \quad i = 1 \dots N \quad 2.28$$

being the “reduced mass” of component i in the sorbate phase, a quantity which according to its definition (2.28) can be calculated from measured experimental parameters of the adsorption system. In order to calculate (m_i^a) from (2.27) we must introduce an approximate value for (V^{as}). Choosing again the helium volume approximation (2.7), the adsorbed mass indeed is the Gibbs surface excess mass of component (i), cp. Chap. 1, for which we get from (2.27)

$$m_{iGE}^a = \Omega_{Vi} + \rho^f V_{He}^S \quad 2.29$$

or in view of (2.28, 2.21, 2.24),

$$m_{iGE}^a = \frac{M_i}{RT} \left(\frac{y_i^* p^* V_{SV}}{Z^*} - \frac{y_i^f p}{Z} (V_{SV} + V_{AC} - V_{He}^S) \right), \quad i = 1 \dots N \quad 2.30$$

Choosing for (V^{as}) in (2.27) instead of (2.7) the approximation (2.9) we get for the absolute adsorbed masses (m_i^a) of components $i = 1 \dots N$ in view of (2.21-2.25, 2.30), the relations

$$\sum_{k=1}^N (\delta_{ik} - y_i^f \frac{M_i p}{\rho_0^L RTZ}) m_k^a = m_{iGE}^a, \quad i = 1 \dots N \quad 2.31$$

This is a system of N linear equations from which the absolute adsorbed masses (m_k^a) of all components $k = 1 \dots N$ can be calculated. The symbol $\delta_{ik} = 0$ for $i \neq k$ and $\delta_{ii} = 1$ for $i = 1 \dots N$ is the Kronecker Symbol. For the reference density of the adsorbed phase an approximate value

$$\frac{1}{\rho_0^L} = \sum_{i=1}^N \frac{w_i^a}{\rho_{0i}^L} \quad 2.32$$

with – according to experience – roughly estimated values of the expected concentrations w_i^a is used. Of course results can be improved by iteration, i. e. using numerical solutions of (2.31) to get a new approximation for (2.32) etc.

From either the set (m_{iGE}^a), (2.30) or (m_k^a), (2.31) the concentrations of masses in the adsorbed phase $w_i^a = m_i^a / (\sum_k^N m_k^a)$, $i = 1 \dots N$ and of mole numbers $x_i^a = M_i m_i^a / (\sum_{k=1}^N M_k m_k^a)$, $i = 1 \dots N$ can be calculated. Hence the *selectivities* of any two components i, k of the gas-adsorption-system

$$S_{ik} = \frac{x_i^a / y_i^f}{x_k^a / y_k^f}, \quad i, k = 1 \dots N \quad 2.33$$

can be determined. These are key quantities for adsorption separation processes.

4.3 Uncertainties or Errors of Measurements

We restrict this discussion to dispersions or mean square deviations (MSD) (σ_{miGE}^2) of the Gibbs excess masses of component $i = 1 \dots N$ of a multicomponent adsorbate as given by Eqs. (2.30). Applying the Gauss law of propagation of error or uncertainty we have in view of (2.28), (2.24), (2.27):

$$\sigma_{miGE}^2 = \sigma_{i*}^2 + \sigma_{if}^2, \quad 2.34$$

$$\sigma_{i*}^2 = M_i^2 [n^* \sigma_{yi*}^2 + y_i^{*2} (\frac{\sigma_{m*}^2}{M^{*2}} + (\frac{m^*}{M^{*2}})^2 \sum_{i=1}^N M_i^2 \sigma_{yi*}^2)] \quad 2.34a$$

$$\sigma_{if}^2 = M_i^2 [n^{f2} \sigma_{yif}^2 + y_i^{f2} (\frac{\sigma_{mf}^2}{M^{f2}} + (\frac{m^f}{M^{f2}})^2 \sum_{i=1}^N M_i^2 \sigma_{yif}^2)] \quad 2.34b$$

Here $n^* = m^* / M^*$ with $M^* = \sum_i y_i^* M_i$ is the mol number of the gas in the storage vessel prior to adsorption, likewise $n^f = m^f / M^f$ with $M^f = \sum_i y_i M_i$ is the mol number of the sorptive gas after equilibration. The dispersions σ_{yi*} , σ_{yif} refer to concentrations in the gas prior (y_i^*) and after adsorption (y_i^f). Approximate values of the dispersions σ_{yi*} , σ_{yif} referring to the total masses of the sorptive gas prior (m^*) and after adsorption are (m^f) given by Eqs. (2.16*) and (2.16f) respectively. Formulae (2.33, 2.34 a, b) clearly show the profound influence of the dispersions σ_{yi*} , σ_{yif} of sorptive's gas molar concentrations y_i^* , y_i^f respectively. Measurements of these should be performed with meticulous care in order to get useful values of the masses (m_{iGE}^a) of the adsorbate components. In practice, concentration measurements (by GC or MS) should maintain uncertainties of $\sigma_{yi*} \approx \sigma_{yif} < 10^{-2}$. Provided uncertainties of all the other measured quantities are of the orders of magnitude given at the end of Sect. 2.3, one may expect relative uncertainties for binary ($N = 2$) mixture measurements of about $(\sigma_{iGE} / m_{iGE}^a) \leq 2\%$, and for ternary ($N = 3$) mixture measurements of $(\sigma_{iGE} / m_{iGE}^a) \leq 5\%$.

4.4 Example

In this section we present data for the coadsorption equilibria of CH_4 / N_2 gas mixtures on activated carbon (AC) Norit R 1 Extra taken at $T = 298$ K and total gas pressure $p = 0.3$ MPa. Measurements were performed using the volumetric – gas chromatographic method described above ($N = 2$). Standard activation procedures of the AC were applied, namely vacuum (10 Pa) at 400 K for 4 hours, then cooling down to ambient temperature under vacuum within 12 hours. First the system was investigated by M. Tomalla at the author's institution in 1993, [2.20]. Measurements were repeated using the same method by St. Dohrmann in the labs of O. Talu, Cleveland State University, Cleveland, USA in 1997. Results of both measurements are shown in Figures 2.7 and 2.8 below. Figure 2.7 shows the partial molar Gibbs surface

excess amounts of CH_4 and N_2 respectively being adsorbed on the AC at constant temperature (298 K) and pressure (0,3 MPa) but at varying molar concentration of methane (y_{CH_4}) in the gas phase. Data show that for an equal molar gas mixture ($y_{\text{CH}_4} = y_{\text{N}_2} = 0,5$) nearly three times as much methane than nitrogen is adsorbed ($S_{\text{CH}_4, \text{N}_2} \cong 3$). The dark full circles represent data taken at Cleveland. The open symbols indicate data taken 4 years earlier at Siegen. Differences between the data basically are due to the fact that AC is not a very stable material and the sample used may have changed somewhat over the period of 4 years. Also slightly different activation procedures may have been applied. In Figure 2.8 the corresponding Mc Cabe – Thiele diagram of the equilibria data is presented. Here the data seem to be nearly identical, thus proving experimental consistency.

Today there is a considerable amount of binary and also of some ternary coadsorption data of technical gas mixtures on a variety of sorbens materials available in the literature. The interested reader is referred to Journals like “Adsorption”, “Adsorption, Science & Technology”, “Langmuir” etc.

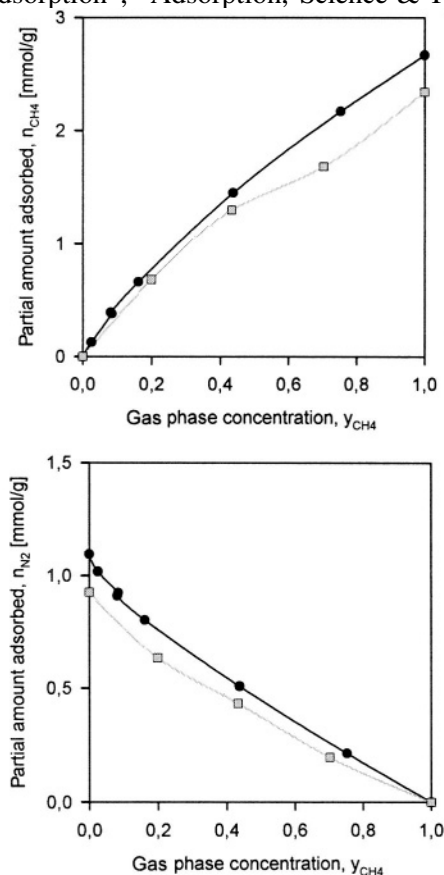


Figure 2.7.

Coadsorption equilibria of CH_4 / N_2 gas mixtures of AC Norit R1 Extra at 298 K, 0.3 MPa. The data indicate partial molar Gibbs excess amounts of CH_4 (upper figure) and N_2 (lower figure) and their dependence on the sorptive gas concentration (y_{CH_4}).

Comparison of Measurements:

- Cleveland State University, Cleveland 1997
- University of Siegen, Siegen 1993

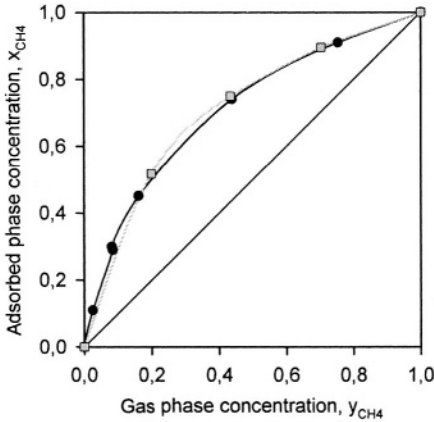


Figure 2.8.

Mc Cabe – Thiele diagram of coadsorption equilibria of CH_4 / N_2 gas mixtures on AC Noit R1 at 298 K, 0.3 MPa. Full circles (●) indicate data taken at Cleveland in 1997, shaded symbols (■) refer to measurements done at Siegen in 1993, [2.20].

5. VOLUMETRIC – CALORIMETRIC MEASUREMENTS THE SENSOR GAS CALORIMETER (SGC)

Assuming the adsorbed phase to be a thermodynamic system in the sense of W. Schottky [2.24], cp. Chap. 1, we can assign it an (integral) enthalpy (H^a) which can be considered as function of either the sorptive gas pressure (p) and temperature (T) or to depend on the mass of the adsorbate (m^a), its temperature (T) and the mass of the sorbent (m^s), i. e.

$$H^a = H^a(p, T, m^s) = H^a(m^a, T, m^s) \quad 2.35$$

This is an important quantity likewise for single and for multi-component adsorbates which characterizes the energetic state of the adsorbed molecules. It normally is determined by measuring the difference (ΔH) between the enthalpies of the mass (m^a) in the gaseous state (H^f) and the adsorbed state (H^a), i.e. the so-called adsorption enthalpy

$$\Delta H = H^a(m^a, T, m^s) - H^f(p, T, m^a) < 0 \quad 2.36$$

Today there are many experimental techniques and instruments at hand to perform measurements of this type both for characterization of the sorbent material, cp. for example [2.25], but also for industrial purposes [2.26]. A good overview of adsorption calorimetric measurement methods is given in [2.2].

On principle calorimetric data of adsorbed phases can be calculated from adsorption equilibria data, i. e. adsorption isotherms, if these are available for different temperatures. From the Clausius-Clapeyron equation applied to the phase equilibrium in the ideal sorptive gas (f) – adsorbate (a) system, one can derive an equation for the isosteric differential adsorption enthalpy or isosteric differential heat of adsorption [2.2, p. 43], [2.26, p. 38]

$$h^a(m^a, T, m^s) = R \left(\frac{\partial \ln(p/p_0)}{\partial (1/T)} \right)_{m^a} < 0 \quad 2.37$$

which here has been assumed to be independent of temperature, cp. Chap. 7, Fig. 7.1. This quantity is related to the enthalpy (H^a) of the adsorbate by

$$h^a = \left(\frac{\partial H^a(m^a, T, m^s)}{\partial m^a} \right)_{T, m^s}, \quad 2.38$$

i. e. we have

$$H^a = \int_0^{m^a} h^a(m^a, T, m^s) dm^a \quad 2.39$$

In practical applications of Eq. (2.37) the r.h.s. differential quotient has to be approximated by a difference quotient, i. e.

$$\begin{aligned} \frac{\partial \ln(p/p_0)}{\partial (1/T)} &\cong \frac{\ln(p_2/p_0) - \ln(p_1/p_0)}{(1/T_2) - (1/T_1)} \\ &= \frac{\ln(p_2/p_1)}{T_1 - T_2} T_1 T_2 \end{aligned} \quad 2.40$$

This may cause considerable deviations of numerical values for (h^a) calculated in this way via (2.37) from measured data of (h^a) or (H^a), which may add up to a 100 % or even more [2.23]. Hence it always is recommended to measure integral adsorption enthalpies (H^a) or integral heats of adsorption (ΔH), (2.36) and to determine the differential heats of adsorption (h^a) by differentiating analytic expressions for $H^a = H^a(m^a, T, m^s)$ to the mass adsorbed, cp. (2.38).

In order to measure simultaneously the mass and the enthalpy of an adsorbed phase, the adsorption vessel in the volumetric instrument, Fig. 2.1, has to be replaced by a calorimeter vessel. Traditionally this vessel is

provided with a large number of thermocouples allowing to measure changes in temperature due to transfer processes of the heat of adsorption flowing from the sorbent/sorbate system to the (isothermal) heat bath covering the sorption system. We here are not going to present this technique in detail as this has been done in literature several times, [2.2], [2.25], [2.27], [2.28] and the literature cited therein. Instead we would like to describe a new type of calorimeter avoiding thermocouples but using instead an inert gas as sensor medium. Hence, we will call it in what follows a sensor gas calorimeter (SGC). In Sect. 5.1 the basic experimental information is provided. The theory of the instrument is outlined in Sect. 5.2 followed by examples of calibration measurements. Examples of simultaneous mass and heat of adsorption measurements are presented in Sect. 5.3. These are compared to results of analytical calculations of the heat of adsorption via Eq. (2.37) and discussed to a certain extent.

5.1 Experimental

In 1994, W. Langer proposed to use a newly designed calorimeter for simultaneous measurements of heats and isotherms of gas adsorption or desorption processes [2.29]. This instrument may be called a sensor gas calorimeter (SGC), as the heat flowing during a gas adsorption process from the sorbent/sorbate system to the sorptive gas will then pass a gas jacket surrounding the adsorption vessel. This gas, normally He or N₂, acts as a sensor. The heat flux introduced changes its temperature and, as the gas volume is constant, also its pressure. Actually, the time-dependent pressure signal can be correlated with the heat flux passing the sensor gas and after integration over time gives a measure of the total heat of adsorption released from the adsorption vessel to the thermostat. A schematics of the instrument is given in Fig. 2.9, followed by a photo of the instrument as designed and built by W. Zimmermann in Lab PB-A 320, IFT, University of Siegen [2.23].

The sensor gas calorimeter (SGC) basically consists of a classical volumetric gas adsorption device complemented by two gas thermometers (cp. Fig. 2.9). The core of the instrument is an adsorption vessel which is placed within a second vessel, the sensor gas jacket. This jacket vessel is filled with gas at pressure (p_{SG}) acting as a sensor via a capillary (1) connecting the vessel with a difference manometer (P3). Additionally, a reference vessel also filled with the (same) sensor gas at pressure (p_{RG}) is placed in the thermostat and connected via capillary (2) to the manometer (P3). Upon opening the valves (V7, V7A) the pressures (p_{SG} , p_{RG}) of the sensor gases in the jacket vessel and the reference vessel are equalized, i. e. we have $p_{SG} = p_{RG}$. Thermal equilibrium at temperature (T^*) in the system

provided, these pressures remain to be equal and constant even after closing valves (V7,V7A). Consequently, in thermal equilibrium there is a constant signal at the difference manometer (P3).

However, if for any reason the temperature of the sensor gas in the jacket vessel is changed, so will be its pressure (p_{SG}). Hence the gas pressures on both sides of the manometer (P3) will be different. This pressure difference signal ($\Delta p = p_{SG} - p_{RG}$) can be displayed and/or monitored by a supporting data acquisition system. As the sensor gas pressure ($p_{SG} = p_{RG} + \Delta p$) is directly related to the temperature (T_{SG}) of the sensor gas via its thermal equation of state it provides a direct indication of any change of this temperature. Such a change may be caused by heat flowing from (or to) the adsorption vessel to (or from) the thermostat fluid via the sensor gas.

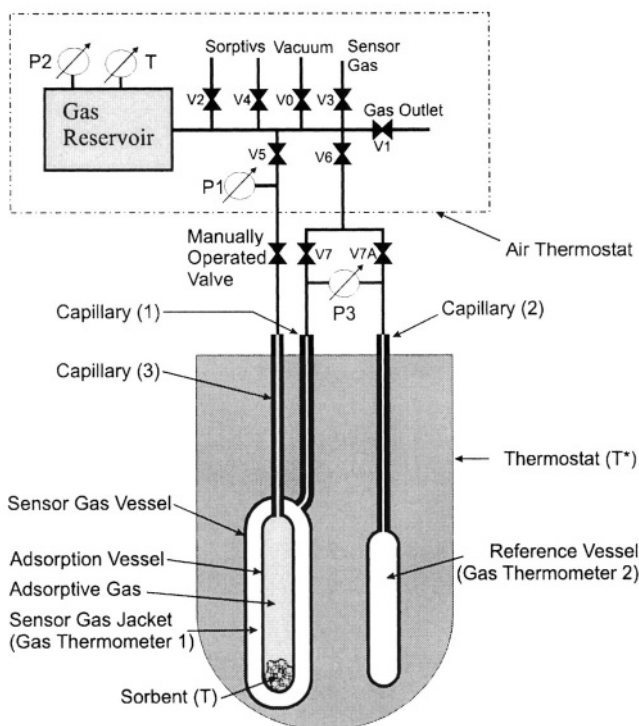


Figure 2.9. Schematic diagram of a sensor gas calorimeter (SGC), [2.23].

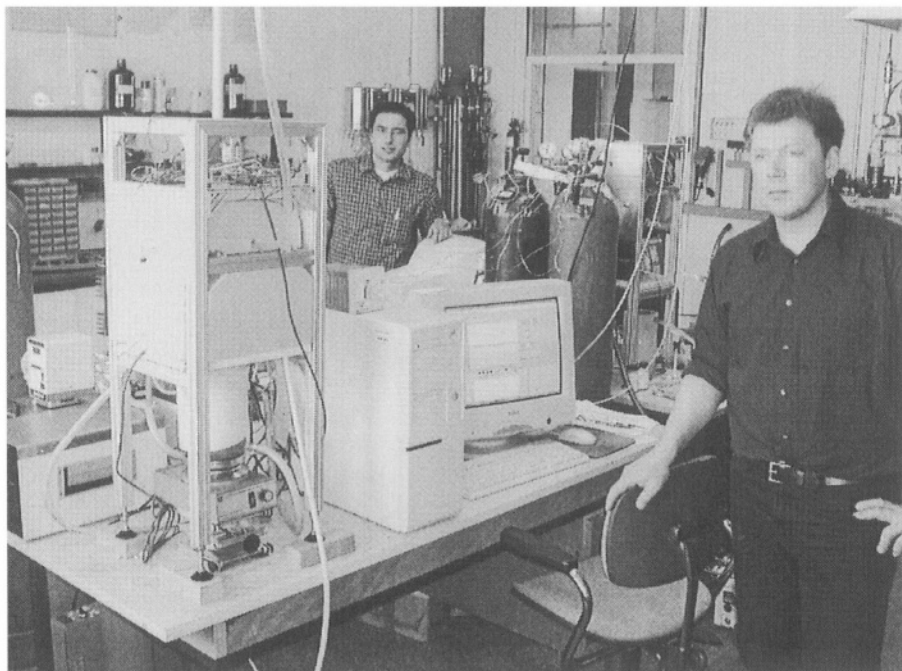


Figure 2.10. Sensor gas calorimeter (SGC) for simultaneous measurements of adsorption isotherms and enthalpies. © IFT, University of Siegen, 2003.

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The instrument is complemented by a gas reservoir and several solenoid valves for the dosing of the gases coming from the gas reservoirs in order to adjust the sorptive gas pressure (p) inside the adsorption vessel. The capillary (3) connecting the adsorption vessel with valves and the sorptive gas reservoir outside the thermostat has to be chosen carefully: diameter and length should be such that the sorptive gas coming from the reservoir assumes the temperature of the thermostat (T^*), but also evacuation of the adsorption vessel, which for example is necessary for activation processes of the sorbent material, does not take too long or even becomes practically impossible.

Auxiliary equipment like vacuum system, thermostat, a data acquisition system including a PC and safety installations also have to be provided. Depending on the specific surface and the density of the material used for examination an amount between 0.5 g and 2g has to be filled into the adsorption vessel. At the beginning of an experiment the sample material is activated by simultaneous evacuation and heating up of the adsorption vessel outside the thermostat. For activated carbon sorbent materials temperatures about (100°C - 150°C) are recommended. For zeolite sorbent materials often activation temperatures about (400°C) and even higher may be needed.

Temperature gradients during heating up and cooling down of the sample as well as the time of activation should be chosen carefully as they may have considerable impact on the properties of the activated sorbent material. After this pre-treatment procedure is completed the whole instrument has to be evacuated. Then sensor gas should be provided to the gas thermometers (1,2). After this the instrument is placed within the thermostat. When thermal equilibrium is reached valves (7,7A) are closed. At this moment the reading of the difference pressure gauge corresponding to equal pressures on both sides of the instruments membrane is a stable signal providing the baseline of any pressure signal measurement and hence also of any calorimetric measurement.

After filling the gas reservoir with an appropriate amount of sorptive gas the adsorption process can be started by opening valve (V5). The sorptive gas is flowing from the reservoir via capillary (3) into the (evacuated) sorption vessel. During this process it is important to make sure that the velocity of the gas flow is small enough to allow thermal equilibration of the gas temperature to thermostat temperature (T^*). Otherwise it would become difficult to set up a concise energy balance of the adsorption process as the enthalpy of the incoming sorptive gas would not be known exactly. As soon as the sorptive gas reaches the sorbent material prepared inside the adsorption vessel adsorption occurs and the heat of adsorption is released to the sorptive gas and then transferred via the wall of the adsorption vessel to the sensor gas inside the sensor gas vessel, cp. Fig. 1. As the temperature of the sensor gas is increased due to this heat transfer so is its pressure (p_{SG}) compared to the pressure in the reference vessel (p_{RG}). Hence there is a pressure difference $\Delta p = p_{SG} - p_{RG} \neq 0$ which is monitored and registered by the difference pressure manometer (P3). Additionally, pressures at manometers (P1) and (P2) also are monitored allowing to determine the amount of gas adsorbed i. e. to evaluate the adsorption isotherm.

A numerical example for a pressure difference signal recorded during a calibration process of an SGC is given in Fig. 2.11. It shows an increase in its first part reaching a maximum value after which it again approaches the baseline i. e. its initial value indicating thermal equilibrium in the overall system. After this, sorptive gas again can be added to the adsorption vessel increasing thus the inside pressure (p) and starting a new adsorption process which finally will lead to a new adsorption equilibrium at some higher pressure ($p' > p$).

5.2 Outline of Theory and Calibration

If heat is generated inside the adsorption vessel of the SGC, Fig. 2.9, it will be transferred via the sensor gas to the surrounding thermostat fluid. According to the Newton-Fourier Law of heat transfer we have for the total heat flow

$$\dot{Q} = K(T(t) - T^*) \quad 2.41$$

Here K is an instrument parameter to be determined by calibration experiments; $T = T(t)$ indicates the time dependent average temperature of the sensor gas and $T^* = \text{const}$ is the temperature of the thermostat fluid surrounding the sensor gas jacket.^{*)} For an ideal sensor gas the temperature T easily can be related to its pressure ($p_{\text{SG}}(t)$) as

$$T = \frac{p_{\text{SG}} V_{\text{SG}}}{m_{\text{SG}} R / M_{\text{SG}}} \quad 2.42$$

In (2.42) V_{SG} , m_{SG} are the (constant) volume and mass of the sensor gas and M_{SG} its molar mass. Combining (2.41, 2.42) we get for the total heat released during a process

$$Q = \frac{K V_{\text{SG}}}{m_{\text{SG}} R / M_{\text{SG}}} \int_0^{\infty} (p_{\text{SG}}(t) - p^*) dt \quad 2.43$$

As $\Delta p(t) \equiv p(t) - p^*$ is the time dependent signal recorded by the pressure difference manometer (P3, Fig. 2.9), with $p^* = p_{\text{RG}}$ indicating the pressure in the reference gas thermometer, the heat (Q) can be calculated from this relation by simple integration. As an example pressure signals ($\Delta p(t)$) as responses to Ohm's heat inputs of (0.5, 1.0, 1.5...5.0) J inside the adsorption vessel are presented in Figure 2.11.

^{*)} The Newton-Fourier Law (2.41) seems to be adequate for the heat transfer process from the sensor gas to the thermostat as long as there is no turbulent convection within the gas, i. e. for Grashof numbers $Gr < 10^6$, [2.30, 2.31]. For situations with $Gr > 10^6$ it has to be generalized taking aftereffects, i. e. the history of the sensor gas temperature $\{T(s), 0 \leq s \leq t\}$ into account. This can be done by using the theory of Linear Passive Systems (LPS), cp. Chap. 6 and the literature cited there. Details will be published in a forthcoming paper [2.32].

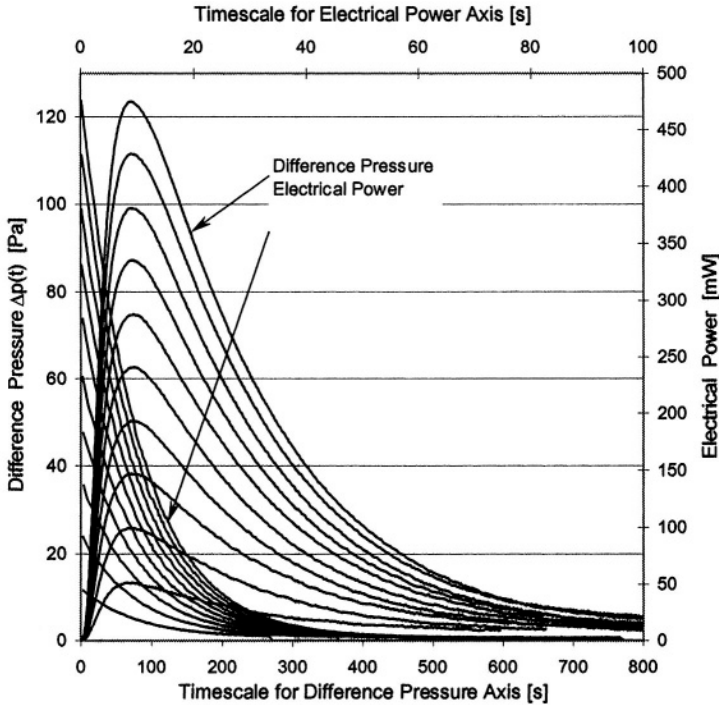


Figure 2.11. Calibration experiments of the sensor gas calorimeter (SGC). Ohm's heat of (0.5, 1.0, 1.5 ... 5.0) J is supplied by electric heating inside the adsorption vessel. The corresponding pressure signals increase in height and size with increasing heat input. The area below these curves is direct proportional to the total heat supplied to the SGC. Sensor gas used: N_2 , 5.0, $p^* = 0.15$ MPa, $T^* = 298$ K.

The monotonously decreasing curves at the left side present the input of electric power in (mW), their time integral the total electric energy supplied to the system. The curves showing a maximum are the pressure signals corresponding to the respective electric energy / Ohm's heat signals. It should be observed that the time scales related to the electric power input (upper scale) and the pressure signal (lower scale) are not identical, but for sake of graphical presentation differ by a factor 8. As indicated by Eq. (2.43) the area

$$A \equiv \int_0^{\infty} \Delta p(t) dt \quad 2.44$$

below the signal pressure curves ($\Delta p = \Delta p(t)$) and the total Ohm's heat supplied (Q) are linearly related, i. e. we have $Q \cong A$. The respective correlation of all curves depicted in Fig. 2.11 is shown in Fig. 2.12.

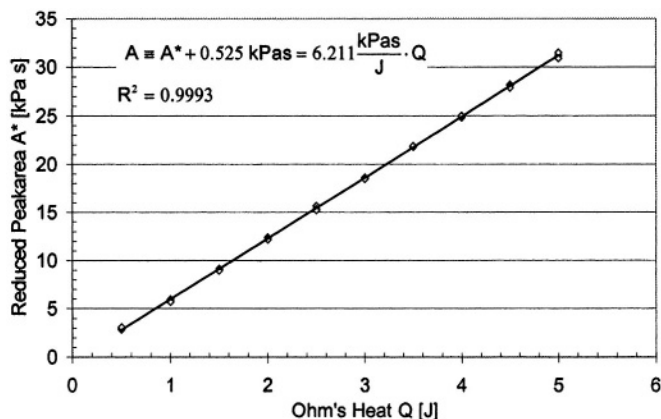


Figure 2.12. Linear correlation of the so-called peak area A , Eq. (2.44) and its actually measured reduced value $A^* = A - 0.525 \text{ kPas}$, to the total Ohm's heat (Q) supplied during calibration experiments, [2.23]. The statistical, i. e. least square correlation function is indicated in the diagram together with the correlation coefficient (R). Sensor gas: N_2 , 5.0 , $p^* = 0.16 \text{ MPa}$, $T^* = 298 \text{ K}$, [2.23].

As data recording during all calibration experiments was always stopped after $t_E = 800 \text{ s}$, only a certain portion (A^*) of the total peak area (A) could be observed, i. e. we have

$$A = A^* + \Delta A \quad 2.45$$

At the time (t_E) all pressure signals Δp ($t \geq t_E$) were at the detection limit of the difference manometer. Hence one could expect ΔA to assume the same numerical value for all experiments performed. This holds true, indeed, and the least square minimization of all data taken led to $\Delta A = 0.525 \text{ kPas}$ for the set of experiments shown in Figure 2.11.

5.3 Example

Integral heats of adsorption and Gibbs excess masses of n-butane (C_4H_{10}) adsorbed on activated carbon (AC BAX 1100) have been measured simultaneously in a SGC at various temperatures for pressures up to 0.2 MPa. Results are sketched in Figures 2.13-2.15. In Fig. 2.13 the Gibbs excess adsorption isotherms are shown for temperatures 273 K, 298 K, 323 K, 343 K. Data were correlated by generalized isotherms of Langmuir type taking into account the fractal character and the energetic heterogeneity of the sorbent material, cp. Chap. 7, Sect. 2.1. Experimental uncertainties are about three times of the size of the graphical symbols of the data points in the figure.

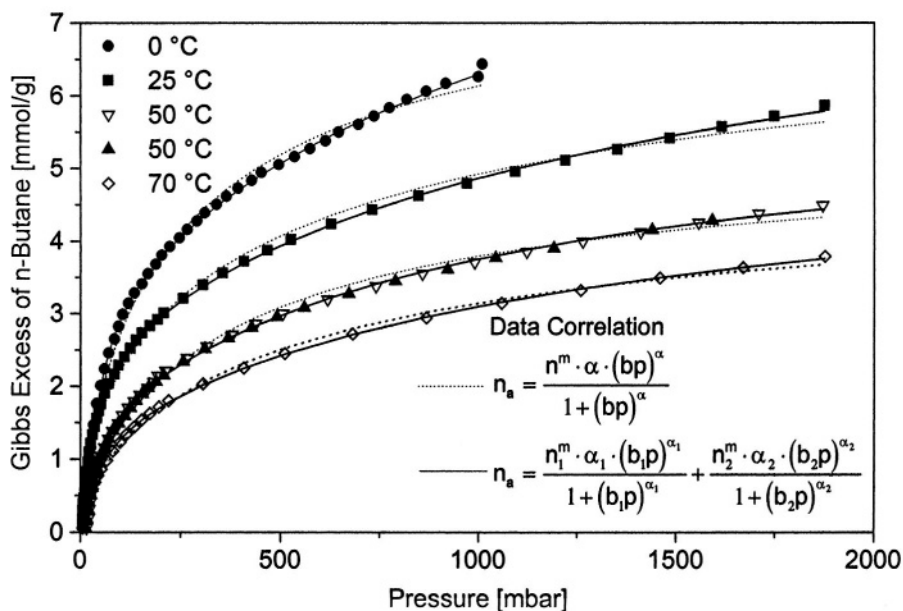


Figure 2.13. Adsorption isotherms of n-butane on activated carbon (AC BAX 1100) at temperatures $T = 273 \text{ K}, 298 \text{ K}, 323 \text{ K}, 343 \text{ K}$ for pressures up to 0.2 MPa.

In Figure 2.14 the integral heats of adsorption (ΔH , cp. (2.36)) per unit mass of sorbent ($m^s = 1 \text{ g}$) are shown as functions of the Gibbs excess mass of n-butane adsorbed. Data were taken for 4 temperatures. Measurements at $T = 323 \text{ K}$ were performed twice. Uncertainties of data are about three times the size of the graphical symbols presenting data points. The experiments performed with the GSC so far indicate that the sensitivity of measurements decreases with increasing temperature but increases with decreasing thermal conductivity of both the sorptive gas and the sensor gas used in the SGC.

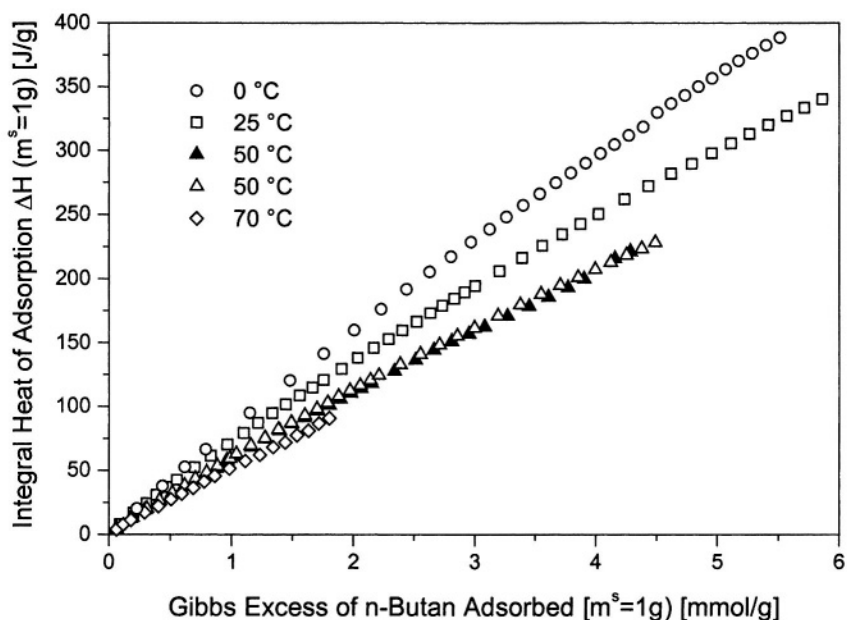


Figure 2.14. Integral heat of adsorption of n-butane (ΔH), per unit mass of sorbent (AC BAX 1100), ($m^s = 1$ g) as function of the Gibbs excess mass of n-butane adsorbed for temperatures $T = 273$ K, 298 K, 323 K, 343 K and corresponding pressures up to 0.2 MPa.

In Figure 2.15 integral and differential heats of adsorption (ΔH , (2.36), h^a , (2.38)) of n-butane on activated carbon (AC BAX 1100) are presented as function of the Gibbs excess amount of n-butane adsorbed per unit mass of sorbent. Measurements refer to $T = 25$ °C and $p \leq 0.2$ MPa. Data of the integral heat of adsorption (Δ) were correlated by a polynomial of order 5, leading by differentiation to the correlation line of the differential heats of adsorption (o).

Uncertainties of ΔH -data are about 3 times the size of the graphical symbols (Δ) representing the data, but of h^a -data about 6 times the size of the respective symbols (o).

The differential heats of adsorption (h^a) decrease with increasing amounts of n-butane (C_4H_{10}) adsorbed approaching values of about 40 kJ/mol near saturation pressure p_s (298 K) = 0.22 MPa which is about twice the value of the heat of condensation ($r_{C_4H_{10}} = 20.9$ kJ/mol). Approximate values of h^a

have been calculated via Eq. (2.37) from adsorption isotherm measurements at two different temperatures.

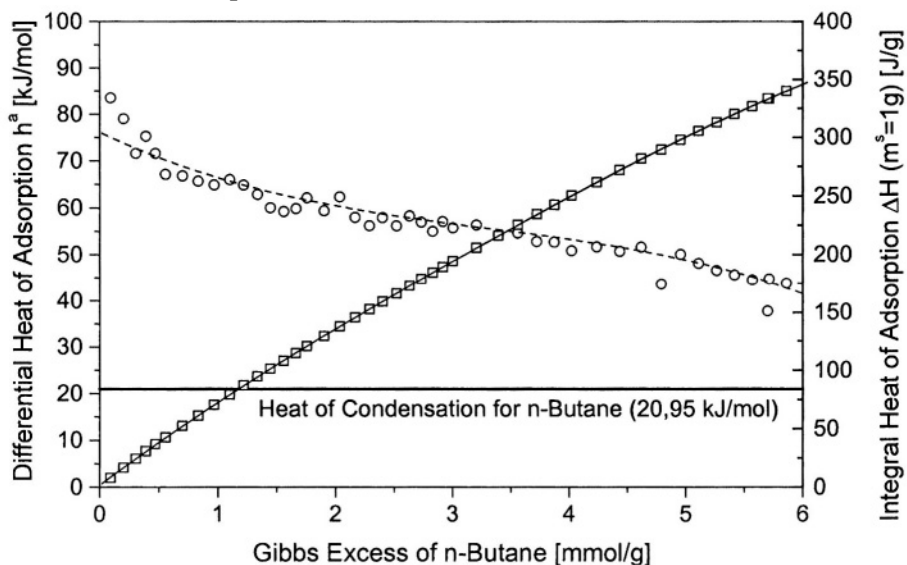


Figure 2.15. Differential and integral heats of adsorption (h^a , (2.38); ΔH , (2.36)) of n-butane on activated carbon (AC BAX 1100) at $T = 298$ K for pressures up to 0.2 MPa. The correlation line for h^a -data (o) is calculated by differentiation of the 5th order polynomial correlation function of the integral heats of adsorption (Δ).

Resulting data are deviating from direct measurement data by up to 30 % at low and 10 % - 20 % at higher adsorption loads. Hence we relinquish to present them here but recommend direct calorimetric measurements if accurate and reliable enthalpy data are needed [2.2, 2.28].

In conclusion it can be said, that the sensor gas calorimeter (SGC) is a very useful instrument for simultaneous measurements of adsorption isotherms and (integral and differential) heats of adsorption. Also hints on the kinetics of the gas adsorption process can be gained from the time dependence of the pressure signal curve, cp. Fig. 2.11. However, to achieve high sensitivity and accuracy of measurements, type and amount of the sensor gas have to be chosen very carefully. At low temperatures (77 K) helium is recommended at reference pressures of about (0.1 – 0.2) MPa. At higher temperatures (298 K) nitrogen should be preferred at the same pressures, [2.23, 2.29].

6. **PROS AND CONS OF VOLUMETRY / MANOMETRY**

In this section we will discuss some of the advantages and disadvantages of the volumetric or manometric method of measuring gas adsorption equilibria as they have appeared to us after more than 20 years of experimental work in this field.

6.1 **Advantages**

1. Simplicity

Volumetric gas adsorption instruments are fairly simple and do not require sophisticated high tech equipment, cp. Figs. 2.1, 2.6. Also the experiment in itself is simple - opening of a valve between gas storage and adsorption chamber. Therefore, volumetric instruments easily can be automated and run without permanent supervision for hours and days [2.3, 2.4]. To achieve this it is recommended that every instrument is equipped with its own personal computer (PC) for data handling, storage and transmission. For screen based operation and control the program "Lab View" (Version 6.1) has proved to be very useful. Combined with the program "PC Anywhere" it could allow remote operation of the measuring instrument from nearly any place around the world.

2. Measuring techniques

Volumetric measurements of gas adsorption equilibria reduce, if the mass of the sorbent sample used has been determined, to measurements of pressures and temperatures in gas phases. For this a variety of high precision measuring instruments operating in a fairly wide range and partly also in corrosive environment are available today. Of course these instruments prior to measurement have to be calibrated with meticulous care which may be laborious and even cumbersome. For pressure measuring devices, calibration with pressure maintaining valves of Desgranges & Huot has proved to be successful.

6.2 **Disadvantages**

1. Amount of sorbent material

For volumetric measurements of technical gas-sorbent equilibria a certain amount of sorbent material is needed, usually several grams. This is caused by the fact that only then considerable changes in the gas pressure which are due to adsorption can be observed. If only tiny

amounts – say several milligrams – of the sorbent are available, gravimetric measurements are strongly recommended.

2. Approach to equilibrium

Gas adsorption processes may last for seconds, hours or – sometimes – even days. Therefore one never can be sure whether thermodynamic equilibrium in a volumetric experiment has been realized. Hence the time which should elapse between opening the expansion valve and reading of instruments, especially thermometer and manometer has to be chosen according to experience or accompanying gravimetric measurements which – contrary to volumetry / manometry – also provide information on the kinetics or the sorption process, cp. Chap. 3.

3. Wall sorption

Upon expansion from the storage vessel the sorptive gas may not only be adsorbed on the surface of the sorbent material but also on the walls of the adsorption vessel and the tube connecting both vessels. This may cause additional uncertainties in measurement. These often but not always can be reduced by performing complementary experiments with gas expansion to the *empty* adsorption chamber including no sorbent material at all. To reduce wall adsorption electropolishing of all inner surfaces is recommended. An experiment allowing to determine wall adsorption is described in Chapter 4, Sect. 3.6.

4. Uncertainties in step-up experiments

In step-up pressure experiments, i. e. gas expansion and adsorption processes with remnant gas in the adsorption chamber, cp. Figs. 2.1, 2.6, the uncertainties of the adsorbed mass accumulate due to the algebraic structure of the sorptive gas mass balance equation

$$\Delta m_{n+1}^* + m_n^f + m_n^a = m_{n+1}^f + m_{n+1}^a, \quad n = 0, 1, 2, \dots \quad 2.35$$

Here Δm_{n+1}^* indicates the mass of gas added to the storage vessel in step (n+1) at closed expansion valve. The quantities m_n^f, m_n^a are the masses of the gas in the sorptive phase and of the adsorbed phase at the end of the n-th experiment respectively. Note that for step-up adsorption experiments $\Delta m_{n+1}^* > 0$, whereas for step-down *desorption* experiments $\Delta m_{n+1}^* < 0$. In practice the total number of steps should not exceed 3-4 as then uncertainties of about 20 % and more typically occur.

5. In situ activation procedures

Prior to adsorption experiments the sorbent sample should be activated by heating the adsorption chamber to (say) 420 K for activated carbons, 670 K for zeolites, degassing etc. During this procedure the mass of sorbent is changed by typically 1 % or more. This change normally can not be included in volumetric experiments but must be taken into account afterwards, at least approximately.

Volumetric / manometric adsorption experiments do not give information on the *kinetics* of the process; they are not useful at extreme low or high pressures as pressure measurements in these regions become difficult and accurate EOS of the sorptive gases not always are available. Also there may be problems with the thermostatisation of the vessels as during expansion the gas (normally) is cooled down due to the Joule-Thomson-effect and it will take some time till heat transfer (and radiation) bring both sorbent and sorptive gas to the same temperature again. This is especially important for desorption experiments which will take even longer till thermal equilibrium is reached [2.7, 2.20].

7. LIST OF SYMBOLS

A collection of most of symbols used in this Chapter including their SI-units is given.

m_{GE}^a	kg	Gibbs excess mass of an adsorbed phase
m_i^*	kg	mass of component $i = 1 \dots N$ of a sorptive gas mixture supplied to the storage vessel prior to adsorption
m_i^a	kg	mass of component $i = 1 \dots N$ being adsorbed on a certain mass of sorbent (m^s)
m_i^f	kg	mass of component $i = 1 \dots N$ of a sorptive gas in an adsorption equilibrium state
m_{iGE}^a	kg	Gibbs excess mass of component i of an adsorbed phase

m^*	kg	mass of sorptive gas in storage vessel prior to adsorption
m^a	kg	mass of adsorbate on the surface of a certain mass (m^s) of sorbent
m^f	kg	mass of fluid, i. e. gaseous or liquid sorptive phase
$M_{He} = 4.0026$	g/mol	molar mass of helium
M_i	g/mol	molar mass of component $i = 1...N$ of a sorptive gas mixture
n^*	mol	number of mols in a gas mixture filled in the storage vessel prior to adsorption
n^f	mol	number of mols of a sorptive gas mixture in a gas-adsorption equilibrium state
p	Pa	pressure of sorptive gas
$R=8.314$	J/Kmol	universal gas constant
S_{ik}	1	selectivity of component i relative to component k in a multi-component gas-adsorption equilibrium state
T	K	absolute temperature
V_{AC}	m^3	volume of sorption chamber
V^{as}	m^3	volume of the combined sorbate and sorbent system
V_{SV}	m^3	volume of storage vessel
V_{He}^s	m^3	volume of a (porous) sorbent measured by helium expansion experiments
$w_i^a = m_i^a / (\sum_k m_k^a)$	1	mass concentration of component i in an adsorbed phase

x	$[x]$	measurable physical quantity
\bar{x}	$[x]$	mean value of a measurable quantity x
x_i^a	1	molar concentration of component i in an adsorbed phase
Δx	$[x]$	experimental uncertainty of the numerical value ($x \pm \Delta x$) of a measurement of the quantity (x)
y_i^f	1	molar concentration of component $i = 1 \dots N$ in a sorptive gas mixture
y_i^*	1	molar concentration of component $i = 1 \dots N$ in a sorptive gas mixture supplied to the storage vessel prior to adsorption
Z	1	compressibility or real gas factor
Z_{He}	1	compressibility or real gas factor of helium
ρ^f	kg/m^3	density of a sorptive gas
ρ_0^L	kg/m^3	density of a sorptive medium in a liquid reference state
ρ_{0i}^L	kg/m^3	density of pure component i of a sorptive in a reference liquid state
σ_x^2	$[x^2]$	dispersion, variance or mean statistical deviation (MSD) of a measurable quantity (x)
$\Omega_v = m^a - \rho^f V^{\text{as}}$	μg	reduced mass of adsorbed phase measured volumetrically, cp. eqs. (2.4, 2.5)

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