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

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Abstract. A new method to determine absolute masses of gas adsorbed on the external and internal surfaces of a porous solid is proposed. It consists on a combination of calorimetric and dielectric measurements. These lead to the enthalpy and the dielectric polarization of the adsorbed phase from which by purely thermodynamic calculations the absolute mass adsorbed can be determined without using the so-called helium volume hypothesis nor any other equivalent assumption.

As example adsorption of subcritical carbon dioxide (CO_2) on zeolite (Degussa DAY) at 298 K and pressures up to 0,4 MPa is considered. As expected data of absolute masses adsorbed are always somewhat larger than the corresponding Gibbs excess masses calculated from both volumetric and gravimetric measurements via the helium volume of the zeolite.

Keywords: absolute mass adsorbed, Gibbs excess mass, helium volume hypothesis, permittivity of adsorbates, enthalpy of adsorption

Introduction

The purpose of this note is to inform readers who are interested in gas-adsorption-phenomena on highly porous solids about a new purely experimental method to measure absolute masses of adsorbed phases without introducing any model hypothesis on sorbent's pore structure nor using the so-called helium volume hypothesis (Sircar, 2002). The reason for considering this problem is threefold:

(1) Only the absolute masses adsorbed form a sound basis for development of thermodynamics in the sense of M. Planck, R. Clausius, L. Boltzmann and W. Schottky (Sandler, 1999; Kestin, 1979; Planck, 1964), whereas the Gibbs excess masses do not as they are differences between two masses referring to different phases and hence may become negative, especially at high sorptive gas pressures. Actually, there has been experimental evidence for this for many years (Sircar, 2002; Rouquerol et al., 1999; Staudt et al., 1997; Malbrunot et al., 1997; Robens et al., 1999), and also similar findings in simulation models of gas-adsorption-systems recently (Gubbins, 2001; Sarkisov and Monson, 2001).

(2) Classical measurements of excess masses of adsorbed phases by either the volumetric/manometric or the gravimetric method require to introduce in addition a hypothesis of the void or impenetrable volume of the sorbent material as seen by sorptive gas molecules. As such traditionally the helium volume is chosen, i.e. the volume of the sorbent sample measured by exposing it to a helium atmosphere. Difficulties with this quantity have been discussed in the literature (Sircar, 2002; Rouquerol et al., 1999; Staudt et al., 1997; Malbrunot et al., 1997; Robens et al., 1999; Keller et al., 1999). Here we only mention that the void volume of a porous material seen by the molecules of a gas naturally

depends on the size of the molecules. Hence the helium hypothesis is deteriorating the more, the larger the molecules of a sorptive gas are in comparison to the size of the helium atoms. Also for sorptive gas mixtures, the concept of "void volume" of a sorbent is becoming obsolete and probably should be replaced by a set of component dependent quantities related to the void volumes of each pure component of the mixture.

(3) Numerical simulation models of gas-adsorption-systems (Malbrunot et al., 1997; Robens et al., 1999) always will give the absolute amount adsorbed on a given amount of a model sorbent. Hence it would be highly desirable to have truly experimental data of this quantity to validate the quality of the simulation model.

Measurement Method

The new method proposed to measure absolute adsorbed masses of pure gas-adsorption-systems consists of a combination of

(A) Measurements of the integral heat of adsorption defined as the difference between the enthalpy of a certain amount of mass in the adsorbed state (H^a) and the enthalpy of the same amount of mass in the fluid, i.e. gaseous or liquid sorptive state (H^f) (Rouquerol et al., 1999; Do, 1998; Keller, 1990), viz.

$$\Delta H^{fa} = H^a - H^f < 0 \tag{1}$$

(B) Measurement of the electric dipole moment (P) of the sorptive/sorbent/sorbate system inside an electric capacitor and/or the macroscopic dielectric polarizability (Ω_{DE}) of the system by applying either a static or an alternating electric field of a suitable chosen frequency (ω).

For quasi-homogenous mass distribution inside the capacitor, both quantities P and Ω_{DE} are related by the equation

$$P = \Omega_{\mathrm{DE}} E, \tag{2}$$

where E is the (possibly time dependent) electric field strength (Jackson, 1993; Fröhlich, 1990; Staudt et al., 1999; Grimnes and Martinsen, 2000). According to our experimental evidence, the quasi-homogeneity assumption holds for pellet like sorbent materials if the ratio of a characteristic length of the capacitor (L) to that of the pellets, say its length or diameter (d), is of order of 10 or larger. In addition, both characteristic lengths have to be much smaller than the wave length of the oscillating electric field ($\lambda = 2\pi c/\omega$) applied. In our experimental equipment, cp. Fig. 1 below the above mentioned parameters were $L = 5$ cm, $d = 0,3\,\mathrm{cm}, (L/d) \simeq 17, 30\,\mathrm{m} < \lambda < 3\,\mathrm{km}$, i.e. $\lambda \gg L$, $\lambda \gg d$.

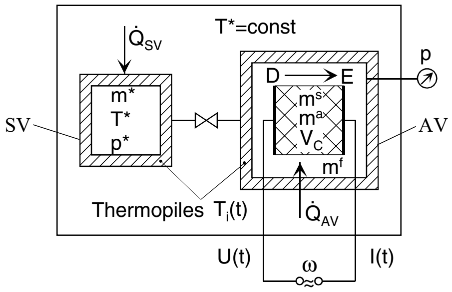

Figure 1. Experimental setup for calorimetric-dielectric measurements of pure gas-adsorption-equilibria (impedance-calorimeter).

Measurements (A) and (B) on principle can be performed simultaneously in a so-called Impedance-Calorimeter (Fig. 1) (Keller, 2000). It consists of a gas expansion system including a gas storage vessel (SV) and an adsorption vessel (AV), both of which are augmented with thermocouples to measure heat flows ($\dot{Q}_{\mathrm{SV}}$, $\dot{Q}_{\mathrm{AV}}$) to and from the vessels by gas expansion experiments. The adsorption vessel also includes an electric capacitor consisting of two parallel metal plates including the sorbent material, mass (m^s), and being connected by electric wires to an impedance analyser outside the thermostat ($T^* = \mathrm{const}$) surrounding the vessels SV and AV, and allowing to measure the dielectric capacity of the sorptive/sorbent/sorbate system (Keller, 2000).

Obviously this instrument also allows to perform simple gas expansion experiments without measuring heat flows and electric capacities, i.e. to determine Gibbs excess masses via the helium volume hypothesis and also, introducing a second hypothesis regarding the density of the adsorbed phase, to approximately calculate absolute masses adsorbed on the sorbent sample (Keller et al., 1999). Hence, results of the caloric-dielectric method can be compared to those of the traditional measurement method of both, the Gibbsian excess and the absolute adsorbed masses.

Outline of the General Theory of Calorimetric-Dielectric Measurements

Calorimetric Measurements of the Integral Heat of Adsorption

Assume a certain amount of gas (m^*) to be prepared in the storage vessel (SV) at pressure (p^*) and thermostat's temperature (T), whereas the adsorption vessel (AV) including a certain amount of sorbent material (m^s) is completely evacuated. Upon opening the valve connecting both vessels the sorptive gas will flow to the adsorption vessel where it is partly adsorbed in the sorbent (m^s) thereby releasing the heat of adsorption (Q_{AV}) which by heat transfer and (possibly) thermal convection is transported to the thermostat fluid. Also some heat or thermal energy (Q_{SV}) may be exchanged between the thermostat fluid and the gas remaining in the storage vessel (SV) at a somewhat different temperature ($T_{\mathrm{SV}}(t) \neq T$) due to the rapid and therefore nearly adiabatic expansion process of the gas. The energy balances of the gas exchange process read for the two vessels:

Storage vessel (SV):

$$U^f(p^*, T, m^*) + Q_{\mathrm{SV}} - \int_0^{m^*-m^f_{\mathrm{SV}}} h^f\,dm = U^f\big(p, T, m^f_{\mathrm{SV}}\big). \tag{3a}$$

Adsorption vessel (AV):

$$\begin{aligned} U^s(p=0, T, m^s) + Q_{\mathrm{AV}} + \int_0^{m^*-m^f_{\mathrm{SV}}} h^f\,dm \\ = U^s(p, T, m^s) + U^f\big(p, T, m^f_{\mathrm{AV}}\big) \\ + H^a(p, T, m^a). \end{aligned} \tag{3b}$$

Here the mass balance

$$m^* = m^f_{\mathrm{SV}} + m^f_{\mathrm{AV}} + m^a \tag{4}$$

has been used with (m^f_{SV}), (m^f_{AV}) being the masses included in the gaseous phases in the storage vessel (SV) and adsorption vessel (AV) respectively and (m^a) being the absolute amount of mass adsorbed on the sorbent's mass (m^s) in the adsorption vessel (AV). Also U^f indicates in (3a, b) the internal energy of the sorptive gas, h^f its specific enthalpy in flowing from SV to AV–the kinetic energy being assumed to be small enough to be neglected-, U^s is the internal energy of the solid sorbent and $H^a = U^a + \pi A^a$ the enthalpy of the sorbate, cp. also the list of symbols at the end of the article.

From Eqs. (3) and (4) two different expressions for the integral heat of adsorption (1) can be deduced assuming only that the sorbent is "thermodynamically inert", i.e. terms U^s in (3b) cancel:

$$\text{(3a, b):}\quad \begin{aligned} \Delta H^{fa} &= Q_{\mathrm{SV}} + Q_{\mathrm{AV}} + U^f(p^*, T, m^*) \\ &\quad - U^f(p, T, m^*) - pv^f(p, T)m^a, \end{aligned} \tag{5a}$$

$$\text{(3b):}\quad \begin{aligned} \Delta H^{fa} &= Q_{\mathrm{AV}} + \int_0^{m^*-m^f_{\mathrm{SV}}} h^f\,dm \\ &\quad - U^f\big(p, T, m^* - m^f_{\mathrm{SV}}\big) \\ &\quad - pv^f(p, T)m^a \end{aligned} \tag{5b}$$

We now restrict to ideal gas adsorptives and to slow i.e. nearly isothermal gas transfer processes between SV and AV. This basically is done to simplify numerical calculations but not for principle reasons. Then we get from (5b)

$$\Delta H^{fa} = Q_{\mathrm{AV}} + pv^f m^f_{\mathrm{AV}}. \tag{6}$$

with $v^f\,(p, T)$ being the specific volume of the sorptive gas at the equilibrium pressure (p) and bath temperature (T). Measured numerical values of the heat (Q_{AV}) and rough approximations of (m^f_{AV}) have shown that the second term in Eq. (6) often is very small compared to the first one, especially at low pressures (p). Hence within this approximation we get from (6) the simple result for the integral enthalpy of adsorption

$$\Delta H^{fa} = Q_{\mathrm{AV}} \tag{7}$$

which herewith is an experimentally measurable quantity. At high pressures, i.e. $p \simeq O(p^f_c)$ with p^f_c indicating the critical pressure of the adsorptive gas, the last assumption does not hold and one should use Eq. (6) instead of Eq. (7). Together with the mass balance Eq. (4), Eq. (6) provides still an implicit relation for determining the unknown mass adsorbed (m^a).

As the integral heat of adsorption (1) clearly is an extensive quantity, it also can be written as

$$\Delta H^{fa} = \Delta h\, m^a, \tag{8}$$

with

$$\Delta h = \Delta h(p, T, B) \tag{9}$$

being the (integral mean) of the specific enthalpy of adsorption which in thermodynamic terms is an intensive quantity of state of the sorbate phase. The symbol "B" in Eq. (6a) indicates a set of constants, characteristic for the caloric equation of state of the adsorbate which has to be determined by measurements, cp. example given in the next section.

Measurement of the Macroscopic Dielectric Polarizability of the Sorbate Phase

The dielectric polarizability (Ω_{DE}) of a material system defined in Eq. (2) is a phenomenological measure describing how easily the material can be polarized, i.e. electric dipoles in it can be generated by applying an electric field.[1] For weak fields ($E < 100$ V/m), according to Debye and Langmuir, the polarizability of a system consisting on more then one quasi-homogenous phases simply is the sum of the polarizabilities of all phases (Jackson, 1993; Fröhlich, 1990; Staudt et al., 1999; Grimnes and Martinsen, 2000). Hence we have

$$\Omega_{\mathrm{DE}} = \Omega^s_{\mathrm{DE}} + \Omega^f_{\mathrm{DE}} + \Omega^a_{\mathrm{DE}}. \tag{10}$$

Here the symbols Ω^i_{DE}, $i = s, f, a$, indicate the macroscopic polarizability of all molecules in phase (i) inside the capacitor.

From Eq. (10) we have

$$\Omega^a_{\mathrm{DE}} = \Omega_{\mathrm{DE}} - \left(\Omega^s_{\mathrm{DE}} + \Omega^f_{\mathrm{DE}}\right). \tag{11}$$

As for most gases at low density and high temperature the polarizability is very small due to the thermal motion of its (nearly free) molecules, in Eq. (11) Ω^f_{DE} can be neglected compared to Ω^s_{DE}, i.e. for near ideal gas sorptives we have

$$\left|\Omega^f_{\mathrm{DE}}\right| \ll \left|\Omega^s_{\mathrm{DE}}\right|. \tag{12}$$

Hence we get from Eqs. (11) and (12)

$$\Omega^a_{\mathrm{DE}} = \Omega_{\mathrm{DE}} - \Omega^s_{\mathrm{DE}}. \tag{13}$$

According to Debye (Jackson, 1993) the polarizability Ω_{DE} of the sorption system is related to its (relative) dielectric constant (ε) by

$$\Omega_{\mathrm{DE}} = 3\varepsilon_0 V_c \frac{\varepsilon - 1}{\varepsilon + 2}. \tag{14}$$

Here $\varepsilon_0 = 8{,}859 \cdot 10^{-12}$ As/Vm is the dielectric constant of the vacuum in SI-units and V_c is the volume of the capacitor.

Likewise we have for the polarizability of the sorbent material in vacuum

$$\Omega^s_{\mathrm{DE}} = 3\varepsilon_0 V_c \frac{\varepsilon_s - 1}{\varepsilon_s + 2}, \tag{15}$$

where (ε_s) is the (relative) dielectric constant of the sorbent material in vacuum inside the capacitor.

Inserting expressions (14) and (15) into Eq. (13) we get for the polarizability of the adsorbed phase

$$\Omega^a_{\mathrm{DE}} = 3\varepsilon_0 V_c \left(\frac{\varepsilon - 1}{\varepsilon + 2} - \frac{\varepsilon_s - 1}{\varepsilon_s + 2}\right), \tag{16}$$

which consequently can be calculated from measured values of ε and ε_s.

It should be noted that Ω^a_{DE} according to its definition by Eqs. (2) and (10) and prerequisites above is an extensive quantity, cp. also Eq. (16). Hence it can be written as

$$\Omega^a_{\mathrm{DE}} = \alpha^a m^a \tag{17}$$

where m^a is the total mass of the adsorbed phase and

$$\alpha^a = \alpha^a(p, T, A) \tag{17a}$$

is its specific dielectric polarizability which in thermodynamics terms is an intensive quantity of state of the sorbate phase. The symbol (A) in this dielectric equation of state of the sorbed phase indicates a set of constants. The numerical values of these constants have to be determined by dielectric measurements and correlation of the experimental data to any analytic function for α^a chosen in (17a).

Calculation of Adsorbate's Absolute Mass (m^a)

The caloric and the dielectric EOSs of the sorbate phase, Eqs. (9) and (17a) formally can be combined by solving–for example–(17a) for the pressure (p) to give

$$p = p(\alpha^a, T, A) \tag{17b}$$

and inserting this in Eq. (9). This leads to the relation

$$\Delta h = \Delta h(\alpha^a, T;\ A, B). \tag{18}$$

Inserting Eqs. (8) and (17) into (18) we get

$$\frac{\Delta H^{fa}}{m^a} = \Delta h\left(\frac{\Omega^a_{\mathrm{DE}}}{m^a}, T;\ A, B\right) \tag{19}$$

or likewise in view of Eq. (7)

$$\frac{Q_{\mathrm{AV}}}{m^a} = \Delta h\left(\frac{\Omega^a_{\mathrm{DE}}}{m^a}, T;\ A, B\right) \tag{19a}$$

Here the heat (Q_{AV}) and the polarizability of the adsorbed phase (Ω^a_{DE}) are measurable, i.e. known quantities. Hence, (19a) is an *algebraic equation* for the absolute mass adsorbed (m^a) which formally can be represented as

$$m^a = m^a\left(Q_{\mathrm{AV},}\Omega^a_{\mathrm{DE}}, T; A, B\right) \tag{20}$$

That is, m_a can be calculated from this equation once the characteristic parameters (A, B) of the equations of state (9), (17a) are known. If instead of the approximate Eq. (7) the exact energy Eq. (6) is used, we get from (4), (6) and (19)

$$\frac{Q_{\mathrm{AV}}}{m^a} + \left[\frac{m^* - m^f_{\mathrm{SV}}}{m^a} - 1\right] p v^f$$
$$= \Delta h\left(\frac{\Omega^a_{\mathrm{DE}}}{m^a}, T;\ A, B\right) \tag{19b}$$

This algebraic equation for (m^a) differs from Eq. (19a) by the bracketed term on its l.h.s. As rough estimations of this term have shown that its numerical value often is small compared to the first term on the l.h.s. of (19b), it has been neglected to simplify further algebraic treatment but not for principle reasons. That is, in the example presented in the next Section of the paper we will use Eq. (19a) instead of Eq. (19b) for determining the absolute mass adsorbed (m^a).

To determine numerical values of the parameters (A, B) we consider the Gaussian minimization procedure

$$\sum_i^I \left\{(Q_{\mathrm{AV}} - \Delta h(p, T, B) m^a)_i^2 + \left(\Omega^a_{\mathrm{DE}} - \alpha^a(p, T, A) m^a\right)_i^2\right\} \to \mathrm{Min} \tag{21}$$

with (m^a) being a function of (A, B) according to Eq. (20).

The sum should be taken over all sets of experimental data ($Q_{\mathrm{AV}i}$, $\Omega^a_{\mathrm{DE}i}$, p_i, T = const.) available. Naturally, the resulting values of parameters A, B will depend on these data and also on the total number (I) of data sets available. However, we expect numerical values of A, B to tend to asymptotic limiting values as $I \to \infty$. The proof of this conjecture is left to cooperative mathematicians. Once parameters A, B are known from (21), the masses adsorbed can be calculated from Eq. (20). Also the specific adsorption enthalpy (Δh_i) and the specific polarizability α_i of the adsorbed phase in state $i = 1 \ldots I$ can be calculated from the respective EOSs (9), (17a). A numerical example will be given in the next section.

Alternatively to (21), the minimization requirement

$$\sum_i^I \left\{\frac{Q_{\mathrm{AV}}}{\Omega^a_{\mathrm{DE}}} - \frac{h(p, T, B)}{\alpha^a(p, T, A)}\right\}_i^2 \to \mathrm{Min} \tag{22}$$

which does not include the function (20) for the (unknown) masses adsorbed, can be used. This can be of importance in case Eq. (20) is not explicit in (m^a), but implicit, i.e. including the unknown quantity (m^a) also on its r.h. side. However, though the minimization principle (22) can be handled numerically much more easily than (21), it does not always allow to actually determine unique values of parameter sets A, B. This easily can be shown by simple numerical examples. Hence we recommend the reader to use Eq. (21) to determine A, B and consider (22) only in order to get–for example–starting values of these parameters within an iterative numerical solution procedure of (21).

The formalism described above may be generalized in several ways. First we expect numerical accuracy to be increased if dielectric measurements not only at one, but at several frequencies are available. Also, by combining the dielectric-caloric method with manometric or gravimetric adsorption measurements, binary coadsorption equilibria of the system can be determined. Details will be given in a forthcoming paper (Keller et al., 2002).

In conclusion we would like to emphasize that using a series expansion of the caloric-dielectric equation of state of the adsorbed phase (18), it is on principle possible to calculate the total amount of mass adsorbed from combined dielectric and caloric measurements without introducing a hypothesis regarding the void volume of the sorbent material. The resulting data will be the more accurate, the more data of the sorption enthalpy and the polarization are available and the smaller uncertainties of these data are. Similar methods comprising combined caloric-magnetic and/or dielectric-magnetic measurements can be envisaged and may be discussed in due time.

Example: Adsorption of CO_2 on Wessalite (DAY-Zeolite) at 298 K

Combined dielectric-calorimetric measurements of the adsorption of carbon dioxide (CO_2) on wessalite, a special type of DAY-zeolite manufactured by Degussa AG, Wolfgang, Germany, have been performed in our laboratory during 2000/2001. Experimental details are described in Staudt et al. (1999), Schein (2001), Dohrmann (1997) and Ohm (2000). Here we restrict to present numerical data as given in Table 1 below.

In this table the integral heat of adsorption ($\Delta H^{fa} < 0$) of CO_2 on wessalite per mass unit of sorbent ($m^s = 1$ g), the specific heat of adsorption ($\Delta h_{\mathrm{GE}} = \Delta H^{fa}/m_{\mathrm{GE}}$) referred to the Gibbs excess mass of the adsorbed phase, the reduced dielectric polarizability ($\Pi = \Omega^a_{\mathrm{DE}}/(3\varepsilon_0 V_c)$), cp. (16, 22) and its specific values ($\hat{\alpha}_{\mathrm{GE}} = \Pi/m_{\mathrm{GE}}$) also related to the Gibbs excess mass are given for five different gas pressures and a temperature $T = 298$ K. Numerical values of the Gibbs excess masses (m_{GE}) are given in Fig. 5 below. The adsorption enthalpies (ΔH^{fa}, Δh_{GE}) are sketched in Fig. 2 below. The (reduced) polarizabilities (Π, $\hat{\alpha}_{\mathrm{GE}}$) are displayed in Fig. 3 below. This is done in order to get insight in what the algebraic structure of the caloric equation of state (EOS) of the adsorbate, Eq. (9) and the dielectric EOS, Eq. (17a) could be, as the quantities (Δh_{GE}, $\hat{\alpha}_{\mathrm{GE}}$) can be considered as "low pressure approximations" for their (actually needed but still unknown) counterparts ($\Delta h = \Delta H^{fa}/m^a$), $\hat{\alpha} = \Pi/m^a$)) related to the absolute mass adsorbed (m^a).

As can be seen from Fig. 2 the pressure dependence of the specific enthalpy of adsorption phenomenologically can be represented by an EOS of the type

$$\Delta h(p, T, b, B) = \Delta h_0 + B(T)e^{-b(T)p} \tag{23}$$

Here $\Delta h_0 = \Delta h(p = \infty, T, b, B)$ is chosen as the enthalpy of condensation at temperature (T) from the vapor to the bulk liquid phase, i.e. for CO_2 we have $\Delta h_0 = -0{,}3455$ J/mg (Wagner et al., 1995). The parameters (B, b) are unknown constants which have to be determined by data correlation, i.e. by the Gauss-minimization procedure Eq. (21) described in more detail below. The curve (23) resulting from this calculation is sketched in Fig. 2. In comparing it to the experimental data symbols it should be emphasized that the line refers to the specific adsorption enthalpy ($\Delta h = \Delta H^{fa}/m^a$) related to the absolute mass adsorbed whereas the data prints represent values of the specific adsorption enthalpy related to the Gibbs excess mass ($\Delta h_{\mathrm{GE}} = \Delta H^{fa}/m_{\mathrm{GE}}$).

From Fig. 3 we similarly deduce that the pressure dependence of the (reduced) specific polarizability

$$\hat{\alpha} = \frac{\Pi}{m^a} = \frac{\alpha^a}{3\varepsilon_0 V_c} \tag{24}$$

with

$$\Pi = \frac{\Omega^a_{\mathrm{DE}}}{3\varepsilon_0 V_c} = \frac{\varepsilon - 1}{\varepsilon + 2} - \frac{\varepsilon_s - 1}{\varepsilon_s + 2} \tag{25}$$

being an auxiliary quantity which may be called "reduced dielectric polarizability" of the adsorbed phase, phenomenologically can be represented by an equation of the type

$$\hat{\alpha}(p, T, a, A) = \hat{\alpha}_0 + A(T)e^{-a(T)p}. \tag{26}$$

Here $\hat{\alpha}_0 = \hat{\alpha}(p = \infty, T, a, A)$ is chosen as the (reduced) specific polarizability of the sorptive gas in its

Table 1. Heat of adsorption (ΔH^{fa}) per unit mass of sorbens ($m^s = 1$ g) and reduced dielectric polarizability ($\Pi = \Omega^a_{\mathrm{DE}}/(3\varepsilon_0 V_c)$) of CO_2 on wessalite (DAY-zeolite) at $T = 298$ K. Also shown are specific values of these quantities ($\Delta h_{\mathrm{GE}} = \Delta H^{fa}/m_{\mathrm{GE}}$, $\hat{\alpha}_{\mathrm{GE}} = \Pi/m_{\mathrm{GE}}$) related to the Gibbs excess mass (m_{GE}) of CO_2 adsorbed, cp. Fig. 5.

No.	P (hPa)	ΔH^{fa} (J/g)	Δh_{GE} (J/mg)	Π	$\hat{\alpha}_{\mathrm{GE}}$ (μg/mg)
1	100	−2,6	−1,83	$13 \cdot 10^{-4}$	900
2	499	−5,3	−0,809	$38 \cdot 10^{-4}$	660
3	1009	−8,25	−0,584	$(95 \cdot 10^{-4})$	(648)
4	1961	−12,8	−0,430	$116 \cdot 10^{-4}$	333
5	4003	–	−0,345	$118 \cdot 10^{-4}$	137
		$m^s = 1$ g	$m_{\mathrm{GE}} = 1$ mg		

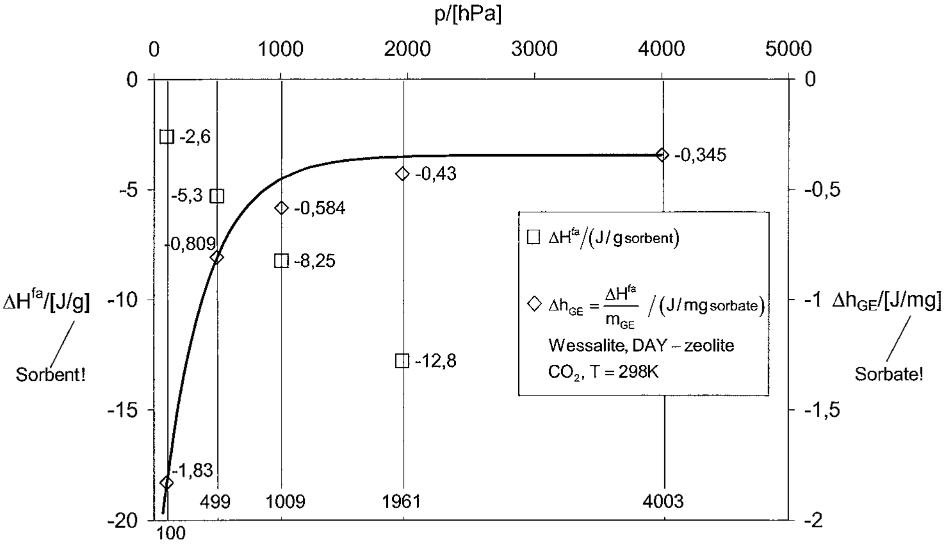

Figure 2. Enthalpy (ΔH^{fa}) and Gibbs excess specific enthalpy ($\Delta h_{\mathrm{GE}} = \Delta H^{fa}/m_{\mathrm{GE}}$) data of CO_2 adsorbed on DAY-zeolite at $T = 298$ K. The curve refers to the specific enthalpy of the absolute mass adsorbed, i.e. $\Delta h = \Delta H^{fa}/m^a$, cp. Eqs. (23) and (30).

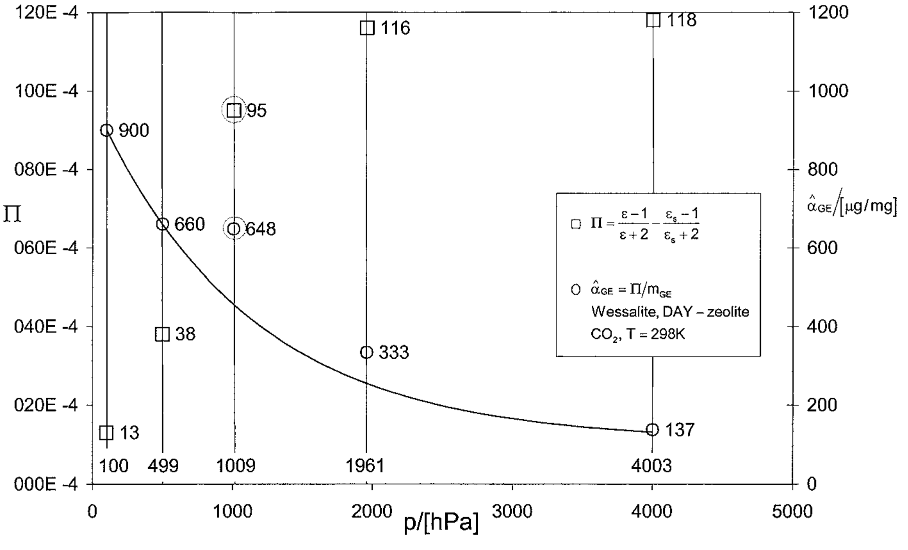

Figure 3. Reduced dielectric polarizability (Π) and Gibbs excess specific polarizability ($\hat{\alpha}_{\mathrm{GE}} = \Pi/m_{\mathrm{GE}}$) data of CO_2 on DAY-zeolite at $T = 298$ K. The curve refers to the specific polarizability of the absolute mass adsorbed, i.e. $\hat{\alpha} = \Pi/m^a$, cp. Eqs. (26) and (30).

bulk liquid state at temperature T. For CO_2 at $T = 298$ K and the capacitor used (Dohrmann, 1997; Ohm, 2000), we have $\hat{\alpha}_0 = 108{,}8$ μg/mg (Wagner et al., 1996). The parameters (A, a) again are unknown constants which also have to be determined by data correlation, i.e. by the Gauss-minimization procedure Eq. (21) as indicated below. The curve (26) resulting from this is already sketched in Fig. 3. In comparing it to the experimental data symbols it should again be taken into account that the line represents the optimal fit of the reduced specific polarization ($\hat{\alpha} = \Pi/m^a$) related to the absolute mass adsorbed whereas the data points represent values of the reduced specific polarizability ($\hat{\alpha}_{\mathrm{GE}} = \Pi/m_{\mathrm{GE}}$) related to the Gibbs excess mass.

From the caloric EOS (23) and the dielectric EOS (26) the *caloric-dielectric EOS* of the adsorbed CO_2 can be derived by eliminating the pressure (p) from

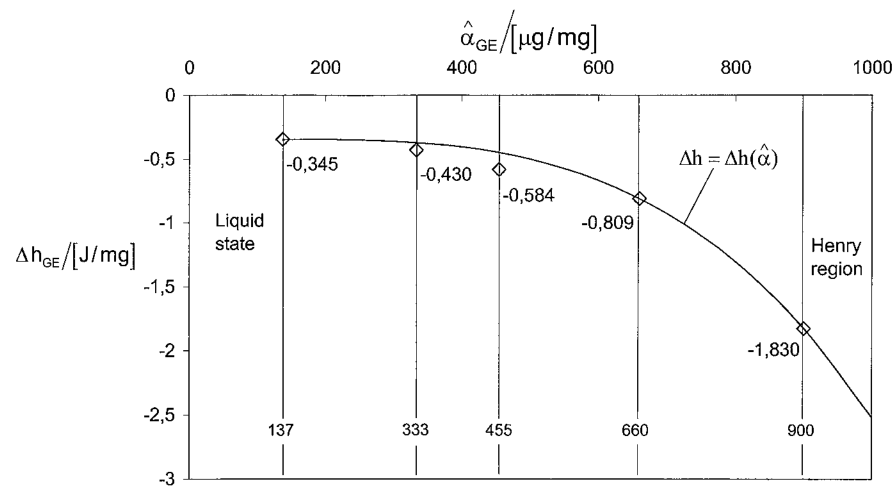

Figure 4. Gibbs excess specific enthalpy ($\Delta h_{GE} = \Delta H^{fa}/m_{GE}$)—reduced Gibbs excess specific polarizability ($\hat{\alpha}_{GE} = \Pi/m_{GE}$) diagram of CO_2 on DAY-zeolite at $T = 298$ K. The curve refers to $\Delta h = \Delta h(\hat{\alpha})$ as given by Eq. (27) with "optimised parameters" (30).

these equations:

$$\Delta h - \Delta h_0 = B\left(\frac{\hat{\alpha} - \hat{\alpha}_0}{A}\right)^{b/a} \qquad (27)$$

This curve is sketched in Fig. 4 using for the parameters their "optimized values" given below, cp. (30). In comparing this curve with the data points depicted in Fig. 4 it should again be taken into account, that the former is related to the absolute masses adsorbed ($\Delta h = \Delta h(\hat{\alpha})$), whereas the later are referred to the Gibbs excess masses ($\Delta h_{GE} = \Delta H^{fa}/m_{GE}, \hat{\alpha}_{GE} = \Pi/m_{GE}$). As can be seen from Fig. 4, the CO_2 adsorbed realizes in the low pressure—or Henry region large specific values of the adsorption enthalpy which correspond to large values of the specific polarizability. Contrary to this for increasing pressures, i.e. approaching the liquid like state of saturation, the enthalpy and polarizability are decreasing to near their liquid state corresponding values.

Inserting now in Eq. (27) the extensivity relations (8) and (24) we get

$$m^a = \frac{\Delta H^{fa}}{\Delta h_0 + B(((T/m^a) - \hat{\alpha}_0)A)^{b/a}} \qquad (28)$$

This is an implicit algebraic equation for the absolute mass adsorbed (m^a) once the parameters a, A, b, B have been determined numerically. To achieve this, we consider the Gaussian mean deviation minimization principle Eq. (21), for correlating the data given in Table 1. Using the reduced polarizability (Π), Eq. (25) instead of (Ω^a_{DE}) it reads:

$$\begin{aligned}&\sum_{i=1}^{4}[\Delta H^{fa} - \Delta h(b, B)m^a(a, A, b, B, \Delta H^f, \Pi)]_i^2\\&\quad + \sum_{i=1}^{5}[\Pi - \hat{\alpha}(a, A)m^a(a, A, b, B, \Delta H^f, \Pi)]_i^2\\&\quad \to \text{Min} \qquad (29)\end{aligned}$$

Here for Δh and $\hat{\alpha}$ Eqs. (23) and (26) have to be introduced whereas the function $m^a = m^a(a, A, b \ldots)$ is defined by Eq. (28). For numerical solution of (28) and (29) one may start by using for m^a in (29) the (volumetrically or gravimetrically measured) Gibbs excess mass (m_{GE}) and determine approximate values of parameters (a, A, b, B). Inserting these in Eq. (28), new values of (A, a, B, b) can be calculated which iteratively may be used in (29). The result of this iteration procedure is

$$\begin{aligned}a &= 9{,}0867 \cdot 10^{-4}(\text{hPa})^{-1}\\A &= 866{,}79\frac{\mu g}{\text{mg}}\\b &= 29{,}17 \cdot 10^{-4}(\text{hPa})^{-1}\\B &= -1{,}9913\ \text{J/mg}\end{aligned} \qquad (30)$$

Using these parameters in Eq. (28) and experimental data as given in Table 1, the absolute masses of CO_2 adsorbed (m^a) can be calculated. Numerical results are given together with the Gibbs excess masses determined volumetrically (m_{GEV}) and gravimetrically (m_{GEG}) in Fig. 5.

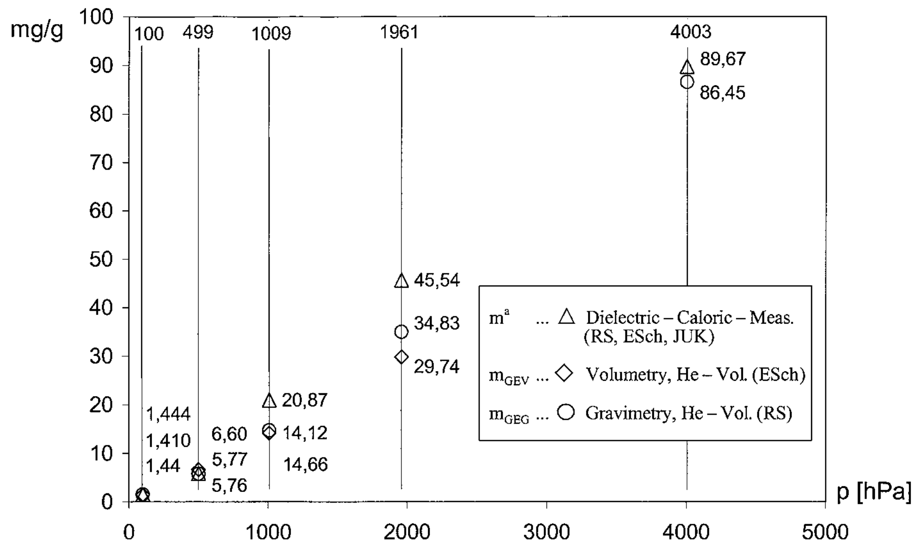

Figure 5. Absolute masses (m^a) and Gibbs excess masses measured volumetrically and gravimetrically (m_{GEV}, m_{GEG}) of CO_2 adsorbed on wessalite (DAY-zeolite) at 298 K.

The absolute masses are always somewhat larger than the Gibbs excess masses as it should be according to the underlying physical concepts. However, we have to emphasize that the results presented only are preliminary, as the data base is fairly small and much more data would be needed to show the absolute–and the Gibbs excess adsorption isotherm over a considerable range of pressure in order to finally answer the question in what range of pressure the later is still a good approximation of the former. Experiments in a new type of adsorption calorimeter are presently performed at IFT and we hope to be able to report on them in due time.

Differences in the volumetrically and gravimetrically measured Gibbs excess masses depicted in Fig. 5 are partly due to different activation procedures of the zeolite samples used in the experiments. This of course should be avoided, but as a matter of fact happened in our experiments and therefore is brought to the reader's attention.

In conclusion we want to emphasize that on principle it is possible to *measure* the absolute amount of a sorptive gas adsorbed on porous solids *without* using the so-called helium volume approximation by combined dielectric and calorimetric measurements. However, experiments are cumbersome and time consuming and probably only will be needed for calibration or standardization purposes or for processes operating at high pressures. It also would be desirable to compare results of measurements of absolute masses adsorbed with those of numerical simulation models to get new inside in both the analytical model used and the experimental technique proposed in this paper.

List of Symbols

Symbol	*SI-Unit*	*Name*
A	(various)	Set of characteristic constants in equation of state (17a) for the specific dielectric polarizability of the adsorbed phase
A^a	m^D	Aerial extension parameter of adsorbed phase of fractal dimension ($1 \leq D \leq 3$)
B	(various)	Set of characteristic constants in the caloric equation of state (9) for the (integral mean) specific heat of adsorption
$1 \leq D \leq 3$	1	Fractal exponent of adsorbed phase

E	V/m	Electric field strength
$H^a = U^a + \pi A^a$	J	Enthalpy of mass m^a adsorbed
H^f	J	Enthalpy of mass m^f of fluid, i.e. gaseous or liquid sorptive
$\Delta H^{fa} = H^a - H^f$	J	Integral heat of adsorption of a gaseous sorptive on a certain mass (m^s) of sorbent
h^f	J/g	Specific enthalpy of sorptive gas
$\Delta h = \Delta H^{fa}/m^a$	J/g	Specific enthalpy of adsorption related to the absolute mass adsorbed (m^a)
$\Delta h_{\mathrm{GE}} = \Delta H^{fa}/m_{\mathrm{GE}}$	J/g	Specific enthalpy of adsorption related to the Gibbs excess mass adsorbed (m_{GE})
m^*	g	Mass of sorptive gas prepared in the storage vessel (SV) prior to expansion
m^a	g	Absolute mass adsorbed on the surface of (m^s)
m^f_{AV}	g	Mass of sorptive gas included in the adsorption vessel after equilibration
m^f_{SV}	g	Mass of sorptive gas included in the storage vessel after equilibration
m^s	g	Mass of sorbent prepared in the adsorption vessel (AV)
P	Asm	Electric dipole moment of a material system
p	Pa	Pressure of sorptive gas
Q_{AV}	J	Heat exchange between the adsorption vessel (AV) and the heat bath in the impedance calorimeter, Fig. 1
Q_{SV}	J	Heat exchange between the storage vessel (SV) and the heat bath in the impedance calorimeter, Fig. 1
T	K	Thermostat temperature
U^f	J	Internal energy of sorptive gas
U^s	J	Internal energy of solid sorbent material
V_c	m^3	Volume of the electric capacitor
v^f	m^3/kg	Specific volume of sorptive gas
$\alpha^a = \Omega^a_{\mathrm{DE}}/m^a$	Asm^2/Vg	Specific dielectric polarizability of the adsorbed phase
$\hat{\alpha} = \Pi/m_a = \alpha^a/3\varepsilon_0 V_c$	g/mg	Reduced specific dielectric polarizability related to the absolute mass adsorbed (m^a)
$\hat{\alpha}_{\mathrm{GE}} = \Pi/m_{\mathrm{GE}}$	g/mg	Reduced specific dielectric polarizability related to the Gibbs excess mass of an adsorbed phase (m_{GE})
$\varepsilon_0 = 8{,}859{\cdot}10^{-12}$	As/Vm	Dielectric constant of the vacuum in SI-units
ε	1	Relative dielectric constant of a material system; in Eq. (14) ε is related to the sorbent and sorbate phase inside an electrical capacitor

ε_s	1	Relative dielectric constant of the sorbent material in vacuum
λ	m	Wavelength of an oscillating electric field
$\Pi = \Omega^a_{DE}/(3\varepsilon_0 V_c)$	1	Reduced dielectric polarizability of an adsorbed phase
π	$J \cdot m^{-D}$	Spreading pressure of adsorbed phase of fractal dimension ($1 \leq D \leq 3$)
$\Omega_{DE} = P/E$	Asm/(V/m)	Macroscopic dielectric polarizability of a material
Ω^a_{DE}	Asm/(V/m)	Macroscopic dielectric polarizability of the adsorbed phase
Ω^f_{DE}	Asm/(V/m)	Macroscopic dielectric polarizability of the gaseous sorptive
Ω^s_{DE}	Asm/(V/m)	Macroscopic dielectric polarizability of the solid sorbent material

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Note

1. We do not consider materials with permanent electric dipole moments—so-called electrets-, i.e. we assume that for $E = 0$, the electric dipole moment of the sorption system also vanishes, $P = 0$, cp. Eq. (2).

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