



A new calorimeter for simultaneous measurement of isotherms and heats of adsorption

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Abstract

A new calorimeter designed for simultaneous measurements of heats and isotherms of gas adsorption and desorption systems is presented. It consists of a volumetric/manometric gas adsorption instrument, the adsorption vessel of which is placed within a second vessel filled with inert gas. This gas acts as a sensor, as not only its temperature but also its pressure is increased if heat is released from the adsorption vessel via the sensor gas to its thermostated surroundings. Indeed, the time integral of the sensor gas pressure signal turned out to be strongly related to the total heat released from the adsorption vessel.

A basic theoretical equation of the measurement procedure is given. Results of numerous calibration measurements are presented. The question of what type and amount of sensor gas should be used to achieve high sensitivity of the instrument is discussed.

Two examples of measurements of heats of adsorption and adsorption isotherms are given, namely adsorption of N₂ on alumina oxide (CRM-BAM-PM-104) at 77 K and CO₂ on zeolite Na13X and wessalite DAY both at 298 K.

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1. Introduction

Sorption processes of gases and vapors on the surface of highly porous solids like zeolites or activated carbons have still a considerable potential for a growing number of processes in separation technology, purification processes of technical gases and air, and also for air conditioning systems [1–5]. This is reflected not only in an increasing number of scientific and technical papers, patents, and engineering reports but also in a still growing world market for plants for air separation, hydrogen and natural gas

purification processes and many more [6–8]. As sorption processes normally are exothermal processes it is very important to know the heat of adsorption (HoA) or the change in enthalpy of the sorptive gas being transferred to the adsorbed state. These heats often are twice as large as the heats of condensation of a (subcritical) sorptive gas and normally range for physical, i.e. reversible sorption processes between 10 and 100 kJ/mol. Heats of adsorption are needed to:

- characterize the sorbent material energetically [9–11];
- provide basic data for development of new theories of adsorption equilibria and kinetics; and
- design engineering adsorption and desorption processes like PSA, VSA, TSA, and combinations thereof [1,12].

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As it is still not possible to calculate heats of adsorption from first principles [13], or even from a few experimental data and a phenomenological theory [14], it is still necessary to measure heats of adsorption, i.e. to perform calorimetric adsorption experiments. The main reasons causing this situation are:

- the energetic heterogeneity of most physico-chemical and engineering sorbent materials; and
- the interaction of simultaneously adsorbed molecules—so-called admolecules—which is becoming the more important, with the higher adsorbate load in the sorbent material [15,16]. In technical sorbent materials, the situation is even more complex as these normally are kind of composite materials consisting on the sorbent material itself and a technical glue or cement providing mechanical stability and several other properties needed in the engineering adsorption process [17].

Today there are several possibilities at hand to determine heats of adsorption from experimental data. Overviews of these are given in [18,19]. Fundamentals are presented in [20]. The most important of these methods are:

- Calculation of HoA from adsorption equilibria data taken at different temperatures, i.e. adsorption isotherms (AI), or adsorption isosteres (AIS) [9].
- Calorimetric measurements: these may be classified as adiabatic or isothermal methods, static or dynamic procedures, Tian-Calvet calorimeters, immersion calorimeters, etc. [18].

Results of measurements by different methods and calculations of HoA often deviate by 10% and more, sometimes by more than 100%. The reason for this is that in procedure A, in which a modified equation

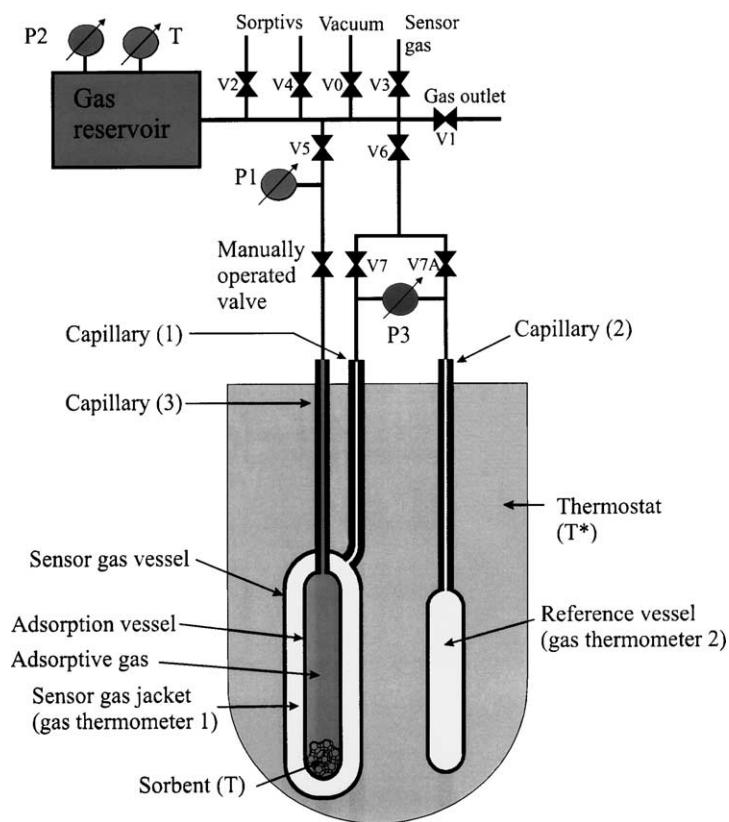


Fig. 1. Schematic diagram of a sensor gas calorimeter. It basically consists of an adsorption vessel surrounded by a sensor gas jacket acting as a gas thermometer (1) being connected to a second gas thermometer (2) by a difference pressure manometer (P3).

of the Clausius–Clapeyron type is used, a differential coefficient has to be approximated by a difference coefficient which unavoidably will lead to numerical uncertainties, especially if only few adsorption equilibria data are available. In procedure B, normally calorimeters are used which were originally designed for other purposes but not for investigation of heterogeneous gas–solid systems [18].

Following a basic idea of Langer [21], a new calorimeter has been designed allowing simultaneous measurements of heats and isotherms of gas adsorption and desorption systems. It may be called a sensor gas calorimeter (SGC), as the heat flowing during a gas adsorption process from the adsorption vessel to a thermostat has to pass a gas jacket surrounding the adsorption vessel. This gas acts as a sensor. Indeed, due to the heat flux its temperature and hence its pressure is changed. Actually, the (time-dependent) pressure signal can be correlated with the heat flux and after integration over time gives a measure for the total heat of adsorption released from the adsorption vessel to the thermostat. A schematic diagram of the instrument is given in Fig. 1. More information on the instrument and the measurement procedure is given in Section 2 of this paper. Section 3 is devoted to the calibration problem of the instrument whereas in Section 4 two examples of measurements of HoA are presented, namely nitrogen (N_2) on alumina oxide (CRM-BAM-PM-104) at 77 K, and carbon dioxide (CO_2) on zeolite NaX13 and wessalite DAY both taken at 298 K. Complementing information on the SGC also may be found in the web on the homepage of the authors.¹

2. Experimental

In this section, a brief description of the instrument followed by an outline of both the volumetric and the calorimetric measurement is given.

The SGC basically consists of a classical volumetric gas adsorption device complemented by two gas thermometers (Fig. 1). 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 differ-

ence 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 and V7A, the pressures p_{SG} and 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 and 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.

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 and 2 g 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,

¹ <http://www.141.99.140.157/d/iff3/index.htm>.

temperatures about 100–150 °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 and 2. After this the instrument is placed within the thermostat. When thermal equilibrium is reached, valves 7 and 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 (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 an adsorption process is given in Fig. 6. 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, thus increasing the inside pressure p and starting a new adsorption process which finally will lead to a new adsorption equilibrium at some higher pressure ($p' > p$).

3. Calibration and reproducibility

In this section, we are going to discuss the problem of calibration and of reproducibility of the difference pressure signals to be observed at the SGC during an adsorption experiment. For this we have performed quite a number of calibration experiments using metal film resistors (100 Ω , 250 mW) placed in the adsorption vessel at ambient atmosphere. The Ohmian heat Q being supplied to the system can be calculated as:

$$Q = IUt, \quad (1)$$

where I is the (constant) electric current, U the electric voltage at the resistor, and t the time interval during which the electric voltage is applied at the resistor. In Fig. 2, three series of identical calibration experiments are depicted showing the series of pressure signals recorded at the pressure difference manometer P3 (Fig. 1). The sensor gas used was helium at $p = 120$ kPa. Temperature of the thermostat LN₂ was 77 K. Each series of experiments consisted of 10 basic experiments during which electric energies:

$$E_n = Q_n = 0.2n, \quad n = 1, \dots, 10, \quad (2)$$

at a power of 80 mW were supplied to the resistor. As can be seen in Fig. 2, each electric power signal is reflected in a pressure signal ($p(t)$) the height and area below the p - t curve of which are consecutively increasing as are the total energies (Eq. (2)) of the signals. More important for us is the fact that the three groups of p - t signals are nearly identical, i.e. heights of maxima and areas under p - t curves in corresponding signals deviate by less than 1%, thus indicating acceptable reproducibility of calibration experiments.

However, the pressure signals themselves cannot be easily related to the total heat released by the electric resistor. This is demonstrated in Fig. 3, showing power inputs and corresponding pressure signals of two calibration experiments performed at 77 K with ambient

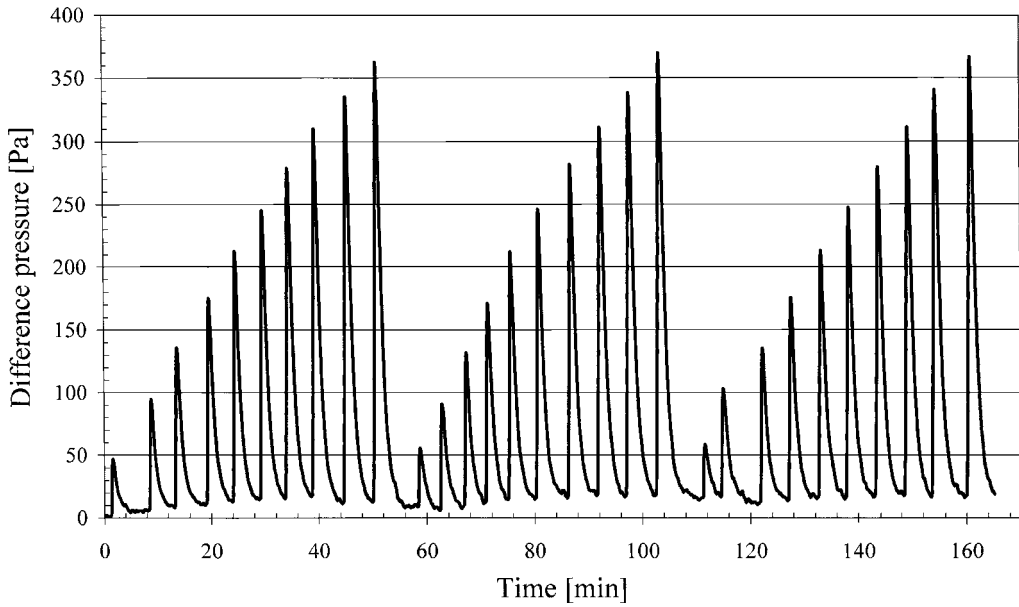


Fig. 2. Signals of the difference pressure manometer P3 of the SGC (Fig. 1), as observed during calibration experiments with Ohmian resistances. Heat supplied, 0.2–2.0 J; power, 80 mW; sorptive gas, He; $T = 77\text{ K}$; $p = 0.1\text{ MPa}$.

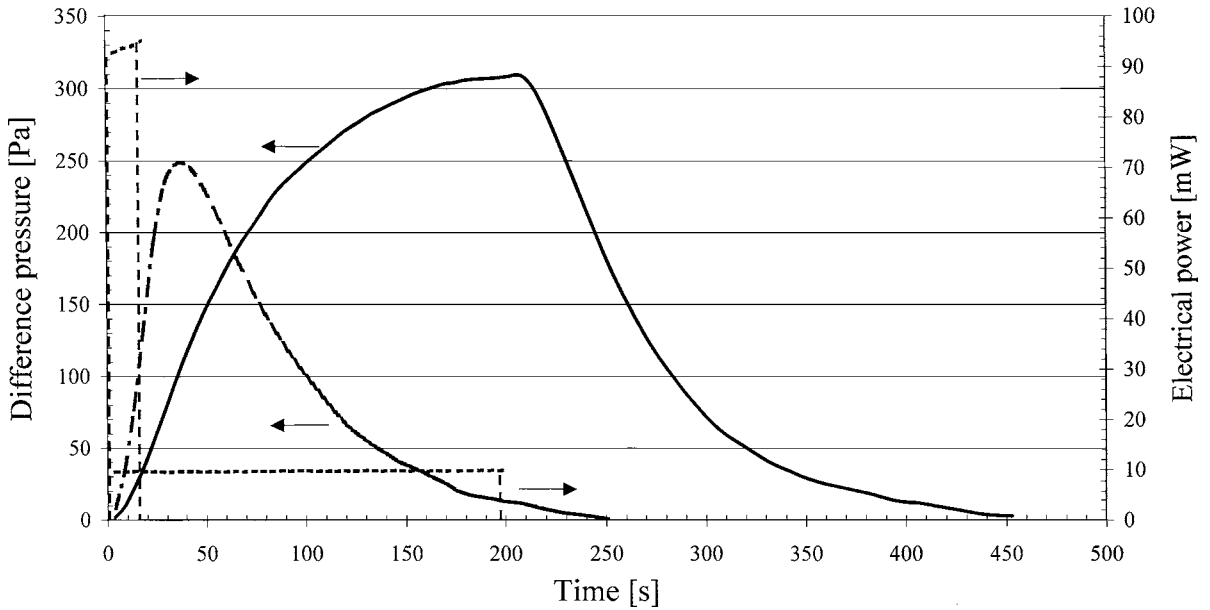


Fig. 3. Signals of the difference pressure manometer P3 of SGC (Fig. 1) for two calibration experiments. Ohmian heat supplied, 2 J. Electric power input: 10 mW (---); 100 mW (- - -).

air at 0.1 MPa as “sorptive gas” in an adsorption vessel made of glass. In both experiments, the same electric energy (2 J) but with different power, namely 10 and 100 mW has been supplied to the electric resistor (dashed lines in Fig. 3). Hence, the areas covered by the electric power signals in Fig. 3 are the same for both experiments. Again helium at 120 kPa and 77 K was used as sensor gas.

Obviously, the pressure difference signals corresponding to the two calibration experiments differ considerably from each other and so do the areas covered by them above the base line, i.e. the time axis in Fig. 3. This is indicating that the curves reflect different mechanisms of heat transfer as they probably are caused by different convective flows initiated by the release of the Ohmian heat from the electric resistor to the air included in the adsorption chamber. In case of the short time but high electric power (100 mW) heat release, the convective flow in the air may well be restricted to a fairly narrow zone in the vicinity of the resistor being turbulent and also accompanied by sublimation and again desublimation of small amounts of water being frozen at the inner walls of the adsorption vessel. Also evaporation and re-condensation of liquid oxygen at the bottom of the adsorption vessel may have an impact to the heat transfer process observed.

In the other calibration experiment where Ohmian heat was supplied at low power (10 mW) but during a much longer time period, the pattern of convective air flow inside the adsorption vessel presumably was basically different from the first one. We suppose the convective flow of air was fairly slow, but spread out in the whole of the adsorption vessel, thus changing the k -value for heat transfer from the vessel to the sensor gas considerably. Also, the pattern of convective flows in the sensor gas surrounding the adsorption chamber, which are initiated by the two calibration experiments, may be different. According to rough estimations of the respective Grasshoff numbers, we expect in the first experiment (100 mW) convection in the sensor gas to occur whereas in the second experiment (10 mW) it seems to be unlikely. This indicates, that the basically different pressure signal curves in Fig. 3 simply reflect different heat transfer mechanisms in both the sorptive gas (air) in the adsorption chamber and the sensor gas (helium) in the gas thermometer 1 (Fig. 1). Taking the different character of the calibration signals (Fig. 3) into account we expect a relation of type:

$$Q = K(P) \int_0^{\infty} (p(t) - p^*) dt, \quad (3)$$

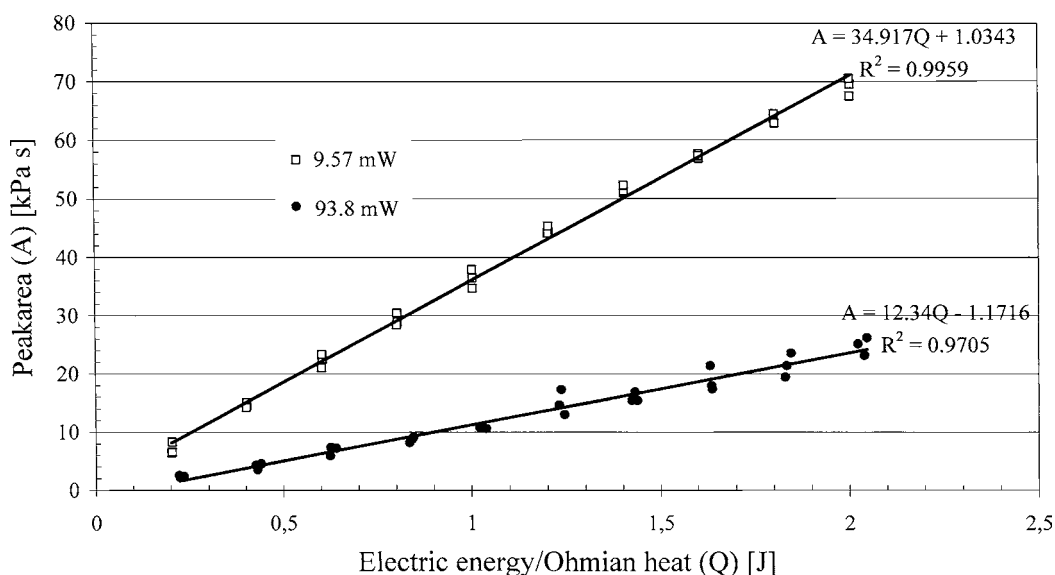


Fig. 4. Time integral of difference pressure signal (A) in kPa as function of the total energy (Q) in J of the Ohmian heat introduced into the SGC. Electric power of calibration signals: 9.57 mW (□); 93.8 mW (●).

to hold between the heat Q released at constant power P from the electric resistor and the time integral of the pressure signal ($p(t) - p^*$). This is the case indeed as can be recognized from Fig. 4, showing fairly linear relations between the electric energy supplied to or heat released from the resistor ($Q < 2$ J) and the area below the $p-t$ curves of the corresponding signals in kPa. The slope of the lines is increasing with decreasing (constant) electric power as indicated in the figure.

The steepness of the lines can be considered as “sensitivity” of the SGC as the “peak area” A below the $p-t$ curves for given heat Q released is the larger, the steeper the corresponding line in Fig. 4 is. This relation for sake of clarity is sketched in Fig. 5, showing that the SGC is highly sensitive for heat signals released slowly, i.e. at low power but during a long time, whereas for highly intensive but short heat pulses the sensitivity is decreasing considerably. However, as can be recognized from Fig. 5, the sensitivity of the SGC is approaching an asymptotic value of ca. 12 kPa/J for calibration signals of power $P > 80$ mW. This corresponds to fast adsorption processes occurring often at low sorptive gas pressure (example given in Fig. 6).

In view of relation 3, it is recommended to provide to any gas adsorption experiment also calibration experiments showing fairly similar $p-t$ curves. Only in

such a situation the values of the $K(P)$ coefficients in Eq. (3) can assumed to be the same for the adsorption and the calibration experiment, i.e. the heat of adsorption to be proportional to the peak area of the pressure signal with the $K(P)$ -value determined from a corresponding calibration experiment. An example for such a situation is shown in Fig. 6 corresponding to adsorption of nitrogen at $T = 77$ K, $p = 250$ Pa on a reference material BAM-CRM-PM-104 developed by the Bundesanstalt für Materialforschung (BAM) (Federal Institute of Materials Research), Berlin, Germany.

As can be recognized from Fig. 6, the pressure signal caused by the heat of adsorption is similar to a signal produced by a calibration experiment providing Ohmic heat of 2 J at a power of 100 mW. Hence, the heat of adsorption Q can be calculated from Eq. (3), i.e. the relation:

$$\frac{Q}{Q_{\text{cali}}} = \frac{\int_0^{\infty} (p(t) - p^*) dt}{\int_0^{\infty} (p_{\text{cali}}(t) - p^*) dt}, \quad (4)$$

yielding the numerical value $Q = 2.3$ J. A more detailed analysis of the relation between a certain amount of heat Q released from the adsorption vessel and the “peak area” A , i.e. the time integral of the pressure signal will be given in a forthcoming paper.

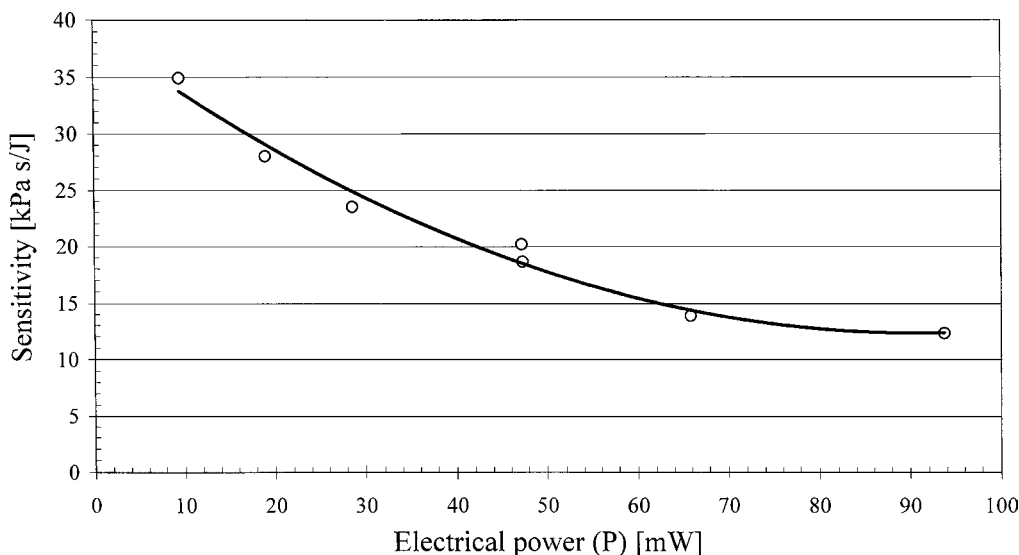


Fig. 5. Sensitivity of a SGC defined as the slope of the calibration lines in Fig. 4 in kPa/J as function of the (constant) power in mW of the Ohmic heat calibration signals introduced into the SGC. Gas in adsorption vessel, He; 77 K; 0.1 MPa. Sensor gas, He; 77 K; 0.12 MPa.

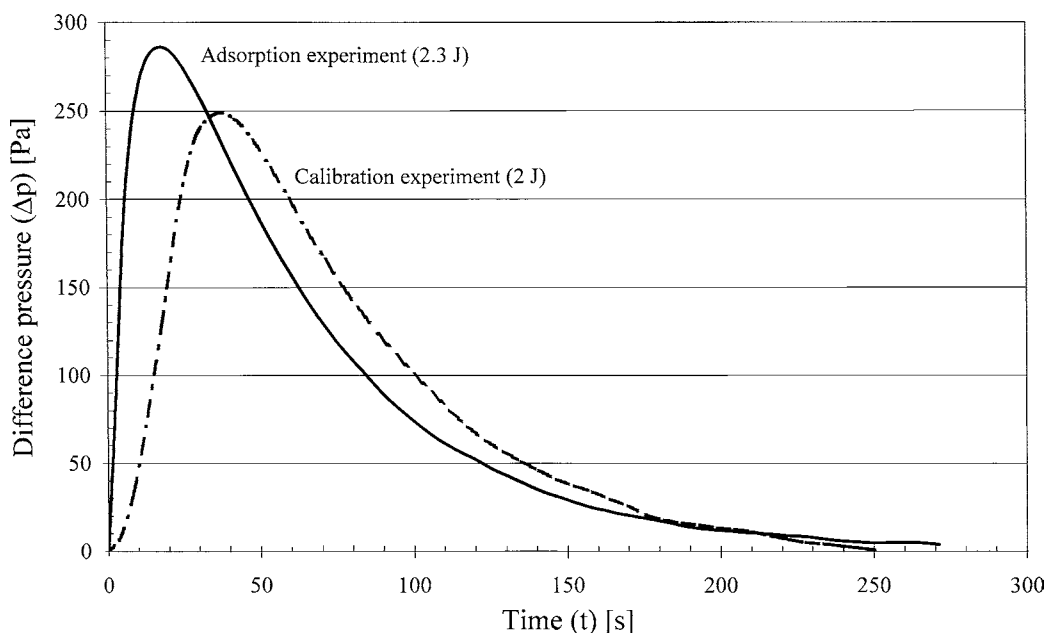


Fig. 6. Signals of difference pressure manometer. (—) Adsorption of N_2 on sorbent BAM-CRM-PM-104 at 77 K; 0.20 kPa. (---) Calibration experiment: Ohmic heat, 2 J; He; 77 K; 0.1 MPa.

4. Examples

Several types of sorption systems already have been analyzed in our laboratory by combined volumetric

and calorimetric measurements using a SGC. Two examples are presented here. In Fig. 7, differential heats of adsorption and desorption (Δh^{ads}) of nitrogen on BAM-CRM-PM-104 at 77 K for specific amounts

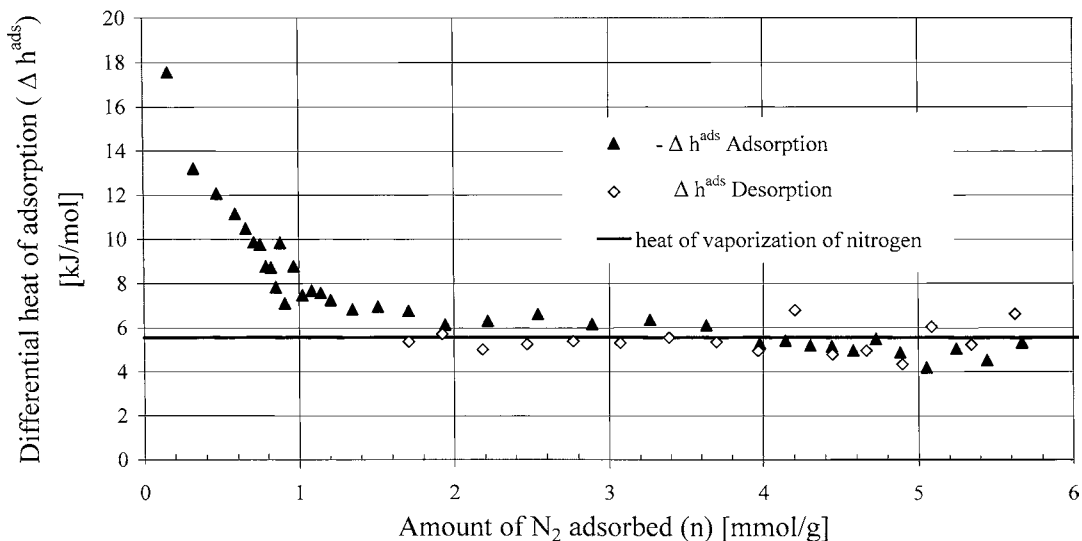


Fig. 7. Differential heats of adsorption and desorption (h^{ads}) of nitrogen on BAM-CRM-PM-104 at 77 K as function of the amount of N_2 adsorbed (n).

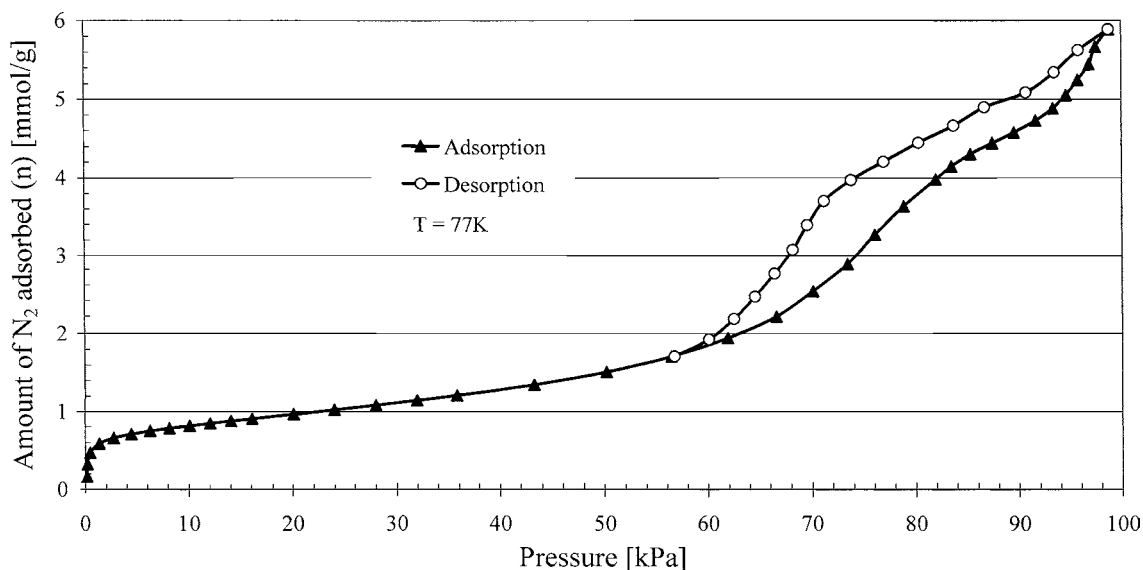


Fig. 8. Adsorption and desorption isotherms of nitrogen on BAM-CRM-PM-104 at 77 K for pressures up to ambient.

adsorbed (n) up to 6 mmol/g corresponding to pressures up to ambient (0.1 MPa) are shown. The corresponding Gibbs excess adsorption isotherms are given in Fig. 8.

Uncertainties of data shown in Fig. 7 are about 5–10%. This unsatisfying situation can be improved by using a sensor gas of low heat capacity such as H_2 or Ne at 77 K and at an “optimized” pressure inside the gas thermometers 1 and 2 (Fig. 1). Experiments performed so far at different temperatures indicate that the sensitivity of SGC (Fig. 5), decreases with increasing temperature but increases with increasing thermal conductivity of both the sorptive and the sensor gas. Results will be reported in a forthcoming paper.

Contrary to the hysteresis shown in the adsorption isotherms (Fig. 8), no such a phenomenon could be observed for the adsorption enthalpies. However, in view of uncertainties of enthalpy data in Fig. 7, more measurements are needed to definitively answer the question of existence of an hysteresis in the heats of adsorption.

The isotherms shown in Fig. 8 are identical to those resulting from interlaboratory tests guided by BAM [23]. Numerical values of data presented in Figs. 7 and 8 are available from the authors as data files upon request. The second example to be presented refers to the adsorption of subcritical carbon dioxide on zeolite

Na13X (UOP) (Si/Al \approx 1–1.5), and Wessalite DAY at 298 K for pressures up to 1 MPa. Mean pore sizes are 0.3 nm for zeolite Na13X and 0.4 nm for Wessalite DAY, respectively.

In Fig. 9, differential heats of adsorption Δh^{ads} are depicted for specific amounts of CO_2 adsorbed up to 4 mmol/g. Uncertainties of data again are about 5–10%. The differential heats of adsorption Δh^{ads} decrease with increasing amounts of CO_2 adsorbed approaching values of about -40 kJ/mol for Na13X and -30 kJ/mol for DAY zeolite. These data are much lower than the bulk heat of condensation of CO_2 which is about -5.2 kJ/mol. However, we could observe convergence of Δh^{ads} data to this value at adsorbate loads of 4–5 mmol CO_2 /g sorbent material. This decrease (of absolute values) of Δh^{ads} is very well known in the literature [23]. It reflects the occurrence of secondary adsorption being characterized by new sites within the zeolite-cages having much weaker interaction energies than the primary adsorption sites being filled in the range of 1–3.5 mmol CO_2 /g sorbent. In Fig. 9 also data from the literature [24] have been added, referring to adsorption of CO_2 on NA13X zeolite at 304.4 K. Taken the different temperatures into account to which our data and data from [24] refer, the coincidence between the two sets of data is reasonably well within the range of mass of adsorbate

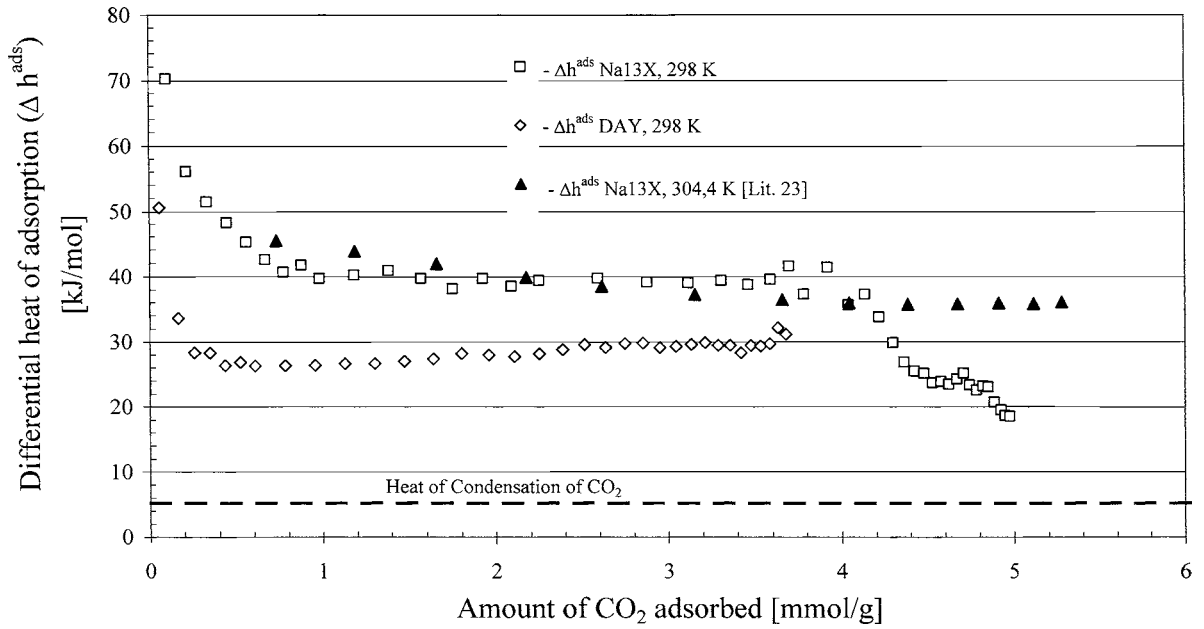


Fig. 9. Differential heats of adsorption of carbon dioxide on zeolite Na13X (UOP) and wessalite DAY at 298 K for specific amounts adsorbed of up to 4 mmol/g, i.e. pressures up to 1 MPa. In addition data from the literature [22] for adsorption of CO_2 on zeolite Na13X at 304.4 K are recorded.

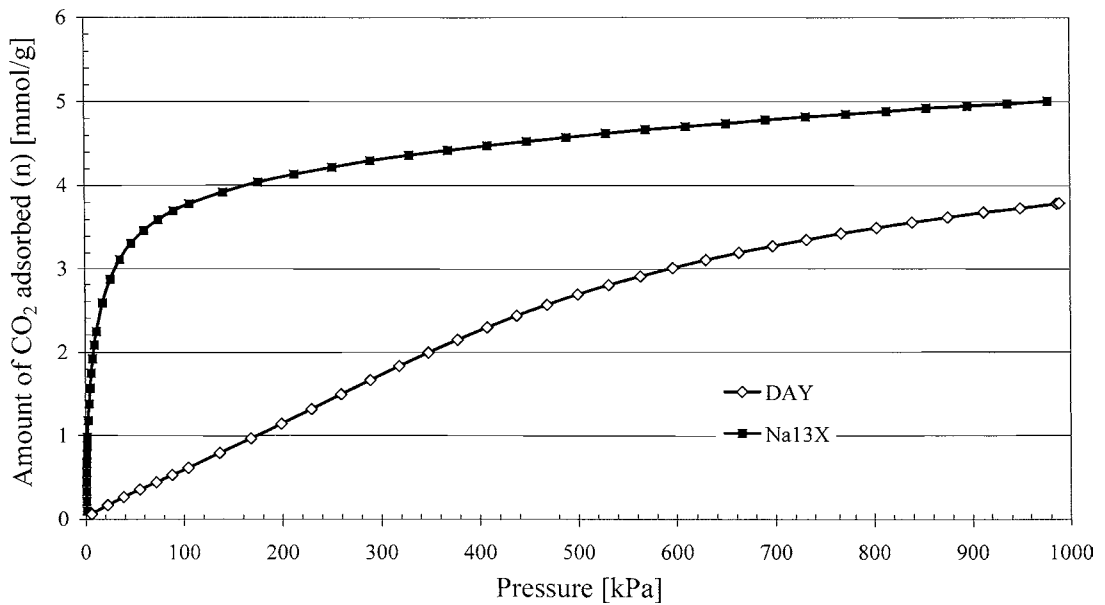


Fig. 10. Adsorption isotherms of carbon dioxide on zeolite Na13X (UOP) and wessalite DAY at 298 K for pressures up to 1 MPa.

1–4 mmol CO₂/g sorbent. The deviation between our data (hollow symbols) from [22] (filled symbols) in the range 4–5 mmol CO₂/g sorbent may well be due to the fact that measurements in [22] refer to pure zeolite Na13X, whereas our data were taken on technical sorbent pellets including not only zeolite Na13X but about 20 wt.% of a technical binder.

The corresponding Gibbs excess adsorption isotherms of the systems mentioned above are given in Fig. 10. They are considerably different for the hydrophilic zeolite (Na13X) and the strongly hydrophobic zeolite (DAY).

No hysteresis phenomena could be observed, i.e. adsorption and desorption branches of isotherms turned out to be identical.

Numerical values of data presented in Figs. 9 and 10 can be provided by the authors upon request. Data show that the heats of adsorption at low coverage for Na13X are nearly twice as large as for DAY. Consequently, one would expect in the low pressure region the adsorption isotherms of Na13X to be much steeper as that of DAY. This indeed is the case and shows physical consistency of data in Figs. 9 and 10. For molecular interpretation of all the data and curves presented above, the reader is referred to the literature [9].

Acknowledgements

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References

- [1] R.T. Yang, *Gas Separation by Adsorption Processes*, Butterworths, London, 1987; Imperial College Press, London, UK, 1997.
- [2] D.M. Ruthven, F. Shamsuzzaman, K.S. Knaebel, *Pressure Swing Adsorption*, VCH Publishers, New York/Weinheim, 1994.
- [3] Sh. Sircar, *Adsorpt. Sci. Technol.* 19 (2001) 347–366.
- [4] Sh. Sircar, *Adsorption* 6 (2000) 359–365.
- [5] M.S. Ray, *Adsorpt. Sci. Technol.* 17 (1999) 205; M.S. Ray, *Adsorpt. Sci. Technol.* 18 (2000) 439; M.S. Ray, *Adsorpt. Sci. Technol.* 19 (2001) 821.
- [6] A. Dabrowski (Ed.), *Adsorption and its Applications in Industry and Environmental Protection*, vols. 1–2, Elsevier, The Netherlands, 1998.
- [7] W. Kast, *Adsorption aus der Gasphase. Ingenieurwissenschaftliche Grundlagen und technische Verfahren*, Verlag Chemie, Weinheim, Germany, 1988.
- [8] K. Kaneko, et al. (Eds.), in: *Proceedings of the Seventh Conference on Fundamentals of Adsorption (FOA7)*, Nagasaki, Japan, May 2001, © International Adsorption Society (IAS), IK International, Chiba-City, Japan, 2002.
- [9] F. Rouquerol, J. Rouquerol, K.S.W. Sing, *Adsorption by Powders and Porous Solids*, Academic Press, San Diego, USA, 1999.
- [10] J. Rouquerol, Chairman, IUPAC Subcommittee on COPS, *Pure Appl. Chem.* 66 (1994) 1739–1758.
- [11] J.U. Keller, et al., *Sorption measurement techniques/instruments*, in: F. Rodriguez-Reinoso (Ed.), *Proceedings of the Sixth International Symposium on the Characterization of Porous Solids (COPS 6)*, Alicante, Spain, 8–11 May 2002, Elsevier, New York, in press.
- [12] D.M. Ruthven, *Principles of Adsorption and Adsorption Processes*, Wiley, New York, 1984.
- [13] D.D. Do, *Adsorption Analysis: Equilibria and Kinetics*, Imperial College Press, Singapore, 1998 (Uto-Print).
- [14] D.U. Rao, S. Sircar, *Adsorpt. Sci. Technol.* 19 (2001) 887–894.
- [15] K. Gubbins, in: K. Kaneko (Ed.), *Proceedings of the Seventh Conference on Fundamentals of Adsorption (FOA7)*, Nagasaki, Japan, May 2001, manuscript in preparation.
- [16] L. Sarkisov, P.A. Monson, in: K. Kaneko (Ed.), *Proceedings of the Seventh Conference on Fundamentals of Adsorption (FOA7)*, Nagasaki, Japan, May 2001, manuscript in preparation.
- [17] VDI-Richtlinien Nr. 3674, *Abgasreinigung durch Adsorption, Prozessgas- und Abgasreinigung*, Ausgabe Mai 1998, VDI/DIN-Handbuch Reinhaltung der Luft, Bd. 6, VDI-Verlag, Düsseldorf, 1998.
- [18] F. Siperstein, R.J. Gorte, A.L. Myers, *Langmuir* 15 (1999) 1570–1576.
- [19] D. Shen, M. Bülow, F. Siperstein, M. Engelhard, A.L. Myers, *Adsorption* 6 (2000) 275–286.
- [20] W. Hemminger, G. Höhne, *Grundlagen der Kalorimetrie*, Verlag Chemie, Weinheim, Germany, 1979.
- [21] W. Langer, *Ein Wärmeleitungs-Gasdruck-Kalorimeter und die simultane Messung von Isothermen und Wärmen der Adsorption von N₂ an SiO₂*, Dissertation, FB Chemie-Biologie, Universität Siegen, 1994.
- [22] Bundesanstalt für Materialforschung und -prüfung, Certificate, reference material alumina TYPE 150 (Al₂O₃) CRM-BAM-PM-104, 13 March 2002.
- [23] V. Solinas, I. Ferino, *Catal. Today* 41 (1998) 179–189.
- [24] J.A. Dunne, M. Rao, S. Sircar, R.J. Gorte, A.L. Myers, *Langmuir* 12 (1996) 5896–5904.