

Dynamic calibration of a sensor gas calorimeter for measurement of heat generation rates during kinetic of adsorption experiments

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Abstract

A procedure for dynamic calibration of a sensor gas calorimeter, resulting with a calibration transfer function, instead with a calibration line, is presented. The main factors influencing the calibration transfer function have been assessed. The calibration transfer function enables measurement of the heat generation rates during adsorption, necessary for obtaining a complete picture about adsorption kinetics.

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1. Introduction

The sensor gas calorimeter, which has been presented in detail in [1], is a new type of calorimeter designed for simultaneous measurement of adsorption isotherms and heats of adsorption. It consists of a volumetric/manometric gas adsorption instrument, the adsorption cell of which is surrounded by a constant volume jacket filled with a chosen sensor gas. When heat is generated inside the adsorption cell, it is transferred to the gas in the jacket, causing increase of its temperature, and consecutively, its pressure. The pressure difference between the sensor gas in the jacket and a reference vessel, kept at constant temperature, is registered and used as a measure of the heat effects within the adsorption vessel. From the continuous measurements of the pressure difference during adsorption, it would be possible to measure the rate of heat generation during the process.

The calibration procedure associated with the equilibrium measurements is based on generation of known amounts of heat inside the adsorption cell, by passing electric current through an electrical resistor placed instead of the adsorbent

sample, and integrating the pressure response curve over time [1].

In this paper we present a different calibration procedure, aimed to application of the sensor gas calorimeter for kinetic measurements, which are as essential for investigation of adsorption systems and design of adsorption processes as the equilibrium ones [2]. For that purpose, a calibration transfer function is needed, instead of a calibration line. These are the results of a preliminary investigation, performed in order to develop a procedure for dynamic calibration and to determine the main factors that have to be taken into account.

2. Definition of the calibration transfer function

The calibration is performed by time-controlled generation of heat inside the adsorption cell, by supplying pulses of electric power $P(t)$ to an electric resistor placed in it, and recording the measured pressure difference signals. By analysis of the input and output signals, the transfer function correlating the change of the pressure of the sensor gas and the electric power G_{cal} can be determined. The idea of dynamic calibration is based on the assumption that the calorimeter can be approximately represented as a series of two elements (Fig. 1): the adsorption cell, in which the heat is generated (as heat of adsorption during real adsorption experiments,

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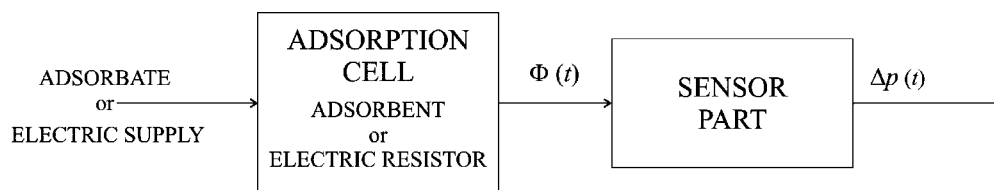


Fig. 1. A schematic block diagram of the sensor gas calorimeter.

or as Joule heat during calibration experiments), and a sensor part, in which the released heat is transferred through the adsorption cell wall to the sensor gas at a rate $\Phi(t)$, and transformed into the differential pressure signal $\Delta p(t)$. During the calibration experiments the dynamics of the process of heat release is supposed to be very fast, i.e. the heat flow rate through the adsorption vessel wall $\Phi(t)$ is considered to

be identical to the electrical power supplied to the resistor $P(t)$. In that case the estimated calibration transfer function is actually corresponding to the sensor part of the calorimeter, and we could say that $G_{\text{cal}} \approx G_{\text{sen}}$, where G_{sen} is the transfer function of the sensor part of the calorimeter, which is essentially the same during the adsorption and the calibration experiments.

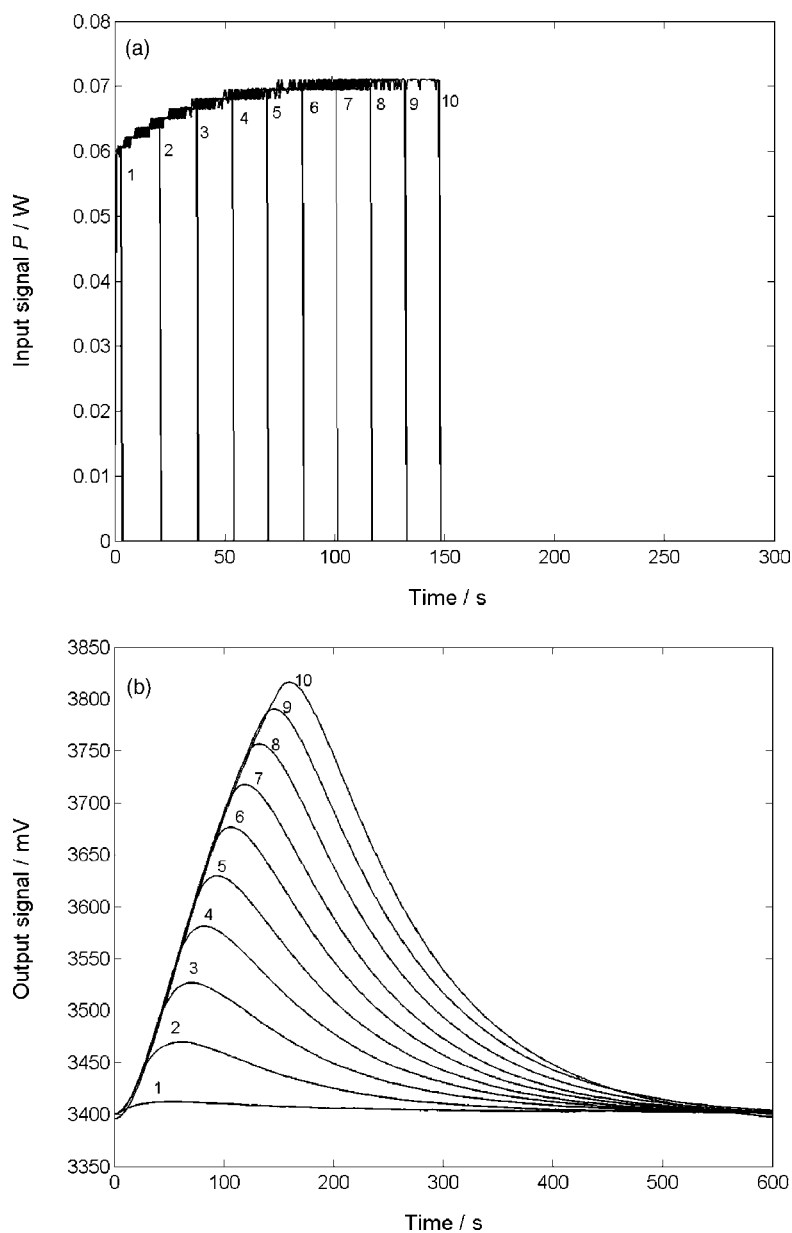


Fig. 2. An example of the input (a) and output (b) signals during calibration (sensor gas N_2 , pressure 100 kPa).

3. Experimental procedure

The experimental calibration procedure is similar to the one presented in [1]. During one experiment a pulse of electric power is supplied to the electric resistor and recorded, together with the pressure difference signal. The resistor used in our experiments had the following characteristics: nominal electrical power 0.25 W, mass 0.082 g, shape cylindrical, size 1.9 mm × 5.5 mm. In order to investigate the influence of the main factors on the calibration transfer function, the calibration was performed with three different sensor gases: He, N₂ and SF₆ and for four starting sensor gas pressures: 100, 120, 140 and 160 kPa. The results presented in this paper were obtained at 25 °C.

The electric power pulses were approximately trapezoidal. In order to check the system linearity, experiments with 10 different input signals with overall energy supply in the range from −0.25 to −10 J were performed. As an example, in Fig. 2b are presented the raw experimental data obtained for N₂ and 100 kPa, and for all 10 different inputs, shown in Fig. 2a (all input pulses shown in this figure start from the origin).

4. Estimation of the calibration transfer functions

The experimental calibration transfer functions were obtained in the frequency domain, as ratios of the Fourier transforms of the output (pressure difference) and input (electric power) pulses [3]:

$$G_{\text{cal}}(j\omega) = \frac{\mathcal{F}\{\Delta p(t)\}}{\mathcal{F}\{P(t)\}} = \frac{\int_0^{\infty} \Delta p(t) e^{j\omega t} dt}{\int_0^{\infty} P(t) e^{j\omega t} dt} \quad (1)$$

The Fourier transforms were calculated by numerical integration over finite time intervals in which the input and output pulses were different from zero. One example of the frequency transfer functions, estimated from the experimental data given in Fig. 2, is presented in Bodé plot form [3], in Fig. 3.

The shapes of the amplitude and phase functions suggest use of a second-order model:

$$G_{\text{cal,m}}(j\omega) = \frac{K}{(\tau_1 j\omega + 1)(\tau_2 j\omega + 1)} \quad (2)$$

The model parameters (gain K and time constants τ_1 and τ_2) were estimated by fitting the amplitude and phase functions obtained from the experimental data, to the ones corresponding to Eq. (2)

$$\text{AR}(\omega) = \frac{K}{\sqrt{(\tau_1^2 \omega^2 + 1)(\tau_2^2 \omega^2 + 1)}} \quad (3)$$

$$\varphi(\omega) = -\arctan(\tau_1 \omega) - \arctan(\tau_2 \omega) \quad (4)$$

The least-squares method was used. The model amplitude and phase functions are also presented in Fig. 3. The agree-

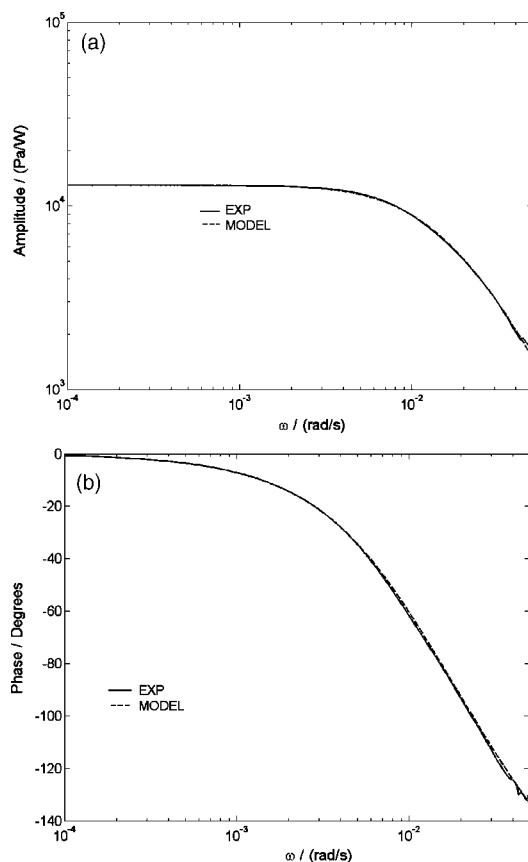


Fig. 3. An example of the calibration transfer function in Bodé plot form: (a) amplitude and (b) phase (N₂, pressure 100 kPa).

ment between the experimental and the model functions is excellent.

Practically, the same transfer functions were obtained when the sensor gas and pressure were kept constant, and the size of the input signal was changed, showing that the sensor part of the calorimeter was linear in the investigated range of parameters. A slight nonlinearity was observed only for SF₆ (the gain K slightly decreased with the increase of the total energy supplied to the electric resistor).

Also, the estimated transfer function was practically insensitive of noise (filtering the raw data resulted with practically no change in the estimated transfer function). This is not unexpected, regarding the fact that the transfer function is obtained by integration, and integration, on the other hand diminishes the influence of noise.

5. Influence of the sensor gas and pressure

The influences of the type and pressure of the sensor gas on the model parameters were investigated. The results are presented in Fig. 4a (the gain K vs. pressure for the three gases investigated) and Fig. 4b (the time constants τ_1 and τ_2 vs. pressure).

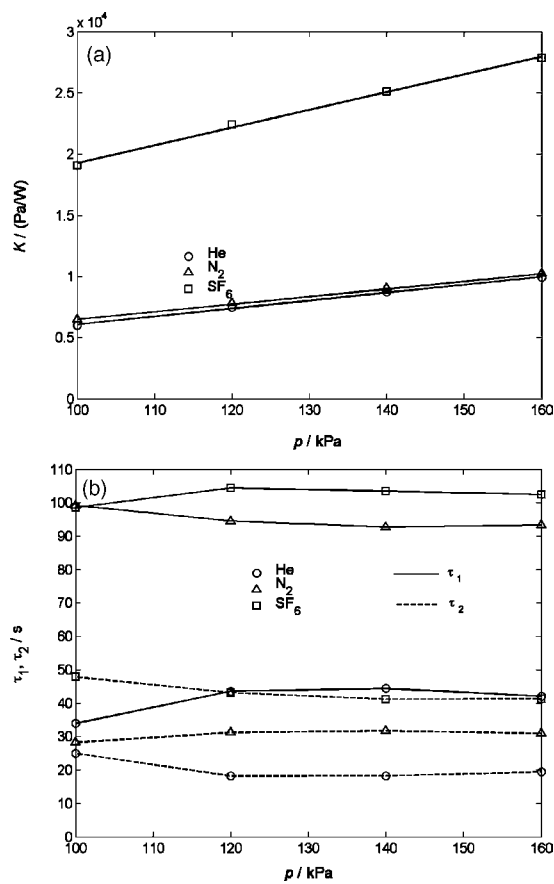


Fig. 4. The calibration transfer function model parameters as a function of the sensor gas pressure, for three sensor gases: (a) gain and (b) time constants.

The following conclusions follow from Fig. 4:

1. The gain increases linearly with the pressure of the sensor gas, while the time constants change with pressure only slightly, and to the opposite direction, meaning that, in the investigated range, the influence of the pressure of the sensor gas on the dynamics of the sensing part of the calorimeter can be neglected.
2. Both the gain and the time constants depend considerably on the sensor gas. The sensitivity of the calorimeter, which is determined by the value of the gain K , is highest for SF_6 , while it is nearly the same for He and N_2 . On the other hand, the fastest response, corresponding to the smallest values of the time constants is obtained for He, and the slowest with SF_6 .

The second-order transfer function of the sensor part of the calorimeter is an approximate mathematical representation of a complex process of heat transfer involving conduction, convection and radiation. The physical parameters of the sensor gas, such as heat capacity and heat conductivity, influence this process, and consecutively the gain and time constants of the sensor part of the calorimeter.

6. Influence of the electrical resistor used for calibration

The calibration procedure using an electrical resistor is based on the assumption that the resistor itself does not influence the results, i.e. that the electrical energy supplied to the resistor is instantaneously transferred to the adsorption cell wall, as heat. In order to check the validity of this assumption, a set of calibration experiments with a different resistor of much larger mass and dimensions (mass 2.261 g, rectangular in shape, size 25 mm \times 6 mm \times 6 mm), was also performed, and analyzed in the same way as previously. The dynamic response for this case was much slower than with the original, smaller resistor, and the transfer function obtained by Fourier transform corresponded to a third-order system. For example: the time constants obtained with He at pressure 100 kPa were 152.2, 15.092 and 15.092 s, as opposed to 33.906 and 25.026 s obtained with the smaller resistor. This difference was a result of the dynamics of the resistor itself, which can be easily showed to be a first-order system [3]. In order to have a reliable calibration system, it is crucial to use a resistor that is small enough, so that its dynamics does not influence the results.

The fact that the transfer function corresponding to the smaller resistor is of the second order, while the one corresponding to the bigger one is of the third order, indicates that the dynamics of the smaller resistor could be negligible. Nevertheless, more detailed analysis is needed for correct choice of the electric resistor for calibration.

7. Conclusions

7.1. Further investigation—need for optimization

The preliminary work on dynamic calibration of the sensor gas calorimeter, presented in this paper, has shown two important things:

1. The calibration transfer function is influenced by the electric resistor used. For that reason, in our future investigations, the choice of the resistor for calibration measurements will be optimized, primarily regarding its size and mass, but also regarding its shape which determines the contact between the resistor and the wall of the adsorption vessel. The influence of the position of the resistor inside the adsorption vessel will also be investigated.
2. The type and pressure of the sensor gas also influences the calibration transfer function. As opposed to equilibrium measurements, when only the sensitivity and linearity are of interest, for kinetic measurements, the dynamics is also important. Our preliminary results, presented in this paper, show that the increase of the sensor gas pressure results with higher sensitivity, and practically no change of dynamics. On the other hand, regarding the choice of sensor gases, SF_6 would be the best choice regarding the sensitivity, but the worse regarding the dynamics and lin-

earity aspects, while He would be the best regarding the dynamics, but the worse regarding the sensitivity. More extensive investigation with different sensor gases and in wider pressure range is planned, in order to optimize the choice of the sensor gas and its pressure. Another aim of this investigation will be to establish some relations between the static and dynamic parameters of the calibration transfer function and the physical parameters of the sensor gas. Influence of temperature and type and pressure of the gas present in the adsorption vessel will also be investigated.

7.2. The significance of the calibration transfer function

Once having a good calibration transfer function $G_{\text{cal}}(j\omega)$ representing the dynamics of the sensor part of the calorimeter (i.e., if $G_{\text{cal}} = G_{\text{sen}}$ is fulfilled), it can be used for estimation of the heat flow rate from the adsorbent to the sensor gas during adsorption, from the pressure difference signal measured during the adsorption process $\Delta p_{\text{ads}}(t)$. This heat flow rate can be obtained by inverse Fourier transform of

the ratio of the Fourier transform of the differential pressure signal and the calibration transfer function:

$$\Phi(t) = \mathcal{F}^{-1} \left\{ \frac{\mathcal{F}\{\Delta p_{\text{ads}}(t)\}}{G_{\text{cal}}(j\omega)} \right\} \quad (5)$$

On the other hand, this heat flow rate is directly correlated to the heat generation rate during adsorption. Not only that these results can be used for estimation of the heats of adsorption, but in addition to that, together with information about adsorption rates (obtained by standard volumetric measurements), they represent an important part of the adsorption kinetics picture.

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