

## **ADSORPTION EQUILIBRIA OF CO/H<sub>2</sub> WITH A MAGNETIC SUSPENSION BALANCE**

### **Purely gravimetric measurement**

*F. Dreisbach\**, *R. Seif* and *H. W. Lösch*

Rubotherm Präzisionsmesstechnik GmbH, Universitäts str. 142, 44799 Bochum, Germany

### **Abstract**

Adsorption equilibria of pure gases and binary gas mixtures can be measured with a new magnetic suspension balance. For this measurement no additional concentration measurement is required, neither for the gas phase nor for the adsorbed phase. The new instrument allows gravimetric adsorption measurements in a wide range of pressure (UHV...50 MPa) and temperature (210 K...570 K) to be performed. The experimental procedure and the instrument set up is fairly easy and can be compared to pure gas adsorption experiments. The new instrument and experimental procedure have been tested by performing coadsorption measurements with CO/H<sub>2</sub> mixtures on a commercial 5A zeolite.

**Keywords:** adsorption, equilibrium, gas mixture adsorption, gravimetry, magnetic suspension balance

### **Introduction**

Adsorption of gas or vapour mixtures on porous solids like activated carbon or zeolite is a widely applied operation in separation technology, such as gas separation, drying of gases, and purification of exhaust air [1]. The development, design and operation of these processes requires knowledge of mixture equilibria, i.e. coadsorption isotherms rather than pure component isotherms.

There are models available in the literature which can predict the mixture behaviour from pure component isotherms. However, the accuracy of these predictions is not usually sufficient to allow an engineer to economically design an adsorption separation process [2].

Therefore, there is a technical and economical demand to measure adsorption equilibria of mixtures on technically applied adsorbents. These measurements are performed nowadays only in a small number of laboratories world-wide. For these measurements in most cases non commercial, i.e. 'self-made', instruments are used, which are not usually automated and therefore need cost consuming operator time.

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\* Author for correspondence: E-mail: dreisbach@rubotherm.de

As a result of this, today gas mixture adsorption measurements are basically limited to non-profit organisations.

The conclusion may therefore be drawn that an instrument for measuring the adsorption equilibria of gas or vapour mixtures is of interest. This instrument should have the possibilities of being automated in order to reduce the experimental effort.

Consequently, a new magnetic suspension balance (MSB) and a new experimental procedure was developed which allows the adsorption equilibria of a binary gas or vapour mixture to be measured purely gravimetrically. This means that only the balance is used without any further analytical instrumentation such as, for example, gas chromatograph (GC) or mass spectrometer for concentration measurement. The principle behind the measurements, the instrument and the measurement procedure will be described in detail. Experimental data referring to the adsorption of the binary mixture CO/H<sub>2</sub> on a 5A zeolite will be given and discussed to a certain extent.

## New magnetic suspension balance

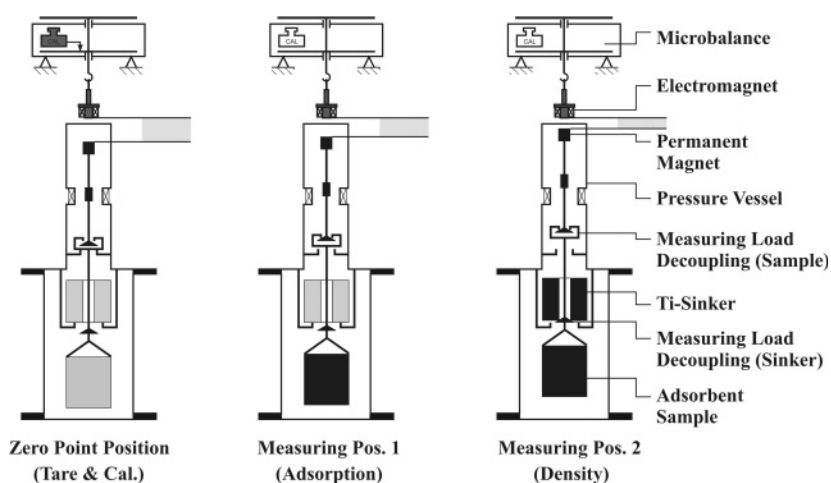
Coadsorption equilibria of gas mixtures can in principle be measured by combining the well known gravimetric method for measuring adsorption equilibria of pure gases with a measurement of gas phase composition, e.g. by GC [3]. One precondition for the application of this measurement method is, that the thermal equation of state (EOS) of the adsorptive gas mixture is known with sufficient accuracy, which is not the case for most technically important mixtures.

The employment of this method was until recently inhibited by the limitation of the commercially available gravimetric instruments to low pressures, a small temperature range and to non-corrosive gases [4]. Moreover, the necessary gas composition measurement device is expensive and the measurement of gas concentrations with these instruments time consuming.

### *Magnetic suspension balance*

The magnetic suspension balance (MSB) overcomes the disadvantages of the commercially available, 'normal' gravimetric instruments by separating the sensitive microbalance from the sample and the measuring atmosphere [4]. The principle of the magnetic suspension balance is shown in Fig. 1.

The mass change of samples in the measuring cell is transmitted through the (pressure and temperature resistant) wall of the pressure vessel. This is realised by an electromagnet/permanent magnet pair. The microbalance is located outside the measuring cell under normal, i.e. ambient, air conditions and carries the electromagnet. This electromagnet attracts the permanent magnet through the wall of the measuring cell in such a way, that the permanent magnet is held in a constant vertical position. The permanent magnet carries the sample and the permanent magnet/sample-system does not touch the measuring cell anywhere. By means of this free magnetic suspension, the mass and mass changes of the samples located under severe atmospheric conditions, (i.e. UHV <math>p < 200 \text{ MPa}</math>,



**Fig. 1** Magnetic suspension balance for the simultaneous measurement of sample mass and density of the gas phase [5]

measuring fluids) can be measured with high accuracy with the microbalance outside the measuring cell.

#### *Simultaneous sorption and density measurement*

A special type of magnetic suspension balance allows two samples located in the same measuring cell (under the same measuring atmosphere) to be measured [5]. This measuring principle is realised by establishing three different vertical positions of the permanent magnet and is also schematically shown in Fig. 1.

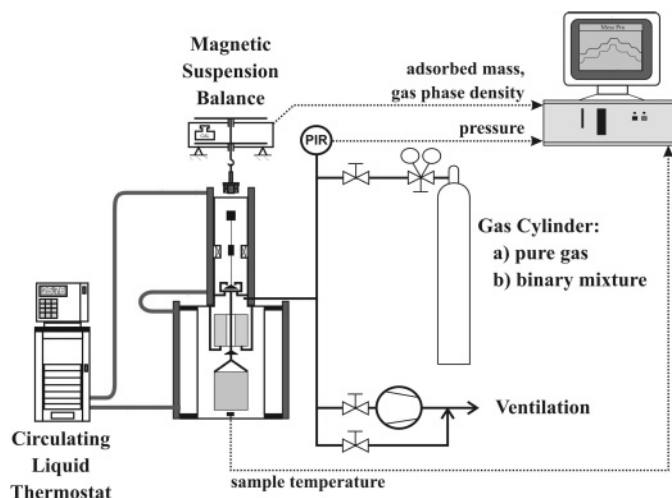
- In the so-called zero point position only the permanent magnet is freely suspended. Both samples rest on fixed supports in the measuring cell. The zero point position is similar to an empty balance, which allows for taring and calibrating the microbalance – even under process conditions. As a result of this, the long term stability and accuracy of the magnetic suspension balance is improved and is far better than those using conventional gravimetric instruments.
- In measuring position 1, the first sample is picked up by means of a controlled position change of the permanent magnet. Since the first sample is the crucible with the adsorbent material the mass and mass changes of the adsorbent are weighed in this position.
- In measuring position 2, the vertical position of the permanent magnet is changed again so that a second sample is picked up from its support. This second sample is a Ti-cylinder with calibrated volume. By weighing this calibrated volume in a gas or vapour atmosphere the buoyancy effect acting on it is measured. With this measurement the density of the gaseous atmosphere is determined according to Archimedes' principle.

With these two instrumental developments, the magnetic suspension balance and the simultaneous sorption and density measurement, the disadvantages previously mentioned of performing gravimetric mixture adsorption measurements are re-

solved. The magnetic suspension balance allows gravimetric measurements to be carried out under almost all conditions and the simultaneous density measurement avoids being dependent on the thermal EOS.

## Experimental procedure and installation

For performing purely gravimetric adsorption measurements with binary gas mixtures the experimental set up shown in Fig. 2 is used.



**Fig. 2** Set up for gravimetric measurements of adsorption equilibria of pure gases or binary gas mixtures

The balance is connected to a gas supply (gas cylinder). In the case of pure component adsorption the pure gas and in the case of mixture measurements the binary mixture with the known concentration ( $y_{\text{CO,FEED}}$ ) is fed from this gas supply to the balance. For activation, i.e. pre-treatment, of the adsorbent the measuring cell can be evacuated by means of a vacuum pump. The constant measuring temperature in the balance is established by a circulating fluid thermostat. The measurement procedure is the same for a single component as well as for a binary gas-mixture isotherm and can be divided into five steps:

- Re-activate the sample (evacuate the sample at elevated temperature).
- Increase the pressure at measuring temperature to the desired value either with the pure gas or with the mixture of known composition ( $y_{\text{CO,FEED}}$ ).
- Wait until equilibrium is established (i.e. mass of sample, pressure and temperature approach constant values).
- Record the equilibrium data: mass of sample and the density of gas phase with the MSB, measuring pressure and temperature.

- Continue measurement by filling gas or gas mixture for the next pressure (step 2.) or, if the maximum pressure to be investigated is reached, start new measurement with re-activation (step 1.).

## Experimental data analysis

In the case of pure gases the mass increase of the sample can be measured directly with the MSB. Only the buoyancy effect acting on the sample has to be corrected. The buoyancy is the product of the gas phase density  $\rho$ , which is measured directly with the balance, and the volume of the adsorbent  $V^S$  (cp. Eq. (1) given below). The quantity  $V^S$  has either to be determined experimentally or has to be known for the used adsorbent. Here experiments have been performed using helium as adsorptive gas for measurement of  $V^S$ .

For handling experimental data in the case of a binary mixture two calibration measurements have to be performed.

- The total inner (void) volume of the measuring cell of the magnetic suspension balance has to be determined (only once per instrument). Here this volume  $V^V$  has been measured by connecting a gas flow meter to the balance gas outlet and filling the empty balance with  $N_2$  to a pressure of 50 MPa and letting the gas flow out through the flow meter. By performing the material balance the resulting void volume was found:  $V^V=85.98\pm 0.06\text{ cm}^3$ .
- The thermal EOS of the binary mixture has to be measured if it is not known analytically (only once for each gas mixture and temperature). For this the magnetic suspension balance is used with an empty sample basket, i.e. without adsorbent material. The balance is filled with a binary gas mixture with known composition (i.e. known concentration of CO in the binary mixture in the gas cylinder,  $y_{CO,FEED}$ ) and the density of this mixture is measured with the density measuring possibility of the MSB described previously. For this work this is done for three different gas mixtures in the pressure range up to 6 MPa at  $T=303\text{ K}$ . The resulting  $\rho/y_{CO}/p$  data for the system CO/H<sub>2</sub> are fitted with a thermal EOS of virial type (Fig. 3).

Once these calibration data are known the handling of the experimental data of the binary gas mixture adsorption measurements can be performed as described below.

The experimental data measured in the isothermal coadsorption equilibrium are pressure  $p$ , balance reading for the adsorbent sample,  $\Delta m(p)$  and the density of the gaseous phase from MSB measurement,  $\rho(p)$ .

From the balance signal the total mass of gas mixture adsorbed  $m_{TOTAL}(p)$  can be determined by performing the buoyancy correction of the experimental data with the volume of the adsorbent  $V^S$  (measured with helium).

$$m_{TOTAL}(p)=\Delta m(p)+\rho(p)V^S \quad (1)$$

The mass of the gas phase  $m^f(p)$  present in the balance surrounding the sample can be calculated by multiplying the (gravimetrically measured) gas density  $\rho(p)$

with the void volume assessable for the gas phase (i.e. the total void volume  $V^V$  measured in the calibration experiment minus the volume of the adsorbent  $V^S$ ).

$$m^f(p) = \rho(p)(V^V - V^S) \quad (2)$$

Since the gas mixture being in the balance can only be adsorbed or be in the gas phase the sum of both masses (the mass adsorbed and the mass in the gas phase) must be equal to the mass of gas mixture which was filled in the balance from the gas supply.

$$m_{\text{FEED}}(p) = m_{\text{TOTAL}}(p) + m^f(p) \quad (3)$$

The gas mixture used for the measurements coming from the gas supply has a known, constant composition ( $y_{\text{CO,FEED}}$ ). This known composition allows calculation of the masses of both components of gas mixture filled into the balance from the gas cylinder:

$$m_{i,\text{FEED}}(p) = m_{\text{FEED}}(p)\omega_i(y_{\text{CO,FEED}}), \quad i = \text{CO}, \text{H}_2 \quad (4)$$

Here  $\omega_i(y_{\text{CO,FEED}})$  is the mass based concentration of component  $i = \text{CO}, \text{H}_2$  in the gas mixture delivered from the gas cylinder. With this treatment of purely experimental data, without any assumption, the mass of gas mixtures' components fed into the balance from the gas cylinder are known (without volumetric type measurement like for example using a gas manifold volume).

From these data a material balance can be made in order to distinguish the total mass adsorbed into the both components. For the component-wise material balance the composition of the gas mixture in the balance in the equilibrium state of adsorption is required.

This information is gained from the gravimetric density measurement. The density of a binary gas mixture at constant (i.e. measured) pressure and temperature is a well defined function of the composition. This function is shown in Fig. 3.

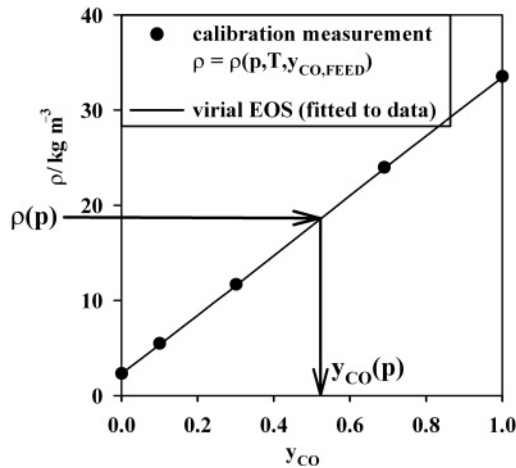


Fig. 3 Measured densities and virial EOS for the mixture of CO and H<sub>2</sub> at constant temperature and pressure ( $p=3$  MPa)

Using this functional dependence the composition of the gas mixture can be determined from the density/pressure measurement, if the thermal EOS is known. For these reasons precisely this thermal EOS for the binary mixture of interest has been measured in the calibration experiment (a virial EOS was fitted to the data from the calibration measurement).

As a result of this, the composition (i.e. concentration of component CO in the binary mixture) can be determined from the density measurement (Fig. 3).

$$y_{\text{CO}}(p) = f(\text{EOS}, \rho(p), p) \quad (5)$$

When the concentration of the gas phase is known, the total mass of gas phase in the balance in adsorption equilibrium  $m^f(p)$  (Eq. (2)) can be separated into both components:

$$m_i^f(p) = m^f(p) \omega_i(y_{\text{CO}}(p)), \quad i = \text{CO}, \text{H}_2 \quad (6)$$

Now all data are available to perform the material balance for the gas mixtures' components and to determine the mass adsorbed for each component of the binary mixture:

$$m_i(p) = m_{i,\text{FEED}}(p) - m_i^f(p), \quad i = \text{CO}, \text{H}_2 \quad (7)$$

From the partial masses adsorbed the number of molecules adsorbed,  $n_i$  can be calculated with the molar masses,  $M_i$  of the components as well as the concentration of the components in the adsorbed phase,  $x_i$  and the selectivity of the coadsorption for CO,  $S_{\text{CO}}$ .

$$n_i(p) = \frac{m_i(p)}{M_i}, \quad x_i = \frac{n_i}{n_{\text{CO}} + n_{\text{H}_2}}, \quad S_{\text{CO}} = \frac{x_{\text{CO}}/y_{\text{CO}}}{x_{\text{H}_2}/y_{\text{H}_2}}, \quad i = \text{CO}, \text{H}_2 \quad (8, 9, 10)$$

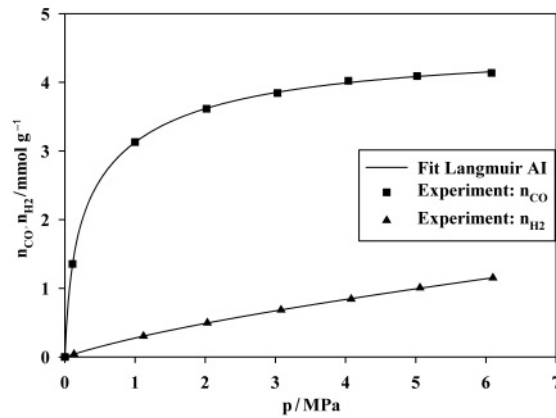
For the previously described data analysis only experimental data measured with the balance without any further analytical instrumentation for the concentration measurements have been applied.

## Results

The adsorption equilibria of the pure gases CO and H<sub>2</sub> and of the binary mixture CO/H<sub>2</sub> have been measured at  $T=303$  K on a 5A zeolite in the pressure range from vacuum to 6 MPa. For the experiments with gas mixtures three different feed gas compositions have been used ( $y_{\text{CO,FEED}}=0.1, 0.3$  and  $0.7$ ). In the Figs 4, 5 and 6 some of the experimental results are shown.

The experimental data for the adsorption of the pure gases are shown in Fig. 4 as symbols. The amount of CO adsorbed is approximately four times higher than the adsorption of H<sub>2</sub>. Both isotherms show the type I behaviour according to the IUPAC classification.

The pure gas adsorption data have been fitted with a Langmuir type isotherm. The data fits are shown as lines.

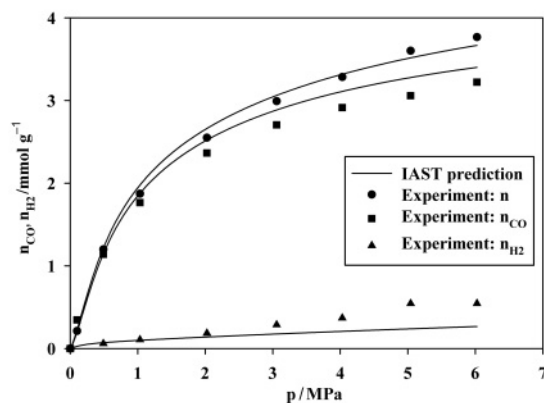


**Fig. 4** Experimental adsorption equilibria of pure gases CO and H<sub>2</sub> on 5A zeolite at 303 K (symbols) and fit of these data with isotherm of Langmuir type (lines)

The data of the adsorption of the gas mixture with the feed concentration  $y_{CO,FEED}=0.3$  are shown in Fig. 5 as symbols. Shown here is the total adsorption as well as the partial adsorption of the both components in the mixture in mmol g<sup>-1</sup>.

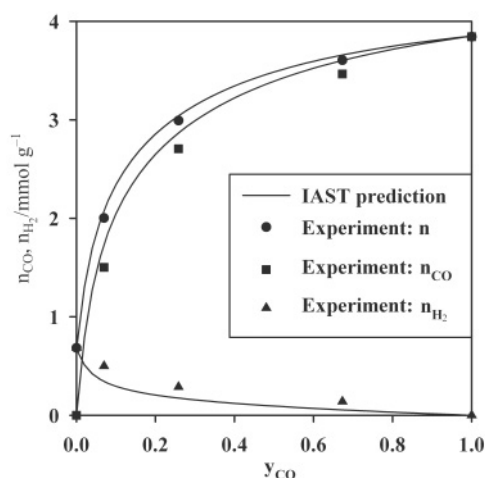
The ideal adsorbed solution theory (IAST) [6] has been used to predict the mixture adsorption from the pure gas data, which were described by the Langmuir isotherms. The IAST predictions are shown as lines. The total load can be predicted well with the IAST, whereas the adsorption of the components in the mixture can only qualitatively be predicted.

The deviations between IAST predictions and experimental data for all three measured mixture compositions are shown in Fig. 6. Here the adsorption of the components is shown over the gas phase composition for the constant pressure of 3 MPa. Shown are the experimental data for the total adsorption and the partial adsorption of the components in the mixture in mmol g<sup>-1</sup> over the gas phase concentration of CO.



**Fig. 5** Adsorption of mixture CO/H<sub>2</sub> ( $y_{CO,FEED}=0.3$ ) on 5A zeolite. Shown is the partial adsorption ( $n_{CO}$  and  $n_{H_2}$ ) and the total adsorption  $n=n_{CO}$  and  $n_{H_2}$  (symbols) and the prediction of the adsorption with the IAST (lines)





**Fig. 6** Adsorption of mixture CO/H<sub>2</sub> on 5A zeolite,  $p=3$  MPa. Shown is the partial adsorption in the mixture ( $n_{\text{CO}}$  and  $n_{\text{H}_2}$ ) and the total adsorption  $n=n_{\text{CO}}$  and  $n_{\text{H}_2}$  (symbols) and the prediction of the adsorption with the IAST (lines)

Generally the measured adsorption of CO in the mixture is smaller as it is predicted by the IAST. Vice versa the adsorption of H<sub>2</sub> in the mixture is measured to be higher as the prediction. Therefore, the experimentally measured selectivity for CO of the mixture adsorption is lower as it is predicted by the IAST from the pure gas data. However, the concentration and pressure dependency of the selectivity is qualitatively predicted right by the IAST.

A reason for this deviation of the IAST predictions from the experimental data may be the relatively small number of experimental pure gas data in the low pressure/low adsorption range. Therefore the determination of the Henry constant from these data, which is essential for performing the IAST predictions, is not sufficiently reliable. The reason for the small number of data points at low pressures is, that the pressure transducer used in the experimental installation has a full scale range of 50 MPa and thus could not be applied at pressures below 0.1 MPa with sufficient accuracy.

## Conclusions

Magnetic suspension balances allow extremely accurate gravimetric measurements of adsorption equilibria in a wide pressure and temperature range to be carried out, even with corrosive and/or toxic measuring gases. As a result of further improvement of the magnetic suspension balances a sorption measuring instrument was developed, which allows the simultaneous gravimetric measurement of adsorption equilibria and the density of the gas phase (adsorptive).

With this new instrument an experimental procedure has been realised, which allows the measurement of coadsorption equilibria of binary gas or vapour mixtures to be performed. Since the density measurement of the binary gas or vapour mixture is used as concentration measurement, no additional analytic instrumentation (e.g. GC) is required.

The handling of this purely gravimetric method of measuring binary gas or vapour adsorption equilibria is as easy as a gravimetric measurement of pure gas adsorption and can therefore be easily automated.

The new instrument was used to measure the adsorption equilibria of CO and H<sub>2</sub> and of three mixtures of these components on a commercial 5A zeolite at 303 K in the pressure range from vacuum to 6 MPa.

The measured pure gas data showed type I behaviour and have been fitted with an analytical isotherm of Langmuir type. The measured coadsorption equilibria showed a lower selectivity for CO compared to the prediction from pure gas data. The prediction of the mixture adsorption was calculated using the IAST and the analytical isotherms fitted to the pure gas data.

As a result of this work the method and instrument described above have proved to be suitable for obtaining fast and reliable measurements of gas mixture adsorption data, e.g. for screening different adsorbent materials. The instrument can be applied in a wide pressure range (UHV...50 MPa) and temperature range (210 K...570 K) with binary mixtures where the components have different molar masses ( $M_1 \neq M_2$ ). Sensitivity calculations have shown, that this method can be applied for measuring the adsorption of N<sub>2</sub>/O<sub>2</sub> mixtures if a sufficiently accurate pressure measurement for the pressure range of interest is used.

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