

SOURCES OF ERROR IN SORPTION AND DENSITY MEASUREMENTS

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Abstract

In sorption measurements, volumetric or gravimetric procedures are commonly used to determine the amount adsorbed. At low pressures, thermomolecular flow and pressure differences according to Knudsen's law disturb measurements. In volumetry, calibration of the dead space is required; in gravimetry, the influence of buoyancy has to be taken into account. In both cases, adsorption of the calibrating gas, usually helium, may disturb the measurements [1]. From the calibration measurements, the density of the sample can in principle be calculated. However, it has been observed in many experiments that its value depends on the calibrating gas.

Keywords: buoyancy, density, helium, Knudsen effect, mass determination, sorption, thermomolecular flow

Introduction

The amount of a gas or vapour adsorbed on the surface of a dispersed or porous solid as a function of pressure and temperature is usually measured by means of a volumetric or gravimetric apparatus [1]. In gravimetry, the mass adsorbed is weighed; in volumetry, the volume of the sorptive gas consumed is measured. Measurement of the nitrogen adsorption isotherm at 77 K is widely used to determine the specific surface area and the pore size distribution of the sorbent.

Measurements begin with degassing of the sample and calibration. A typical gravimetric record of such a preparation is depicted in Fig. 1. Similar records of the variation in time of the gas pressure may also be obtained by means of volumetric measurements.

Preparations

Prior to sorption measurements, it is necessary to remove physically adsorbed material from the surface of the sample by degassing, while avoiding irreversible

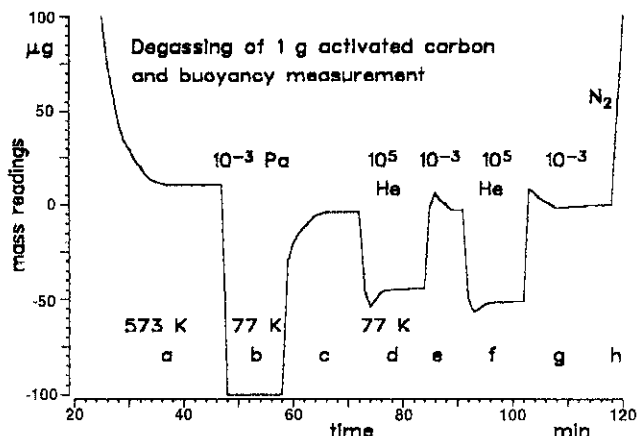


Fig. 1 Gravimetric record of the activation process of a sorbent sample of 1 g activated carbon, counterbalanced by quartz glass, in vacuum and in helium atmosphere. a) Degassing in vacuum at 573 K; b) Cooling of the sample to 77 K in vacuum. Initial temperature differences generate a thermal gas flow, resulting in a sudden decrease in the mass indication; c) Initial zero point; d, f) Helium is introduced and the buoyancy causes a fast decrease in the mass indication, followed by a slow increase due to helium adsorption; e, g) Evacuation causes a fast increase in the mass indication, due to vanishing buoyancy, followed by a slow decrease due to helium desorption; g) Zero point shift due to sorption of contaminating vapour; h) Beginning of the nitrogen adsorption isotherm at 77 K

changes to the surface. In volumetric measurements, optimal degassing conditions may be found in trial experiments, using different degassing conditions as far as duration and temperature are concerned. For this activation procedure, thermogravimetric methods are recommended, since they allow determination of the limiting temperature below which the structure of the sorbent sample remains unchanged.

Thermomolecular flow and Knudsen effect

In our example, activated carbon is heated at 573 K in vacuum. As soon as the degassing curve (a) assumes a constant value (after approximately 40 min), the oven is substituted for a Dewar vessel filled with liquid nitrogen. Since heat conduction in vacuum is poor, the sample temperature levels out very slowly, and a thermal gas flow acts on the balance. After a sharp decrease (b), the mass indication returns slowly to a certain plateau (c). The final plateau after calibration (g) is somewhat higher, due to the adsorption of contaminating vapour, and may be used as 'zero point' on the ordinate.

The thermostat surrounds the balance pans from the side and from the bottom. From above, heat is irradiated to the sample. A sample temperature of up to 15 K

above that of the thermostat has been observed [2]. A remnant thermomolecular flow will therefore shift the zero point downwards, and at higher pressure convection is observed. The thermomolecular flow has a maximum at a pressure at which the mean free path of the gas molecules is comparable to a characteristic length l , here the diameter of the balance tube [3]. The Knudsen number Kn satisfies the condition

$$Kn = \frac{\lambda}{l} = 1 \quad (1)$$

In the usual arrangement of a microbalance with balance tubes 2 cm in diameter, the maximum thermomolecular flow is observed in the pressure range 0.1 to 1 Pa.

Through the use of reflecting metal shields mounted above the sample, and long (1 m) and very thin (30 μm) hangdown wires, the disturbances can be reduced to about 10 μg . The zero point should be measured at a pressure below 10^{-2} Pa. Measurements within the region 10^{-2} Pa to 10^2 are cumbersome and do not always lead to reproducible results.

For pressures below $Kn=1$, the thermomolecular flow generates a pressure difference. The maximum pressure difference is given by the Knudsen's law

$$\frac{P_1}{P_2} = \sqrt{\frac{T_1}{T_2}} \quad (2)$$

In particular for volumetric measurements in the region below 10^3 Pa, the indicated pressure should be corrected. However, in contrast with gravimetric measurements, the zero point of the isotherm is not disturbed [3–5].

Calibration error

Gravimetric measurements are seriously affected by buoyancy [1]. Since density values of dispersed or porous matter are vague, the complete compensation of buoyancy by means of the counterweight on the basis of given density values fails in general. It is therefore necessary to measure the remaining buoyancy effect by using helium at 77 K or at ambient temperature, or with nitrogen at ambient temperature. In our example, the mass of activated carbon is compensated by a counterweight consisting of quartz glass. On the introduction of helium, an instantaneous decrease in the mass indication is observed as a result of the buoyancy difference (Fig. 1: d, f). After this, a slow increase in mass occurs, due to the adsorption of helium. Evacuation causes a fast increase in the mass indication as a result of vanishing buoyancy, followed by a slow mass decrease due to the desorption of helium.

From the buoyancy effect, the sample density can be roughly estimated (Section 4). Buoyancy can be cancelled by means of a correct counterweight. Such a counterweight may be prepared from a mixture of quartz and gold pieces for densities above $2.2 \cdot 10^3 \text{ kg m}^{-3}$, or with hollow glass globules for densities below $2.2 \cdot 10^3 \text{ kg m}^{-3}$.

For asymmetric balances (spring balances or magnetic suspension balances), the influence of buoyancy must be corrected computationally, taking into account the fact that the buoyancy of the balance parts occurs at a temperature different from that of the sample.

In volumetric measurements, known amounts of sorptive gas are introduced into the sample vessel and partly adsorbed on the surface of the sample or condensed in pores. Another part of the gas remains in the free space (dead volume) of the sample vessel, in equilibrium with the adsorbate. In order to be able to calculate the amount adsorbed by means of the thermal equation of state of the gas, the volume of the free space is calibrated in advance. This is usually done with helium at 77 K or at ambient temperature. Though the boiling point of helium is far below this temperature, some of it is adsorbed, simulating a larger free space. From helium isotherms measured on mesoporous materials [6, 7], we should reckon with an insignificant error from this effect. Sometimes, however, large amounts of helium are adsorbed [8]. This is indicative of micropores with diameters below 0,26 nm [9], which are accessible for the small helium atoms, but not for larger molecules such as nitrogen [10, 11].

Determination at ambient temperature reduces the error of adsorption, but increases the error due to the different temperature of the sample tube. If a sample is suspected of being microporous, it is recommended to perform the calibration at ambient temperature with other noble gases or nitrogen, taking into account the error due to adsorption.

Density determination

Density can be determined gravimetrically by using the buoyancy effect, or volumetrically by filling the free volume with gas in a calibrated bottle. In both cases, the mass of the sample is to be weighed in addition. As buoyancy, the force F_s exerted from the volume of gas displaced by the sample V_s is measured in the gravitational field g .

$$F_s = g\rho_{\text{He}}V_s \quad (3)$$

Assuming arms of the balance beam of equal mass, density and length, we can observe in our experiment the mass difference F/g from buoyancy between sample and counterweight, namely

$$\frac{\Delta F}{g} = \rho_{\text{He}}\Delta V = \rho_{\text{He}}\left(\frac{m_s}{\rho_s} - \frac{m_c}{\rho_c}\right) \quad (4)$$

where m_s and m_c are the masses of the sample and the counterweight and ρ_{He} , ρ_s , ρ_c the densities of helium at 77 K, m_s and m_c the masses of the sample and the counterweight, respectively. For the sample of activated carbon, we obtain a density of $1.9 \cdot 10^3 \text{ kg m}^{-3}$, which is about 10% higher than that measured with nitrogen at ambient temperature!

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