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VOLUMETRIC AND GRAVIMETRIC METHODS OF DETERMINING MONOLAYER CAPACITIES

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ABSTRACT

A comparison is made between the volumetric and the gravimetric methods for measuring adsorption isotherms. The discussion includes equipment, handling, price, accuracy and sensitivity. Dead space and buoyancy errors are calculated and compared. The aim of the work is to initiate a detailed discussion of these methods of determining specific surface area and pore size distribution.

1. COMPARISON OF CHARACTERISTIC FEATURES

For the determination of the specific surface area with nitrogen at 77 K, Brunauer, Emmett and Teller used a volumetric apparatus, and many researchers used similar apparatus to measure the entire isotherm to determine the pore size distribution using the Kelvin equation[1,2]. Soon afterwards, gravimetric measurements were performed using Gulbransen- and McBain-type balances.

The volumetric method is used more widely because the apparatus is much simpler, can be cheaper, and is easier to use than microgravimetry. As far as prices are concerned, a simple volumetric apparatus without any electronics can be constructed for less than DM 5,000, whereas a gravimetric measurement can hardly be expected to be performed without an electronic microbalance, which brings the price to at least DM 30,000.

On the other hand, the gravimetric method is more versatile. By simply replacing the liquid nitrogen bath by a furnace, one can perform measurements of controlled chemical reactions of the sample with a gas, as well as thermal decomposition or thermogravimetric analysis. Different investigations can be performed sequentially without having to remove the sample. Several examples of such measuring sequences are described in other papers of the conference, e.g. degassing, surface area and pore size determination, controlled oxidation, followed by a second surface area and pore size determination[3].

In addition, the gravimetric method has the outgassing advantage. The diameter of the tubes connecting the sample space to the vacuum pump can be much larger in the balance. The sample bulb of a volumetric apparatus must be connected through a capillary tube in order to reduce the effect of variations in the level of the liquid nitrogen. This leads to a much more time-consuming outgassing procedure with higher residual gas pressures over the sample. Attention should be drawn to the fact that the different outgassing procedures may well lead to different pore structures of the degassed sample and consequently to different shapes of isotherms measured on them.

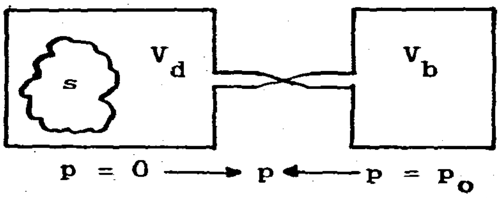
Using the gravimetric method, the sample mass is continuously observed, and therefore the rate and extent of the outgassing procedure can be controlled. The mass loss versus time curve may reveal temperature-dependent reactions of the material[4] or decomposition. A third outgassing advantage is the possibility of correcting the sample mass for material lost during outgassing. This correction might easily be as high as 5 percent and would be very difficult indeed to estimate using the volumetric method.

2. COMPARISON OF ERRORS

In the following the most serious errors of both methods will be compared. In the volumetric measuring method, this is the error involved in the calibration of the dead space in the sample vessel, whereas in the gravimetric method it is the buoyancy error[5-7]. In both calibrations the error is due to unexpected adsorption.

2.1. ERROR DUE TO THE CALIBRATION PROCEDURE FOR THE DEAD SPACE IN THE VOLUMETRIC METHOD

Consider a calibration procedure using helium as an inert gas with respect to the sample material and is for practical



purposes not adsorbed at room temperature. In Fig. 1 two volumes are shown connected by a tube with a valve where V_b is the volume of the burette from which the sample vessel V_d will be provided with proportioned amounts of nitrogen. The sample vessel, which contains the sample and the dead space, is at first evacuated, whereas V_b is filled with helium at the pressure p_o. Before opening the valve, room temperature T_r is established in both volumes.

After the valve has been opened, the gas pressure in both volumes becomes p. By assuming the conservation of mass, we obtain:

$$\frac{V_b p_o}{RT_r} = \frac{V_b p}{RT_r} + \frac{V_d p}{RT_r} + \varkappa \frac{A_s}{A_{He}} \frac{1}{6x10^{23}}$$

where A_s is the surface area of the sample and walls of V_d, A_{He} is the surface area occupied by one helium atom, and $\varkappa$ is the specific covering factor of the surface defined as the number of sites occupied divided by p x number of available sites. By ignoring the volume of the adsorbed helium, the resulting error δV_b is given by

$$\delta V_b = -RT\varkappa_{He} A_s / A_{He} \cdot 6x10^{23} \ .$$

When performing the actual adsorption measurement gas from V_b at p_o is added to the sample at temperature T_s using a gas of molecular weight M_w. The adsorbed mass is calculated from the measured final pressure p_f using

$$\frac{V_b p_o}{RT_r} = \frac{V_b p_f}{RT_r} + \frac{V_d p_f}{RT_s} + \frac{m_{ads}}{M_w}$$

The error δm_{ads} now satisfies

$$\delta m_{ads} = M_w \frac{p_f}{RT_s} \quad \text{and} \qquad \delta V_d = M_w \frac{T_r}{T_s} p_f \varkappa_{He} \frac{A_s}{A_{He}} \frac{1}{6x10^{23}}$$

As an example, for $M_w = 30$; $p_f = 10^5$ Pa; $T_r/T_s = 4$; $\varkappa_{He} = 10^{-1}$ Pa^{-1}; $A_s = 10^2$ m^2; and $A_{He} = 3x10^{-20}$ m^2:

$$V_b = 100 \ mm^3 \quad \text{and} \quad m_{ads} = 5x10^{-4} \ g.$$

The error increases with pressure and cumulates in each step of the incrementally measured isotherm.

2.2. ERROR DUE TO BUOYANCY IN THE GRAVIMETRIC METHOD

Using compensating loads of selected density, the buoyancy force of the balance beam may be cancelled completely. In the same way the buoyancy force of the sample can be compensated by using a counterweight with negligible surface area and similar mean molecular mass[3]. To determine the buoyancy one can perform weight determinations at room temperature under vacuum and under helium, corresponding to the procedure of the volumetric method. As the difference of the force measured we obtain:

$$F_{vac} - F_{He} = V_s g \varrho_{He,r} + g \varkappa p \frac{A_s}{A_{He}} \frac{1}{6\mathrm{x}10^{23}}$$

where g stands for the acceleration due to gravity and $\varrho_{He,r}$ for the density of He at room temperature and pressure p. If the adsorbed amount is ignored the error δV_s becomes

$$\delta V_s = -RT_r \varkappa \frac{A_s}{A_{He}} \frac{1}{6\mathrm{x}10^{23}}$$

This expression surprisingly enough equals the error of the dead space calculated above.

When performing the actual adsorption measurement at temperature T_s, the related error satisfies

$$m_{ads} = M_w T_r p \varkappa / T_s A_{He} \cdot 6\mathrm{x}10^{23}$$

which again is identical to the final error in the volumetric case. However, during the measurement of an isotherm, this error only increases proportionally to the pressure of the measuring gas. In the volumetric method the error is also accumulated at each step. So attempts to secure detailed shapes of isotherms must become counterproductive because of the cumulative error.

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