Adsorption, 1, 283–290 (1995)

Theory of Measurement of Gas-Adsorption Equilibria by Rotational Oscillations*

J.U. KELLER
Institute Fluid- and Thermodynamics, University of Siegen, D-57068 Siegen, Germany

Received January 19, 1994; Revised March 8, 1995; Accepted April 25, 1995

Abstract. The gas adsorbed on the inner surface of a highly porous material like activated carbon or zeolite can be measured by slow damped oscillations of a torsional pendulum. The physical principles and the theory of this method are outlined. Formulas are given relating the increase in mass due to adsorption to changes of the frequency and the logarithmic decrement of slow, damped rotational oscillations of the pendulum. Preliminary measurements of gas adsorption equilibria of nitrogen on activated carbon show that the ratio of the mass adsorbed m, to the mass of the adsorbent m^s, can be determined by this method with mean absolute error $\delta|m/m^s| \leq 0.04\%$.

Keywords: gas adsorption equilibria, measurement techniques, gas phase, rotational oscillations

1 Introduction

Adsorption phenomena provide an effective tool to clean gases and liquids, i.e. to remove for example hazardous and poisonous components from exhaust air and waste water (Brauer, 1985; Kast, 1988). For proper design of adsorption reactors, adsorption equilibria should be known, describing the amount of mass, m, of a gas (or liquid) which at given temperature, T, and pressure, p, can be adsorbed on a mass, m^s, of a porous adsorbent like activated carbon (AC) or zeolite (Sing and Gregg, 1983; Ruthven, 1984; Suzuki, 1993). Traditional measurement methods like microbalance gravimetry and volumetry only allow us to determine the quantity

$$\Omega = m - \rho V^{as}, \tag{1}$$

i.e. the difference between the adsorbed mass and a buoyancy related product of the gas density, ρ, and a "volume", V^{as}, of the adsorbate (a)-adsorbent (s) system realized by the gas-loaded porous solid. Since V^{as} normally is unknown, approximations for this quantity are introduced, for example, the so-called Helium-volume of the adsorbent (Sing and Gregg, 1983; Ruthven, 1984; Sing et al., 1985). However, this assumption may lead to contradictions and thermodynamic inconsistencies, especially at higher pressures ($p \sim 10$ MPa) and low temperatures ($T \sim 77$ K), (Staudt et al., 1993).

In order to measure m directly, we here propose another method using the inertia of mass and not its gravity as in microbalance technology or its extensivity as in the volumetric method: slow rotational oscillations of disks consisting of a porous adsorbent and being fixed to a suspension wire of known physical properties. Indeed, by observing the frequency and the logarithmic decrement of damped oscillations of the pendulum in vacuum and in gas, m can be calculated without introducing an assumption on the "volume" of the porous disk! Also, as a side result, the kinematic viscosity of the gas can be determined with reasonable accuracy.

The torsional pendulum with a dense disk moving in a viscous fluid has been developed by J. Kestin and coworkers (Kestin, 1980). Today it is used for viscosity measurements in gases (Michels et al., 1931; Vogel, 1972) and more recently in liquids (Krall, 1992; Krall et al., 1992). Its theory, especially the coupling of the smooth surface disk motion to the fluid flow is well established (Newell, 1959; Nieuwoudt et al., 1975). However, the pendulum does not seem to have been considered for determining masses or changes of masses as they occur during adsorption processes in porous solids. Nevertheless, in literature there are other methods to determine adsorbed masses enjoying the same advantage of not requiring knowledge of the

*Dedicated to the memory of Joseph Kestin (1913–1993).

volume of the adsorbent. We here only mention acoustic techniques described by Yan and Bein (1992) and the piezoelectric method suggested by Ward and Buttry (1990). Both methods use *high* frequency oscillations. These however may cause microcavitation in the surroundings of the sample by which its damping properties are changed considerably as is well known from viscosity measurements using piezoelectric transducers, (Nieuwoudt et al., 1975). Also, to fix the sorbent to the piezo-quartz, some glue is required which not only adds to the mass to be determined, but often changes part of the sorbent in an unreproducible way.

Slow, damped oscillations of a linear oscillator, i.e. a sample adsorbent fixed to a spring, do not provide a useful technique, because the hydrodynamics of the surrounding fluid is to complicated to be taken into account, which is not the case for rotational oscillations!

The purpose of this paper is to outline the theory of measurement of the mass of a porous solid loaded with an adsorbed phase by slow, damped rotational oscillations. In addition, results of preliminary experiments are reported showing that the ratio of the mass adsorbed to adsorbent's mass (m/m^s) can be measured by this method with mean absolute error $\delta|m/m^s| \leq 0.4$ mg/g.

2 Motion of Pendulum in Vacuum

Let us consider a simple rotational pendulum, Fig. 1. It may consist of a cylindrical disk, radius R, height d, made of a highly porous material like activated carbon or zeolite, and a suspension wire, length L, diameter $2r_w$, fixed at the center of the plate. For mechanical stability a stem may be fixed below the disk, bearing a small mirror. Thus, by reflections of a laser beam the angular displacement or the amplitude $\alpha = \alpha(t)$ of the pendulum can be detected. For further experimental details the interested reader is referred to the literature (Krall, 1992; Krall et al., 1992).

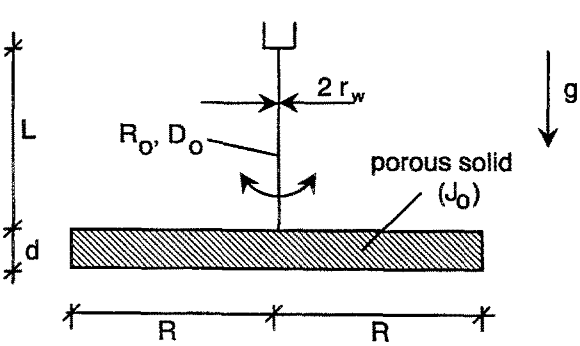

Fig. 1. Rotational pendulum.

The motion of the pendulum in vacuum is described by the equation

$$J_0\ddot{\alpha} + R_0\dot{\alpha} + D_0\alpha = 0. \tag{2.1}$$

Here

$$J_0 = \int_{m^s} r^2 dm^s = m^s R^2/2, \tag{2.2}$$

is the moment of inertia of the "empty disk", R_0 is the damping coefficient caused by internal damping of the torsional wire, and D_0 is the retarding moment related to the wire's length L, diameter, r_w, elasticity modulus, E, and its Poisson number, μ, by the relations

$$\begin{aligned} D_0 &= G J_{TW}/L, \\ G &= E/(2(1+\mu)), \\ J_{TW} &= \pi r_w^4/2. \end{aligned}$$

Experiments show that after fading away of initial disturbances the motion of the pendulum always can be described by a simple damped harmonic oscillation. For a proper time scale, t, and initial conditions, $\alpha(0) = \alpha_0$, $\dot{\alpha}(0) = 0$, it reads

$$\alpha(t) = \alpha_0 e^{-\Delta_0\omega_0 t} \cdot [\cos(\omega_0 t) + \Delta_0 \sin(\omega_0 t)]. \tag{2.3}$$

Here α_0 is the amplitude, $\omega_0 = 2\pi/T_o$ is the angular frequency with T_o indicating the period of oscillation, and Δ_0 is the logarithmic decrement defined by the relation

$$2\pi\Delta_0 = \ln\frac{\alpha(t)}{\alpha(t+T_o)} \qquad \text{all } t \geq 0. \tag{2.4}$$

The quantities ω_0 and Δ_0 are related to the pendulum's parameters J_0, R_0, and D_0 via the relations

$$\omega_0^2 = \frac{D_0}{J_0} - \left(\frac{R_0}{2\cdot J_0}\right)^2, \tag{2.5}$$

$$\Delta_0\omega_0 = R_0/2\cdot J_0. \tag{2.6}$$

Conversely, we have from Eqs. (2.5, 2.6)

$$J_0 = \frac{D_0}{\omega_0^2(1+\Delta_0^2)}. \tag{2.7}$$

From this equation the moment of inertia of the disk, J_0, and therefore its mass, m^s, can be determined, if the retarding moment, D_0, is known from calibration measurements and if ω_0 and Δ_0 have been experimentally determined. Typical orders of magnitude of these quantities being $\omega_0 \cong 10$ s and $\Delta_0 \cong 10^{-4}$. Introducing a dimensionless time variable by

$$\tau = \omega_0 t = 2\pi t/T_o, \tag{2.8}$$

the equation of motion (2.1) may be rewritten as

$$J_0\omega_0^2\big(\ddot{\alpha}(\tau)+2\Delta_0\dot{\alpha}(\tau)+\big(1+\Delta_0^2\big)\alpha(\tau)\big) = 0. \tag{2.9}$$

The dot now denotes the derivative to the variable τ! The solution, Eq. (2.3)

$$\alpha(\tau) = \alpha_0 e^{-\Delta_0\tau}\cdot[\cos\tau + \Delta_0 \sin\tau] \tag{2.3a}$$

also may be represented via the Laplace transform

$$\hat{\alpha}(s) = \int_0^\infty \alpha(\tau)e^{-s\tau}\, d\tau, \tag{2.10}$$

as a contour integral in the complex s-plane:

$$\alpha(\tau) = \frac{\alpha_0}{2\pi i}\oint_{c-i\infty}^{c+i\infty} \frac{(s+2\Delta_0)}{(s+\Delta_0)^2+1} e^{s\tau}\, ds, \tag{2.11}$$

where the path of integration has to be taken right to the poles

$$s = -\Delta_0 \pm i, \tag{2.12}$$

of the integrand, i.e. such that $C > -\Delta_0$. Thus we can characterize the damped harmonic motion of the pendulum in vacuum by a single pair of complex conjugated first order poles in the complex s-plane, the abscissa of which simply is the negative logarithmic decrement $-\Delta_0$ of the motion.

3 Motion of Pendulum in Gas

If the motion of the pendulum takes place in a viscous fluid, i.e. a gaseous atmosphere or a liquid at constant pressure and temperature, its equation is

$$J\ddot{\alpha}(t) + R_0\dot{\alpha}(t) + D_0\alpha(t) = M(t). \tag{3.1}$$

Here

$$J = \int_{m^s+m} r^2(dm^s + dm) \tag{3.2}$$

is the moment of inertia of the porous disk consisting of the mass of the adsorbent, m^s, and the mass of the molecules adsorbed, i.e. the adsorbate, m. Assuming the disk to be quasi-homogeneous, i.e. the ratio

$$\mu = \frac{dm}{dm^s} = \text{const.}, \tag{3.3}$$

to be a (temperature and pressure dependent) constant, Eq. (3.2) in view of Eq. (2.2) can be rewritten as

$$J = (1+\mu)J_0. \tag{3.4}$$

Conversely, we may calculate the key quantity, μ, from this relation if J and J_0 have been determined experimentally, i.e. by observing the pendulum's motion (cp. Eq. (3.36)).

The quantity $M(t)$, in Eq. (3.1) is the torque exerted by the fluid flow on the pendulum. Physically this is caused by the internal friction of the fluid, i.e. in Newtonian fluids to which we here restrict, by the velocity gradient in the fluid's flow perpendicular to the surface of the porous disk. Basically, the torque, $M(t)$, is an unknown quantity. However, since the motion of the disk and the fluid flow caused by it are strongly coupled systems, in addition to Eq. (3.1) there should be a relation between α and M rooted in the equations of motion of the fluid and in the shape and physical properties of the porous disk. Assuming the density, ρ, of the fluid to be constant, the equations of motion of the fluid are the well known Navier-Stokes-equations (Landau and Lifschitz, 1966),

$$\partial_t v_\alpha + v_\beta\partial_\beta v_\alpha = -\frac{1}{\rho}\partial_\alpha p + \nu\Delta v_\alpha, \qquad \alpha = 1,2,3 \tag{3.5}$$

complemented by the continuity condition

$$\partial_\alpha v_\alpha = 0. \tag{3.6}$$

Here $\partial_t = \partial/\partial t$ and $\partial_\alpha = \partial/\partial\alpha$, $\alpha = 1,2,3$ indicate partial derivatives of time t and space coordinates x_α respectively; $v_\alpha = v_\alpha(\underline{x}, t)$ is the velocity field and $\nu = $ const. is the kinematic viscosity of the fluid. The symbol, $\Delta = \partial_\alpha\partial_\alpha$, is Laplace's operator. The summation convention is applied. To facilitate discussion we restrict to slow motions of the pendulum, i.e. we only consider low Reynolds numbers flows, i.e. $\text{Re} \equiv (\omega_0 R^2/\nu) \to 0$ and also exclude secondary flows. This condition can be realized experimentally by considering only "thick" disks (cp. Eq. (3.14)) and by adding auxiliary plates above and below the disk (Michels et al., 1931; Vogel, 1972). Hence, in Eq. (3.5) the nonlinear term $v_\beta\partial_\beta v_\alpha$ can be neglected. Also we assume in view of the fact that the fluid basically is in an equilibrium state at constant pressure and temperature, that pressure gradients in the fluid possibly induced by pendulum's motion dissipate very quickly, i.e. in time intervals much shorter than those characterizing the fluid flow itself ($2\pi/\omega_0$). Hence, we can neglect the pressure gradient term in Eq. (3.5), too.

Finally we assume the velocity field to be rotationally symmetric, only having a component in the azimuthal direction. Therefore, introducing cylindrical coordinates we have

$$\underline{v} = r\Omega(r, z, t)\hat{\Phi} \tag{3.7}$$

with Ω being a function of the radial coordinate, r, the z coordinate in the direction of the torsional wire, and time, t, but not of the azimuthal coordinate, φ, the unit vector of which being directed perpendicular to the radius vector is indicated by $\hat{\Phi}$. Introducing Eq. (3.7) into the reduced Navier-Stokes equations Eq. (3.5)

$$\partial_t v_\alpha = \nu \Delta v_\alpha, \qquad \alpha = 1, 2, 3, \tag{3.8}$$

we get a single equation for the $\hat{\Phi}$-direction:

$$\partial_t \Omega = \nu\left(\partial_r^2 + \frac{3}{r}\partial_r + \partial_z^2\right)\Omega. \tag{3.9}$$

Here $\partial_r = \partial/\partial r$ and $\partial_z = \partial/\partial z$ indicate the respective partial derivatives. The boundary conditions (BC) of the fluid flow are:

1) On any fixed surface, e.g. the cover of the instrument or the auxiliary plates above and below the disk we have

$$\Omega = 0. \tag{3.10}$$

2) On pendulum's surface we have

$$\Omega = \dot{\alpha}(t) = \omega_0 \dot{\alpha}(\tau). \tag{3.11}$$

We now introduce dimensionless coordinates

$$\xi = \frac{r}{\delta}, \quad \eta = \frac{z}{\delta}, \tag{3.12}$$

by using the characteristic length δ of the system defined by

$$\delta^2 = \frac{\nu}{\omega_0}. \tag{3.13}$$

Also we would like to mention that assumption Eq. (3.7) on the velocity field predominantly holds for "thick disks", i.e. if the inequalities

$$d \gg \delta, \quad R \gg \delta \tag{3.14}$$

for the height, d, and the radius, R, of the disk hold.

Introducing the Laplace transform with respect to the dimensionless time τ,

$$\hat{\Omega}(s, \xi, \eta) = \int_0^\infty \Omega(\tau, \xi, \eta) \cdot e^{-s\tau}\, d\tau, \tag{3.15}$$

the boundary value problem Eqs. (3.9–3.11) can be reformulated as

$$s\hat{\Omega}(s, \xi, \eta) - \Omega(\tau = 0, \xi, \eta) = \left(\partial_\xi^2 + \frac{3}{\xi}\partial_\xi + \partial_\eta^2\right)\hat{\Omega}(s, \xi, \eta) \tag{3.16}$$

$$\hat{\Omega} = 0 \ldots \text{ on fixed surfaces} \tag{3.17}$$

$$\hat{\Omega} = \omega_0(s\hat{\alpha} - \alpha_0) \ldots \text{on pendulum's surface.} \tag{3.18}$$

Finally, let us introduce a reduced angular velocity, w, by the equation

$$\hat{\Omega}(s, \xi, \eta) = \omega_0(s\hat{\alpha}(s) - \alpha_0)w(s, \xi, \eta). \tag{3.19}$$

Assuming the fluid to be initially at rest, i.e. $\Omega(\tau = 0, \xi, \eta) = 0$, the boundary value problem Eqs. (3.16–3.18) can be recast to

$$sw = \left(\partial_\xi^2 + \frac{3}{\xi}\partial_\xi + \partial_\eta^2\right)w, \tag{3.20}$$

$$w = 0 \ldots \text{ on fixed surfaces,} \tag{3.21}$$

$$w = 1 \ldots \text{ on pendulum's surface.} \tag{3.22}$$

Now the fluid flow formally has been decoupled from the pendulum's motion since Eqs. (3.20–3.22) do not include any quantity referring to it. The solution is a formal mathematical problem not pursued here. There are already solutions available in literature referring to various types of geometry (Kestin and Wang, 1957; Krall et al., 1992; Nieuwoudt and Shankland, 1975). The coupling between the fluid flow and pendulum's motion formally is described by Eq. (3.19), the key-relation connecting the Laplace transforms of the angular velocity $\hat{\Omega}$ and the amplitude of the pendulum $\hat{\alpha}$! Note that the auxiliary field w also depends on the Laplace variable s, i.e. $w = w(s, \xi, \eta)$!

The retarding torque exerted by the fluid on the pendulum generally can be represented as a surface integral of the velocity gradient, i.e. in view of Eq. (3.7) by

$$M(t) = -\eta \int_0 r^2(\underline{n}_r\partial_r + \underline{n}_z\partial_z)\Omega\, d\underline{\vec{f}}, \tag{3.23}$$

or, after introducing reduced coordinates Eq. (3.12) by

$$M(t) = -\eta\delta^3 \int_{0^*} \xi^2(\underline{n}_\xi\partial_\xi + \underline{n}_\eta\partial_\eta)\Omega\, d\underline{\vec{G}}. \tag{3.24}$$

Here η is the dynamic viscosity of the fluid; the quantities $\underline{n}\ldots$ indicate unit vectors in the respective directions $\ldots$ and $d\vec{f} = \delta^2 d\vec{G}$ is a vectorial element of the disk's surface, 0 and 0*, in cylindrical and reduced coordinates, respectively.

Introducing the dimensionless time coordinate, $\tau = \omega_0 t$, and applying Laplace's transformation to Eq. (3.24) we get after inserting Eq. (3.19) for the Laplace transform of the torque

$$\hat{M}(s) = -\eta\delta^3\omega_0(s\hat{\alpha}(s) - \alpha_0)W, \tag{3.25}$$

with

$$W = \int_{0^*} \xi^2(\underline{n}_\xi \partial_\xi + \underline{n}_\eta \partial_\eta) w d\vec{G}. \tag{3.26}$$

This quantity is a characteristic numerical constant of the pendulum. It can be calculated by integrating the solution function $w(s, \xi, \eta)$ of the boundary value problem Eqs. (3.20–3.22) on the surface, 0*, of the disk as indicated in Eq. (3.26). It should be noted that the integral exists as long as the surface, 0*, is continuous, i.e. even if it is non-analytic but of fractal character (Mandelbrot, 1977).

We now consider the Laplace transform of the equation of motion Eq. (3.1). It formally can be solved to give the Laplace transform of the pendulum's amplitude

$$\hat{\alpha}(s) = \frac{(2\Delta\theta + s)\alpha_0 + \hat{M}(s)/J\omega_0^2}{(s+\theta\Delta)^2 + \theta^2}. \tag{3.27}$$

Here the abbreviations

$$\theta = \frac{\omega}{\omega_0}, \tag{3.28}$$

$$\omega^2 = \frac{D_0}{J} - \left(\frac{R_0}{2J}\right)^2, \tag{3.29}$$

$$\Delta\omega = \frac{R_0}{2J}, \tag{3.30}$$

and the initial conditions $\alpha(0) = \alpha_0$, $\dot{\alpha}(0) = 0$ have been used. Introducing for the Laplace transform of the torque $\hat{M}$, expression Eq. (3.25) and taking the inverse Laplace transform, the pendulum's amplitude can be represented by the integral

$$\alpha(\tau) = \frac{\alpha_0}{2\pi i}\oint \frac{2\theta\Delta + Fj + s}{(s+\theta\Delta)^2 + Fjs + \theta^2} e^{s\tau}\, ds, \tag{3.31}$$

with the abbreviations

$$F = \frac{W}{J_0}\frac{\eta\delta^3}{\omega_0}, \tag{3.32}$$

$$j = \frac{J_0}{J}. \tag{3.33}$$

Note that the auxiliary quantities Δ and Θ defined by Eqs. (3.28–3.30) can be written as functions of the (unknown) parameter, j, via Eqs. (2.6, 2.7) as

$$\Theta^2 = (1+\Delta_0^2)j - (\Delta_0 j)^2, \tag{3.34}$$

$$\Delta\Theta = \Delta_0 j. \tag{3.35}$$

Since experiments show, that the pendulum after an initial period—which is of order of magnitude of $2T_o = 4\pi/\omega_0$—always exhibits a damped harmonic oscillation with angular frequency ω_E and decrement Δ_E we have for the l.h.s. of Eq. (3.31) with $\tau = \omega_0 t$

$$\alpha_E(\tau) = \alpha_0 e^{-\Delta_E\Theta_E\tau}\cdot[\cos(\Theta_E\tau) + \Delta_E\sin(\Theta_E\tau)], \tag{3.36}$$

$$\Theta_E = \frac{\omega_E}{\omega_0} \tag{3.37}$$

or likewise for the Laplace transform

$$\hat{\alpha}_E(s) = \frac{\alpha_0(s + 2\Delta_E\Theta_E)}{(s - s_E^+)(s - s_E^-)}, \tag{3.38}$$

with the first order poles

$$s_E^\pm = (-\Delta_E \pm i)\Theta_E. \tag{3.39}$$

Comparing Eq. (3.38) with (3.31), one recognizes that the denominator of the integrand also must vanish at $s = s_E^\pm$, given that $F(s)$ is analytic in $s_E^\pm$ which can be concluded from Eqs. (3.26) and (3.32). Hence we have the working equation(s)

$$(s_E^\pm + \Theta\Delta)^2 + jF(s_E^\pm)s_E^\pm + \Theta^2 = 0. \tag{3.40}$$

Introducing Eq. (3.39) in (3.40) and observing that $F(s)$ generally will be a complex quantity, i.e.

$$F(s_E^\pm) = F_1 \pm iF_2, \tag{3.41}$$

we get from the real part the equation

$$(1-\Delta_E^2)\Theta_E^2 + j\Theta_E(\Delta_E F_1 + F_2 + 2\Delta_0\Delta_E) - j(1+\Delta_0^2) = 0, \tag{3.42}$$

and likewise from the imaginary part the relation

$$-2\Delta_E\Theta_E + j(2\Delta_0 + F_1 - \Delta_E F_2) = 0. \tag{3.43}$$

In deriving Eqs. (3.42) and (3.43) from (3.40) the auxilary relations Eqs. (3.34) and (3.35) have been used.

Applying in view of Eq. (3.40) the residue theorem to Eq. (3.31) and comparing the result with Eq. (3.36) we get the relation(s)

$$\frac{1}{\Theta_E}\left(2\Delta\Theta + s_E^{\pm} + jF\left(s_E^{\pm}\right)\right) = \pm(\Delta_E + i). \quad (3.44)$$

The real part and imaginary part of the relations lead to

$$jF_1 = 2(\Delta_E\Theta_E - \Delta\Theta), \quad (3.45)$$

$$F_2 = 0, \quad (3.46)$$

which combined with Eqs. (3.42), (3.35) and (3.37) yield for the ratio of the moments of inertia

$$j = \frac{J_0}{J} = \frac{1+\Delta_E^2}{1+\Delta_0^2}\left(\frac{\omega_E}{\omega_0}\right)^2. \quad (3.47)$$

Hence, we have in view of Eqs. (3.3) and (3.4)

$$\frac{m}{m^s} = \frac{1+\Delta_0^2}{1+\Delta_E^2}\left(\frac{\omega_0}{\omega_E}\right)^2 - 1. \quad (3.48)$$

This relation allows to calculate the mass, m, of gas adsorbed in the mass, m^s, of porous solid forming the "empty" disk from the measured frequencies and logarithmic decrements of the pendulum's oscillations performed in vacuum (ω_0 and D_0) and in the gaseous atmosphere (ω_E and Δ_E) respectively. It should be emphasized that in this method no buoyancy correction is needed and, hence, no numerical value of any kind of "volume" of the porous solid is introduced. Indeed, the concept of "volume" of the disk is only needed in a marginal sense, namely to make sure the surface integral W defined by Eq. (3.26) exists, its numerical value however being irrelevant for determining the adsorbed mass, m! Once this quantity is known it may be introduced in Eq. (1) to determine an equivalent volume, V^{as}, of the adsorbent and adsorbate by additional gravimetric measurements! Let us finally note that once the auxiliary quantity, W, defined by Eq. (3.26) has been calculated numerically, the kinematic viscosity, ν, of the adsorptive can be determined from the same measurements (ω_0, Δ_0, ω_E, and Δ_E) via relations (3.32, 3.35, 3.45, and 3.47).

4 Preliminary Experiments

To check the sensitivity and accuracy of the proposed method, experiments with a torsional pendulum designed in our laboratory were performed. The diameter of the disk was $2R = 12$ cm, its thickness, $d = 1.5$ cm. The disk was connected to a torsional wire (Goodfellow, Pt/W) of diameter, $2r_w = 0.13$ mm, and length, $l = 20$ cm. It also was provided with a stem to stabilize it and to bear a small mirror to reflect a laser beam. Using pairwise photodiodes, optical signals were recorded allowing to calculate pendulum's frequency and decrement. The inaccuracies of measurement of pendulum's amplitude $\delta\alpha = \pm 0.05°$ and of time resolution $\delta t = \pm 10\ \mu$s, led to error bounds of the frequency $\delta\omega = \pm 5 \times 10^{-5}\ \text{s}^{-1}$ and of the decrement $\delta\Delta = \pm 5 \times 10^{-4}$. According to these error bounds, the average error of the mass ratio has been dtermined via Eq. (3.48) by

$$\delta\left(\frac{m}{m^s}\right) = \pm 0.04\%.$$

This is two orders of magnitude greater than can be achieved by gravimetric measurements with today's microbalances. However, it should be emphasized that the proposed oscillometric method does not contain systematic errors! These, in principle, cannot be avoided in gravimetric or volumetric measurements of adsorbed masses due to the fact that the buoyancy related volume of the sample generally is not known (cp. Eq. (1))! Also it should be mentioned that the accuracy of oscillometric measurements can be improved by at least one order of magnitude by increasing the diameter of the pendulum and the length of the torsional wire and by improving the pendulum's stand.

Measurements of adsorption equilibria of nitrogen at $T = 292$ K on activated carbon Norit $R1$ in the range $p < 0.5$ MPa are shown in Fig. 2. The symbols (□) indicate the mass adsorbed per unit mass of adsorbent which has been measured with the rotational pendulum (m_{RP}). Simultaneously, we have taken gravimetric measurements with a microbalance (Mettler AT 201). These led to reduced masses $\Omega = m - \rho V^{as}$ represented by symbols (○). A "geometric" density of the nearly cylindrical AC-pellets has been determined as $\rho_G^S = 650$ g/l, corresponding to a specific volume of the sorbent of $V_G^S = 1.54\ \text{cm}^3/\text{g}$. Using this as an approximate value for the volume $V^{as} \cong V_G^S$ in the defining Eq. (1) for Ω, we have calculated a microbalance measured mass of the adsorbate by $m_{\text{MB}} = \Omega + \rho V_G^S = m + \rho(V_G^S - V^{as})$. Its values are symbolized by (△). Table 1 below includes the basic data of the measurements, namely the adsorptive's pressure, p, density, ρ, the rotational pendulum measurements, m_{RP}, the reduced mass, Ω, the approximative buoyancy term, ρV_G^S, the microbalance measured mass, m_{MB}, and the

Table 1. Basic data of gas adsorption equilibria measurements of nitrogen (N_2) on activated carbon (Norit *R*1) at $T = 292$ K.

p/MPa	ρ/mg/cm^3	m_{RP}/mg/g	Ω/mg/g	ρV_G^S/mg/g	m_{MB}/mg/g	δm/%
0.0773	0.8916	9.50	7.828	1.37	9.20	3.3
0.1036	1.1950	12.56	10.72	1.84	12.56	0.01
0.2215	2.5550	26.30	19.87	3.94	23.81	10.4
0.3196	3.6886	32.31	26.76	5.68	32.44	0.4
0.4161	4.8040	39.42	32.17	7.40	39.57	0.4

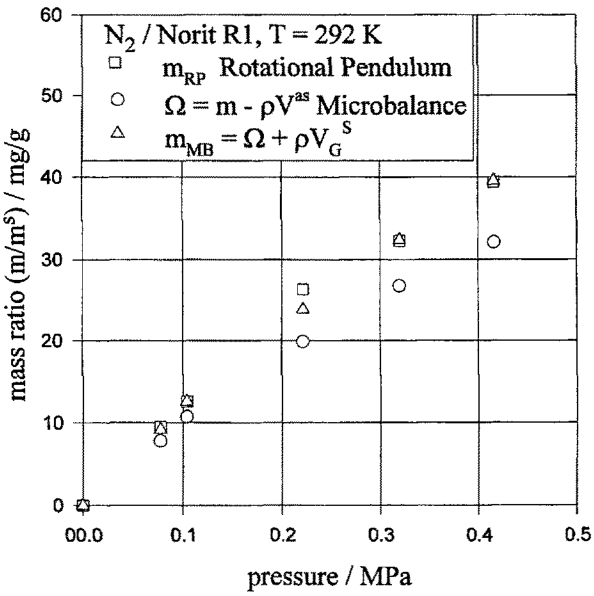

Fig. 2. Gas adsorption equilibria of nitrogen (N_2) on activated carbon (Norit *R*1) at $T = 292$ K.

relative deviation, $\delta m = |m_{RP} - m_{MB}|/m_{RP}$. As one can recognize from both the figure and the table, the coincidence of m_{RP} and m_{MB} is fair—except one measurement taken 0.2215 MPa where oscillations seemingly have been disturbed during the measurement period of nearly 30 minutes. Further measurements are underway and will be reported in a forthcoming paper.

Nomenclature

D_0	retarding moment of suspension wire	kg m^2 s^{-2}
d	height of disk	m
$d\vec{f}$	vectorial element of the surface of the porous disk	m^2
E	elasticity modul of suspension wire	kg m^{-1} s^{-2}
F	numerical constant of pendulum defined by Eq. (3.32)	1
J	moment of inertia of porous disk loaded with adsorbate	kg m^2
J_{TW}	moment of inertia of suspension wire	kg m^2
$j = \frac{J_0}{J}$	ratio of moments of inertia	1
J_0	moment of inertia of porous disk in vacuum	kg m^2
L	length of the suspension wire	m
$M(t)$	torque exerted by the gas flow on the pendulum	kg m^2 s^{-2}
m	mass of adsorbate	g, kg
m^S	mass of porous disk	kg
R	radius of disk	m
R_0	damping coefficient of pendulum in vacuum	kg m^2 s^{-1}
Re	Reynold's number of gas flow	1
r_W	radius of suspension wire	m
r, z, φ	cylindrical coordinates	m, m, rad
s	Laplace variable	1
$s_E^{\pm}$	Laplace coordinates of poles characterizing pendulum's motion in the gas	1
t	time coordinate	s
T_o	period of oscillation of pendulum in vacuum	s
V^{as}	buoyancy related volume of adsorbent and adsorbate	m^3
v_α	velocity field of gas flow	m s^{-1}
W	numerical constant of pendulum defined by Eq. (3.26)	1
x_α	space coordinates	m
α	angular coordinate of the pendulum	rad, Deg.
α_0	initial amplitude of the pendulum	rad, Deg.
$\hat{\alpha}$	Laplace transform of angular coordinate α	rad, Deg.
Δ	Laplace operator	m^{-2}

$2\pi\Delta$	logarithmic decrement of pendulum's damped oscillations in gas	1
$2\pi\Delta_0$	logarithmic decrement of pendulum's damped oscillations in vacuum	1
$\delta = (\nu/\omega_0)^{1/2}$	characteristic length of pendulum-gas system	m
$\eta = z/\delta$	dimensionless height coordinate	1
η	dynamic viscosity of gas	kg m^{-1} s^{-1}
$\Theta = \omega/\omega_0$	ratio of angular frequencies	1
$\mu = m/m^S$	ratio of mass adsorbed to mass of adsorbent	1
μ	Poisson number of suspension wire	1
ν	kinematic viscosity of gas	m^2 s^{-1}
ρ	density of adsorptive	kg m^{-3}
$\xi = r/\delta$	dimensionless radial coordinate	1
$\tau = \omega_0 t$	dimensionless time	1
$\Omega(r, z, t)$	auxiliary velocity function	s^{-1}
$\Omega \equiv m - \rho V^{as}$	difference between mass adsorbed and buoyancy term	g, kg
ω	angular frequency of pendulum's oscillation in gas	s^{-1}
ω_0	angular frequency of pendulum's oscillation in vacuum	s^{-1}

Acknowledgments

The author is grateful to the late Professor J. Kestin, Providence, and to Professor Geropp, Siegen, for valuable discussions. He also appreciates the work of his coworkers Dr. R. Staudt, F. Dreisbach and U. Göbel who designed the torsional pendulum and took the gas adsorption equilibria measurements. Also the work of Mrs. Decker who typed the manuscript and of F. Dreisbach who did the formating of formulas and wording is gratefully acknowledged.

References

Behrens, D. and R. Eckermann, *Chemistry Data Series, DECHEMA*, Frankfurt M., 1977.

Brauer, H., "Die Adsorptionstechnik—ein Gebiet mit Zukunft," *Chem.-Ing.-Tech.* (*German Chemical Engineering*), **57**, 650 (1985).

Göcke, F., R. Staudt, and J.U. Keller, "Bestimmung von Massen durch Messung niederfrequenter Schwingungen eines Torsionspendels," Student Research Project, Institute of Fluid- and Thermodynamics, University of Siegen, Siegen, Germany, 1994.

IUPAC, Chemical Data Series No. 20, Thermodynamic Tables Project, S. Angus et al. (Eds.), Pergamon Press, Oxford, 1976.

Kast, W., "Adsorption aus der Gasphase, Ingenieurwissenschaftliche Grundlagen und technische Verfahren," *Verlag Chemie*, Weinheim, Germany, 1988.

Kestin, J., R. Paul, J.R. Shankland, and H.E. Khalifa, *Bunsen-Ber. Phys. Chem.*, **84**, 1255 (1980).

Kestin, J. and H.E. Wang, "Corrections for the Oscillating-Disk Viscometer," *J. of Applied Mechanics*, 197 (1957).

Krall, A.H., "Oscillating-Body Viscometry and its Application to Phase-Separating Liquid Mixtures," *Dissertation*, University of Maryland, College Park, Maryland, 1992.

Krall, A.H., J.V. Sengers, and J. Kestin, "Viscosity of Liquid Toluene at Temperatures from 25 to 150°C and at Pressures up to 30 MPa," *Journal of Chemical & Engineering Data*, **37**, 349 (1992).

Landau, L.D. and E.M. Lifschitz, *Lehrbuch der Theoretischen Physik*, Bd VI Hydrodynamik, Akademie Verlag, Berlin (Ost), 1966.

Mandelbrot, B.B., *Fractals: Form, Chance and Dimension*, W.H. Freeman & Co., San Francisco, 1977.

Michels, A. and R.O. Gibson, "The measurement of the viscosity of gases at high pressures—The viscosity of nitrogen to 1000 atms," *Proceedings of the Royal Society of London, Series A*, **134**, 288 (1931).

Newell, G.F., "Theory of oscillation type viscometer V: Disk oscillating between fixed plates," *Z. Angew-Math. Phys.*, **10**, 160 (1959).

Nieuwoudt, J.C. and I.R. Shankland, "Oscillating-Body Viscometers, article in: Measurement of the Transport Properties of Fluids," *Experimental Thermodynamics, Vol. III, IUPAC Series*, W.A. Wakeham et al. (Eds.), Blackwell Scientific Publications, London etc., 1975.

Ruthven, D.M., *Principles of Adsorption and Adsorption Processes*, Wiley-Interscience, New York, etc., 1984.

Sing, K.S.W. (Ed.) et al., "Reporting Physisorption Data for Gas/Solid Systems etc.," *Pure Appl. Chem.*, **57**, 603 (1985).

Sing, K.S.W. and S.J. Gregg, *Adsorption, Surface Area and Porosity*, Academic Press, Inc., London etc., 1983.

Staudt, R., G. Saller, M. Tomalla, and J.U. Keller, "A Note on Gravimetric Measurements of Gas-Adsorption Equilibria," *Ber. Bunsenges. Phys. Chem.*, **97**, 98 (1993).

Suzuki, M. (Ed.), *Proceedings of 4th Int. Conference on Fundamentals of Adsorption*, Kyoto, May 1992, Kodansha Ltd., Tokyo, 1993.

Vogel, E., "Konstruktion eines Quarzglas-Schwingscheibenviskosimeters und Messungen an Stickstoff und Argon," *Wiss. Z. Univ. Rostock*, **21**, 169 (M2, 1972).

Ward, M.D. and D.A. Buttry, "In Situ Interfacial Mass Detection with Piezoelectric Transducers," *Science*, **249**, 1000 (1990).

Yan, Y. and T. Bein, "Molecular Recognition on Acoustic Wave Devices: Sorption in Chemically Anchored Zeolite Monolayers," *J. Phys. Chem.*, **96**, 9387 (1992).