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DISTURBANCES IN WEIGHING DUE TO BUOYANCY*

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SUMMARY

Methods to determine and to compensate buoyancy effects, which disturb gravimetric investigations and which include temperature and pressure variations, are discussed. For typical arrangements of vacuum microbalances equations to calculate the pressure and temperature depended effect are given.

INTRODUCTION

Buoyancy is the most typical weighing error and the first one theoretically described as early as Archimedes (ref. 1). Its effect may exceed mass changes by orders of magnitude. Buoyancy produces serious errors in thermogravimetry, adsorption and susceptibility investigations because it produces ficticious mass indications which do not vary with time and, thus, may be overlooked. These disturbances, therefore, were often discussed at the preceding microbalance conferences (ref. 2,3) and are also reviewed in books (ref. 4,5). Whereas the effect itself is very simple and clear, in practice thermal and geometrical conditions produce unforeseen results. In the following we will calculate the effect for typical microbalance arrangements. On the other hand buoyancy can be a useful tool for density determination and may even be used as a method of weighing. These applications are discussed in another paper at this conference (ref. 6).

DISTURBANCES DUE TO BUOYANCY

As an example in Fig. 1 the influence of buoyancy on an adsorption isotherm is shown. Obviously, it is not possible to evaluate this curve without corrections. Therefore, buoyancy should be reduced or compensated for as far as possible, and the remainder has to be computed.

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If a solid is within a fluid the buoyancy forces are directed against the force of attraction in the gravitational field acting on the sample mass. The buoyancy force F_b equals the fluid mass displaced by the sample:

$$F_b = - g \, \varrho_f(p,T,M) \, V_s(T) \tag{1}$$

where ϱ_f = density of the fluid / kg m^{-3}; g = gravitational acceleration = 9.81 m s^{-2}; V_s = volume of the sample or of the gas volume displaced by the sample, respectively / m^3; p = gas pressure / Pa; T = abs. temperature / K; M = molecular mass of gas / kg; n = number of moles; R = gas constant = 8.314 / J mol^{-1} K^{-1}. The displaced mass m_b indicated by the balance is

$$m_b = - \varrho_f \, (p,T,M) \, V_s(T) \tag{2}$$

All three parameters influencing density and also the sample volume may vary during the experiment, whereas the thermal expansion of solids is below 10^{-4} K^{-1} and can mostly be neglected as a second order effect.

For a gas obeying the equation of state equation (2) becomes

$$m_b(p) = - \frac{p \, V_s \, M}{R \, T} \tag{3}$$

Investigations using non-ideal gases or near the saturation line modified equation of state or respective values of densities inserted in equation (2) may be used. Also this is a second order effect, which in many cases is swamped by other experimental difficulties.

In thermal analysis the sample volume is reduced with rising temperature, accompanied by a change of sample density. As a result of chemical reactions a volume increase can also occur. The resulting variation of the buoyancy should be considered by determining the effect at the beginning and the end. Then, as the simplest approximation a correction proportional to the indicated mass should be made.

In adsorption experiments the buoyancy of the adsorbate volume depends on the relative pressure p/p_0 and can be determined from the isotherm. To assess the effect we insert in the following equation

$$m_b = - \varrho_f \, \frac{m_a}{\varrho_a} \tag{4}$$

the density of nitrogen at 77 K: ϱ_a = 808 kg m^{-3}, the density of the fluid gas ϱ_f = 1.251 kg m^{-3} and calculate for p/p_0 = 1:

m_b = - 0.0015 m_a.

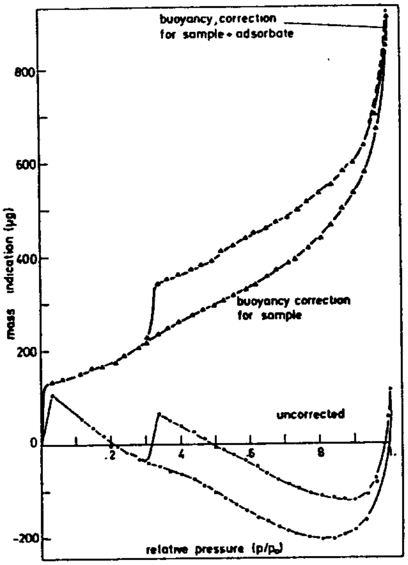

Fig. 1: Measured and corrected nitrogen isotherm on graphite at 77 K

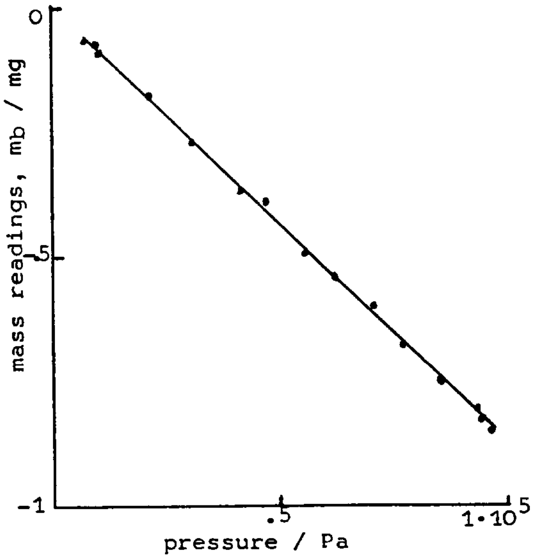

Fig. 3: Determination of buoyancy and regression line

THE BUOYANCY EFFECT FOR TYPICAL MICROBALANCES

In the following we confine ourselves to an invariable sample and neglect all second order effects including the buoyancy of the adsorbate.

To reduce buoyancy the volume of balance parts (beam, suspensions, pans) should be kept small and low density materials (aluminium, quartz) should be avoided. With a beam balance it is possible to compensate for the buoyancy effect using a counterweight of the same density and held at the same temperature. Compensations can be made for one-arm balances using a second balance equipped with a dummy sample. It should be noted that compensating for large buoyancy effects means making differences between two large numbers. If the compensation is not made very accurately, the results can be seriously falsified.

The total or – after compensation – residual buoyancy of a balance in a closed case is composed of the buoyancy of the mass sensor held in general at constant temperature and that of the sample exposed to varying temperatures, and it is a function of the gas density ϱ_f or of p,T and M, respectively.

$$m_b = -\,(m_{b,sensor}(p,M) + m_{b,sample}(p,T,M)) \qquad (5)$$

Both components of buoyancy must be measured separately.

The Spring Balance

In a spring balance the spring is held either at a constant temperature (Fig. 2) or is thermostatted at the variable sample temperature. In the latter case the buoyancy of the spring should be regarded as a part of the sample's buoyancy and term 1 in eq. 5 vanishes.

Alternately, first the buoyancy of the spring is determined, loading the balance with a gold mass as big as a typical sample mass, thermostatting the whole arrangement at the normal temperature of the spring. After degassing in vacuum, the measuring gas, e.g. nitrogen, is introduced and the mass indication read between widely differing pressures, e.g. at 10^3 and 10^5 Pa. The results are drawn in a diagram m_b/p (Fig. 3) and the measuring points are connected by a regression line. The slope of this line is the pressure related total buoyancy $m_{b,total}$.

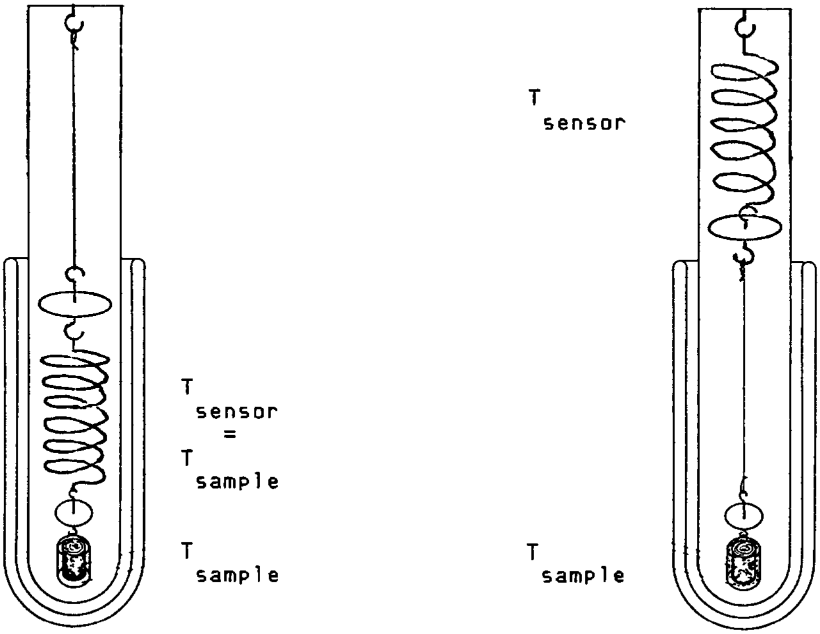

Fig. 2: Sources of buoyancy in the spring balance

Multiplication by 10^5 yields the buoyancy at atmospheric pressure. The buoyancy of the spring results using

$$m_{b,\mathrm{sensor}} = m_{b,\mathrm{total}} - \frac{m_{\mathrm{Au}}}{\varrho_{\mathrm{Au}}} \varrho_f \qquad (6)$$

After replacing the gold dummy by the sample the measurement is repeated and the buoyancy of the sample calculated using

$$m_{b,\mathrm{sample}} = m_{b,\mathrm{total}} - m_{b,\mathrm{sensor}} \qquad (7)$$

The (always negative) correction of the mass than can be calculated using

$$m_b(p) = (m_{b,\mathrm{sensor}} + m_{b,\mathrm{sample}} \frac{T_{\mathrm{sensor}}}{T_{\mathrm{sample}}})\, p \qquad (8)$$

and in the case of replacing the initial gas of molecular mass M_1 by another gas or gas mixture with (mean) molecular mass M_2:

$$m_b(p) = (m_{b,\mathrm{sensor}} + m_{b,\mathrm{sample}} \frac{T_{\mathrm{sensor}}}{T_{\mathrm{sample}}}) \frac{M_2}{M_1}\, p \qquad (9)$$

The Beam Balance

The beam balance - equal or unequal armlength - provides a means to compensate for buoyancy. On account of simplicity we confine ourselves to the symmetrical design of an automatically deflection compensating balance. As indicated by four circles in Fig. 4 buoyancy may arise from four sources: sample + adsorbate, counterweight and both sides of beam with suspensions.

The symmetrical design of the balance beam with parts of the indicator system ensures that the buoyancy of those parts is kept small. After both sides of the beam have been balanced in mass, the residual buoyancy is measured with the balance loaded on either side with identical pieces of gold corresponding to the later load, because the zero point is somewhat load dependent. The measurement is performed as described above. The effect can be offset by suspending an aluminium wire at the knife edge hanger at the side of lower volume and a gold wire at the opposite side. The identical masses of the wires are calculated as follows:

$$m_{\mathrm{Au}} = m_{\mathrm{Al}} = \frac{\varrho_{\mathrm{Au}}\, \varrho_{\mathrm{Al}}\, m_b^p\, 10^5}{\varrho_f\, (\varrho_{\mathrm{Au}} - \varrho_{\mathrm{Al}})} \qquad (10)$$

with $\varrho_{\mathrm{Au}} = 19.3 \times 10^3$ kg m^{-3}, $\varrho_{\mathrm{Al}} = 2.7 \times 10^3$ kg m^{-3}, $\varrho_f = 1.15$ kg m^{-6}.

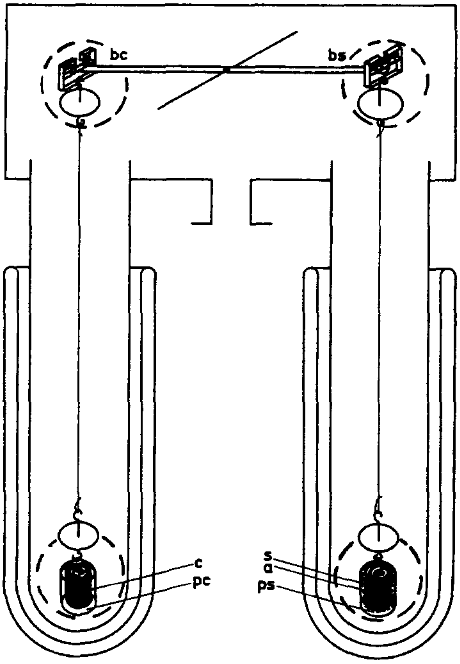

Fig. 4: Sources of buoyancy in the symmetrical beam balance. bc: beam + suspension at the counterweight side; bs: - at the sample side; pc, ps: pans; c: counterweight; s: sample; a: adsorbate

The interpretation of buoyancy effects using a beam balance is somewhat puzzling because the balance indicates a mass defect proportional to the volume difference on both sides of the balance and this may be positive or negative. A typical sequence of effects when performing the measurement of a sorption isotherm (ref. 7) is demonstrated in Fig. 5: The bigger volume of sample + pan may be at the right side. On evacuating the balance, the mass of the sample decreases as a result of drying. On account of buoyancy this decrease is reduced and even an apparent mass gain may be indicated (Fig. 5a —> 5b). When degassing is finished the balance is electrically compensated to zero (Fig. 5c). On measuring the isotherm, the mass increases but the indicated mass is lower and may go even to negative values on account of buoyancy (Fig. 5d and Fig. 1). On measuring an isobar, the temperature is increased and desorption takes place. However, because the gas density decreases the buoyancy counteracts producing a smaller decrease or even an increase of the indication.

Suspension parts on both sides should be made of identical materials and equal mass. Careful correction using quartz pieces is important for the quartz pans.

The buoyancy of the sample can be eliminated by using a counterweight of the same density if this is kept at the same temperature. Pieces of quartz and gold produce counterweights with densities between 2.2 and 19.3 x 10^3 kg m^{-3}. The masses of the counterweight components are calculated as follows:

$$m_Q = m_s \frac{\rho_Q (\rho_{Au} - \rho_s)}{\rho_s (\rho_{Au} - \rho_Q)} \qquad (11)$$

$$m_{Au} = m_s - m_Q \qquad (12)$$

where m_s = mass of sample, ρ_s = density of the sample, m_{Au} = mass of gold, ρ_{Au} = density of gold, m_Q = mass of quartz, ρ_Q density of quartz. Counterweights with apparent densities below 2.2 x 10^3 kg m^{-3} may be realised by hollow quartz beds.

Frequently, however, the density of the degassed material is not known with sufficient accuracy, so that after compensation there is still a residual buoyancy. From that the real density can be calculated (see ref. 6) and the effect corrected at once.

Buoyancy determinations of microporous samples like activated

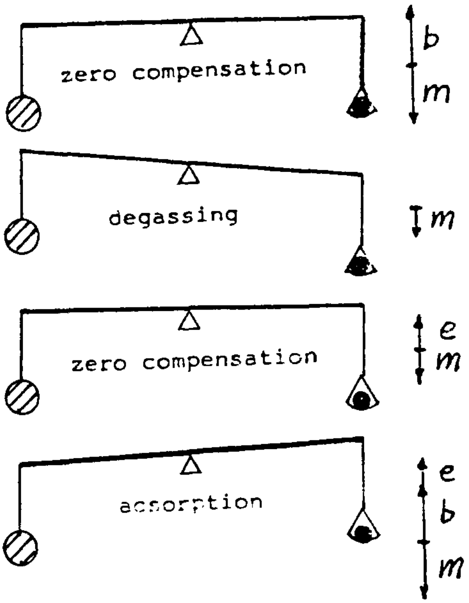

Fig. 5: Mass indication at an adsorption measuring sequence

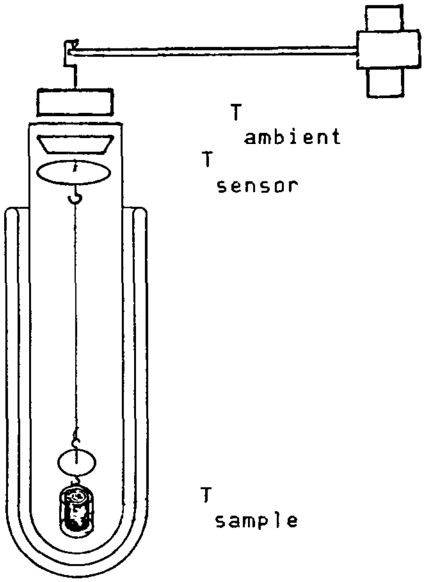

Fig. 6: Sources of buoyancy in the magnetic suspension balance

carbon sometimes fail because the samples adsorb surprisingly large amounts of the measuring gas at room temperature. At room temperature a gas may have access to micropores which are blocked at low temperatures. This means that the surface at room temperature may be much higher than that at 77 K. In this case a residual buoyancy error is usually not of importance in view of the large amounts of adsorbed gas.

For the subsequent measurements, sample and counterweight should be kept at equal temperature. To avoid condensation in the counterweight pan, however, in adsorption experiments the temperature on this side should be somewhat higher e.g. by adding a small quantity of oxygen to the nitrogen bath.

The Suspension Balance

In the magnetic suspension balance (Fig. 6) the suspension magnet must be held near room temperature, generally deviating from the sample temperature. In addition, a buoyancy effect may be observed at the beam balance which carries the electromagnet controlling the suspension magnet. This beam balance is outside the reaction vessel, thermostatted at room temperature but exposed to the variations of the atmospheric pressure. The resulting buoyancy effect should be cancelled out applying a quartz piece or an aluminium wire to the beam at its low volume side.

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