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VACUUM FOR BALANCES*

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Abstract

.This paper deals with the design of gravimetric apparatus with regard to the requirements of vacuum. Items discussed include the calculation of suction speed and ultimate vacuum, the choice of the pump and of the method of pressure control, and the design of the balance and the balance stand.

Keywords: balance, vacuum, weighing

Introduction

Mass determinations are carried out in vacuum for various reasons [1]:

– to avoid re-contamination of a freshly-prepared surface or cleaned sample before the measurement starts,
– to remove gases acting as a diffusion barrier and slowing down evaporation or the reaction of a gas component with the sample surface,
– to examine mass variations due to physical or chemical reactions below atmospheric pressure, e.g. the measurement of adsorption isotherms.

The different tasks require different qualities of the vacuum and this should be considered in the choice of the pump. The balance needs to be suitable for vacuum, and the tubes of the apparatus should be designed in such a way that the gas flow is not restricted. For this purpose, simple rules should be observed, but these seem to be unknown for many balance manufacturers and experimenters. The present paper deals with the design of gravimetric apparatus with regard to the requirements of vacuum.
We have several possibilities to weigh a sample in vacuum [2] (Fig. 1):

a) The sample can be weighed in a closed, evacuated bottle. This may be used to check the sample mass after enclosure.

The main application is in the determination of the mass of a gas filled in an empty cylinder. From the pressure and mass of the gas in a calibrated volume, the density and the molecular mass can be derived.

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* Dedicated to Dr. ir. Carel H. Massen on his 60th birthday

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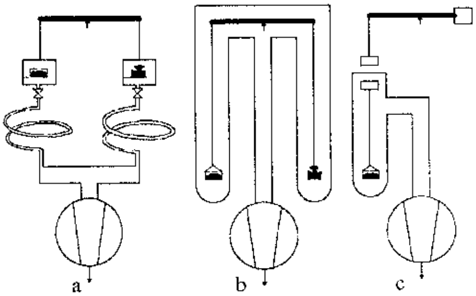

Fig. 1 Methods of mass determination in vacuum. a – Weighing in evacuated bottles, connected by means of flexible tubes to the vacuum pump and the gas supply, b – weighing by means of a vacuum balance arranged in the vacuum vessel, c –weighing of a sample suspensed by means of a magnetic coupling and enclosed in a separate bulb

In order to control the gas pressure, the bottle can be connected by means of a flexible tube to a vacuum pump and gas supply. In this arrangement, weighings are not affected by buoyancy, but disturbances by the flexible tube will decrease the sensitivity. If the counterweight vessel is connected simultaneously, the gas mass does not influence the weighings either. Such arrangements are applied for the investigation of catalytic processes, in particular at high pressure and with occasional evacuation for gas exchange. As conventional balances are used in all such cases, we abstain from discussing these methods.

b) The balance with pans and sample is arranged in a vacuum vessel. For this purpose, special vacuum balances are needed.

c) The sample is in a separate vacuum vessel, suspended by means of a controlled magnet from the balance, which is in the atmosphere.

Theory

The basic equation describing the pressure in a vacuum chamber is

$$pS_{\mathrm{eff}} = -V\frac{\mathrm{d}p}{\mathrm{d}t} + q \tag{1}$$

where p is the pressure, t is the time, S_{eff} is the effective pumping speed and q is the influx of gas. To obtain a low ultimate pressure, it is necessary to have a high pumping speed and a low influx. It might appear from Eq. (1) that the volume of the chamber affects only the pumpdown speed. However, since the desorption of gas contributes to the influx, the extent of the walls and the geometry of the chamber will influence the ultimate pressure as well. The ultimate pressure is reached at the steady state between gas influx and removal, i.e. $\mathrm{d}p/\mathrm{d}t=0$. In this case, Eq. (1) reduces to

$$p = \frac{q}{S_{\mathrm{eff}}} \tag{2}$$

S_{eff} is to be determined near to the sample, because 'vacuum is a very viscous liquid' and the flow is hindered markedly by the tubing system, including the valves and other obstacles. This is expressed by

$$\frac{1}{S_{\text{eff}}}=\frac{1}{L}+\frac{1}{S_{\text{p}}} \tag{3}$$

where S_{p} is the speed of the pump and L is the total conductance of the tubing system, which results from the conductance of the parts L_{i} according to

$$\frac{1}{L}=\sum\frac{1}{L_{\text{i}}} \tag{4}$$

The conductance of a circular aperture in the molecular flow region is expressed as

$$L_{\text{a}}=9.18d_{\text{a}}^{2} \tag{5}$$

where L_{a} is the conductance in l s^{-1} for air at 20°C and the diameter d_{a} in cm. The molecular flow region is the region where the mean free path of a gas molecule λ is much larger than the diameter of the tubing d_{t}, characterized by the Knudsen number

$$Kn=\frac{\lambda}{d_{\text{t}}} \tag{6}$$

For typical microbalance arrangements, this corresponds to a pressure of about 0.1 Pa. For negligible outgassing tubes, the conductance can be calculated by using

$$L_{\text{t}}=\frac{12.12d_{\text{t}}^{3}}{l_{\text{t}}+\frac{4d_{\text{t}}}{3}} \tag{7}$$

The conductance of commercially produced parts is in general indicated. For outgassing parts, such as bellows, the pressure drop due to gas influx must be considered.

Ultimate vacuum

Demands on vacuum should correspond to the requirements, because the costs for vacuum apparatus increase exponentially from the rough vacuum generated by means of a water jet pump to the fine vacuum produced by a rotary vane pump, and to high and ultrahigh vacuum.

If physical or chemical reactions with the sample surface should be observed, the surface needs to be cleaned at the beginning of the investigation. A clean surface can be generated by vapour deposition or by sputtering in UHV below 10^{-5} Pa. Cleaving of bulk material in UHV may also be applied, but the new surface may be covered with contaminants occluded in the bulk material. A widely used cleaning technique is baking under vacuum. As a preparatory step for thermogravimetric or sorption measurements, a high vacuum better than 10^{-3} Pa may be sufficient.

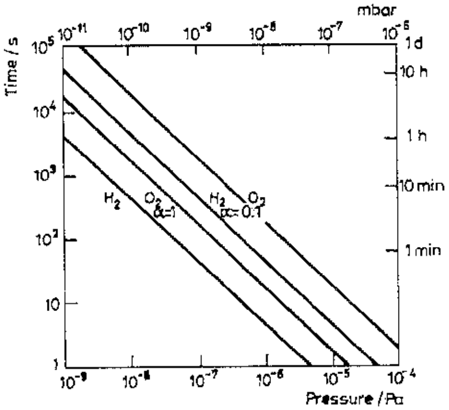

Fig. 2 Time required for the coverage of a smooth surface with a 10 per cent contaminating layer as a function of pressure and sticking probability α

After preparation of the sample, some time is required to adjust the measuring conditions, e.g. the temperature. Within this period of time, the sample surface may be contaminated again. Figure 2 shows the time period in which a smooth surface will be covered with a 10 per cent sorbate layer, as a function of the partial pressure of the sorptive gas and for different sticking probabilities α. The diagram demonstrates that, after degassing, the measurements should be initiated without delay, beginning in a very good vacuum free from considerable components of the pump fluid, of monomers from the sealing material and from active molecules such as oxygen.

If a dry pump is not used, the apparatus must be kept free of condensable constituents by means of a cold trap or catalysts. When the sample is cooled, the walls of the cooled balance tubes (Fig. 3) act as a cold trap, and the oven for sample degassing should therefore be exchanged by the cryostat as quickly as possible. Fortunately, with the balance, contamination can be observed.

Another value for the required ultimate vacuum is given by thermo-molecular flow. By temperature gradients, a gas flow is generated which gives rise to reactive forces on the hangdown wires and the pans in the vicinity of temperature gradients. For typical arrangements, as depicted in Figs 3, 5 and 6, the maximum of the Knudsen forces is observed at $Kn=1$. To avoid disturbances, the ultimate pressure should be below 10^{-2} Pa.

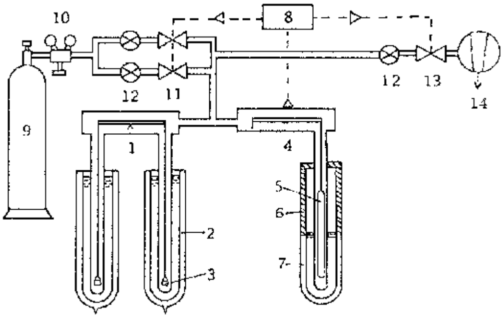

Fig. 3 Pressure control for a microbalance for the pressure range 10^{-2} Pa to 10^{6} Pa according to Robens and Sandstede/Massen *et al.* 1,4 – compensating vacuum microbalances, 2 – cryostat or heater, 3 – sample pan, 4 – buoyancy/Knudsen pressure gauge, 5 – void glass balloon, 6 – thermostat, 7 – cryostat, 8 – pressure control, 9 – (N_2) gas cylinder, 10 – reducing valve, 11 – solenoid valves, 12 – needle valves, 13 – motor metering valve, 14 – vacuum aggregate: turbo molecular pump+rotary vane pump

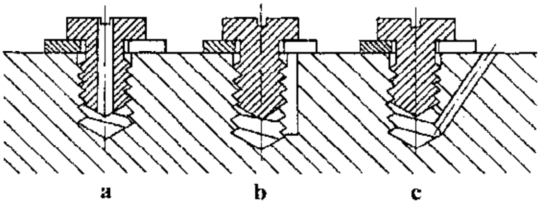

Fig. 4 Several possibilities to vent screw-holes. a – central drill hole, b – lateral groove pin, c – lateral drill hole. In addition, the washer should be provided with a sparing

It may be mentioned that in such arrangements disturbances by Knudsen forces vanish in the pressure region above 10 Pa, whereas disturbances due to convection are still negligible up to 100 Pa. The region between 10 and 100 Pa, therefore, is very suitable for thermogravimetric investigations.

Choice of the pump

Any pump which produces the required ultimate vacuum is suitable for combination with a balance. The transmission of vibrations from the backing pump can be prevented by means of a plastic tube and vibrations of modern turbo molecular pumps are virtually insignificant. By means of baffles and cold traps, the balance vessel must be protected from vapour backstreaming from jet pumps. For all types of pumps after turn-off, dry air or a protecting gas should be fed into the apparatus from above the pump, so that no pump oil or contaminants from the traps are swept into the balance chamber.

It follows from Eq. (3) that the speed of the pump need not be much larger than the total conductance of the tubular system. By experience, however, we

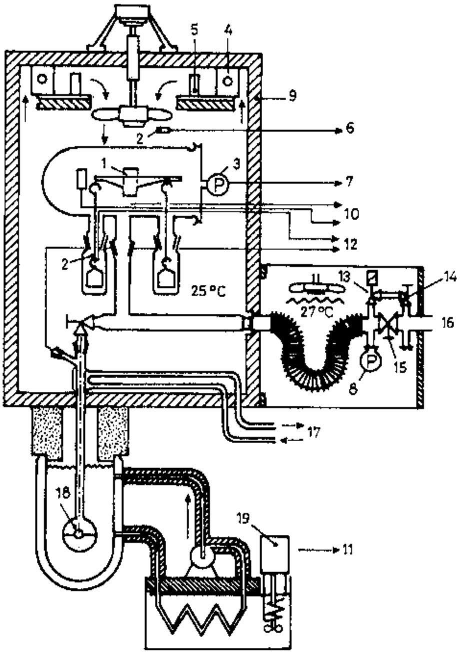

Fig. 5 Gravimetric apparatus according to Willems for the measurement of water adsorption isotherms. 1 – microbalance, 2 – vacuum chamber, 3 – diaphragm pressure gauge, 4 – water cooler, 5 – heater, 6 to temperature control and record, 7 – to pressure control and record, 8 – Pirani vacuum gauge, 9 – heat-insulated case, 10 – to balance control and mass record, 11 – thermostat control, 12 – to temperature record, 13 – solenoid valve, 14 – metering valve, 15 – main suction valve, 16 – suction port, 17 – thermostat (25.0°C), 18 – thermostat water bulb for pressure control, 19 – thermostat

have found that a speed of about 100 l s^{-1} is required to obtain a good vacuum in an appropriate time for arrangements shown in Figs 1b and 1c.

Pressure control

The gas pressure for the range above 10^{-2} Pa in the balance chamber can be regulated by means of metering and solenoid valves controlled by a pressure gauge. An example of a gravimetric apparatus is shown in Fig. 3. In this special case, a second balance using buoyancy and Knudsen forces is the pressure sensor [3, 4]. If the pressure gauge indicates a deviation from the set point, gas is either introduced by means of the opening of solenoid valves of different sizes (depending on the pressure) or pumped off by slow operation of a motor-controlled metering valve.

For high vacuum and UHV, a dynamic procedure may be applied [5]. A steady gas stream is introduced into the balance chamber and steadily pumped off by the pump.

Choice of the balance

For sorption and thermogravimetric measurements, high-resolution beam balances are most suitable (Fig. 1b). The relative resolution (discrimination threshold related to maximum capacity) of commercial instruments is of the order of 10^{-8} and may be improved to 10^{-10}. Disadvantageously, the sensor cannot be baked at temperatures above 100°C. Further, the electronic parts and coils may be affected by organic or corrosive vapour [7]. In order to attain UHV, it is necessary to place the transducer outside the vacuum system [8]. This is not the case in any commercial beam balance. On the contrary, ancillary equipment such as sample changers is to be tolerated, which may additionally worsen the vacuum.

The vacuum chamber of the magnetic suspension balance (Fig. 1c) contains only the suspension magnet, sample pan and sample. It can be baked up to 200°C. The magnet may be protected against aggressive gases by a quartz envelope. In some suspension balances, however, so many parts are built in that the advantage of separation of the sensor and sample is called into question.

With regard to the low surface and bakability, spring balances of quartz, tungsten or special alloys are most suitable for vacuum. In consequence of the low relative resolution of 10^{-5}, application is limited.

Quartz resonators and other oscillating sensors are used for special tasks, e.g. thickness monitoring and contamination measurements. For such devices, the sample needs to be connected strongly to the sensor surface. Strain gauges and other force sensors exhibit a low relative resolution comparable to that of spring type balances.

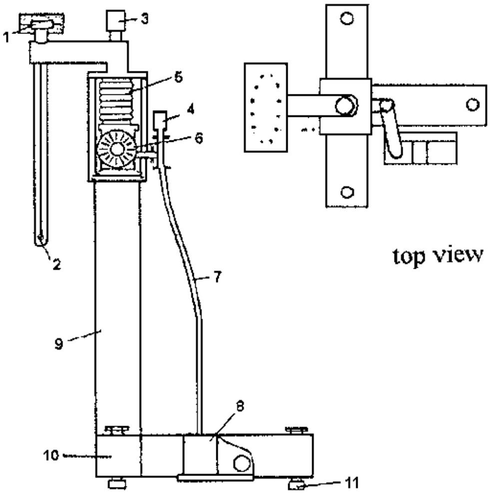

Fig. 6 Arrangement of a beam-type vacuum microbalance in a vacuum apparatus. 1 – microbalance, 2 – sample pan, 3 – Penning vacuum gauge, 4 – Pirani vacuum gauge, 5 – stainless steel bellows, 6 – turbo molecular pump, 7 – flexible tube, 8 – rotary vane pump, 9 – hollow pillar, 10 – footing of massive steel, 11 – shock absorbers

Design of the apparatus

As a general rule for the design of the apparatus, the diameter of the connection between the high-vacuum pump and the vacuum chamber should correspond to the diameter of the suction flange of the pump. The tube should be short, long bellows should be avoided. Parts built in should not have any hollow space with a small entrance. In such a void, liquids such as oil or water may be trapped, which evaporate slowly and worsen the ultimate vacuum. Screw holes and the like need to be vented by means of drill holes, as shown in Fig. 4. In addition, washers should be provided with a sparing.

Typical microgravimetric apparatus with beam balances [9] are shown in Figs 5–7. In the apparatus for water vapour measurements described by Willems [10] (Fig. 5), the speed of the 80 l s^{-1} oil diffusion pump drops gratuitously to about 1 l s^{-1}, because of the long tubes and a stainless steel bellows. The pressure sensor is arranged in the vacuum chamber, not far from the sample.

In Fig. 6, a 120 l s^{-1} turbomolecular pump is seen to be suspended freely from a short and wide stainless steel bellows. The pumping speed is limited, mainly by the long balance tubes, to about 8 l s^{-1}. The backing pump (of rotary vane type) is placed separately on the ground and connected via a flexible tube. A Penning gauge arranged just above the suction valve provides only a rough picture of the vacuum in the manifold.

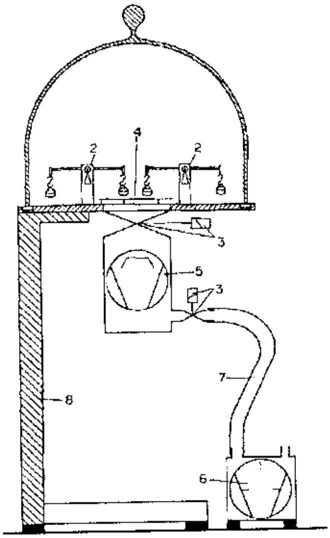

Fig. 7 Arrangement of several vacuum microbalances under a bell jar. 1 – bell jar, 2 – microbalances, 3 – solenoid valves, 4 – flow protection shield, 5 – high-vacuum pump, 6 – rotary vane pump, 7 – flexible tube, 8 – stand

Figure 7 depicts an apparatus with several balances. The pump with the main suction valve is clamped directly to the vacuum chamber. The vibrations of a

500 l s^{-1} turbomolecular pump do not disturb the weighings. A parallel small suction line including a metering valve is not shown. This is required for slow prepumping in order to avoid the scattering of powdery samples.

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