

A.4. VAPOUR PRESSURE

1. METHOD

The majority of the methods described are based on the OECD Test Guideline (1). The fundamental principles are given in references (2) and (3).

1.1. INTRODUCTION

It is useful to have preliminary information on the structure, the melting temperature and the boiling temperature of the substance to perform this test.

There is no single measurement procedure applicable to the entire range of vapour pressures. Therefore, several methods are recommended to be used for the measurement of vapour pressure from $< 10^{-4}$ to 10^5 Pa.

Impurities will usually affect the vapour pressure, and to an extent which depends greatly upon the kind of impurity.

Where there are volatile impurities in the sample, which could affect the result, the substance may be purified. It may also be appropriate to quote the vapour pressure for the technical material.

Some methods described here use apparatus with metallic parts; this should be considered when testing corrosive substances.

1.2. DEFINITIONS AND UNITS

The vapour pressure of a substance is defined as the saturation pressure above a solid or liquid substance. At the thermodynamic equilibrium, the vapour pressure of a pure substance is a function of temperature only.

The SI unit of pressure which should be used is the pascal (Pa).

Units which have been employed historically, together with their conversion factors, are:

$$1 \text{ Torr} (\equiv 1 \text{ mm Hg}) = 1,333 \times 10^2 \text{ Pa}$$

$$1 \text{ atmosphere} = 1,013 \times 10^5 \text{ Pa}$$

$$1 \text{ bar} = 10^5 \text{ Pa}$$

The SI unit of temperature is the kelvin (K).

The universal molar gas constant R is $8,314 \text{ J mol}^{-1} \text{ K}^{-1}$

The temperature dependence of the vapour pressure is described by the Clausius-Clapeyron equation:

$$\log p = \frac{\Delta H_v}{2,3RT} + \text{const.}$$

where:

p = the vapour pressure of the substance in pascals

ΔH_v = its heat of vaporization in Jmol^{-1}

R = the universal molar gas constant in $\text{Jmol}^{-1} \text{ K}^{-1}$

T = thermodynamic temperature in K

1.3. REFERENCE SUBSTANCES

Reference substances do not need to be employed in all cases when investigating a new substance. They should primarily serve to check the performance of the method from time to time and to allow comparison with results from other methods.

1.4. PRINCIPLE OF THE TEST METHODS

For determining the vapour pressure, seven methods are proposed which can be applied in different vapour pressure ranges. For each method, the vapour pressure is determined at various temperatures. In a limited temperature range, the logarithm of the vapour pressure of a pure substance is a linear function of the inverse of the temperature.

1.4.1. Dynamic method

In the dynamic method, the boiling temperature which pertains to a specified pressure is measured.

Recommended range:

10^3 up to 10^5 Pa.

This method has also been recommended for the determination of normal boiling temperature and is useful for that purpose up to 600 K.

1.4.2. Static method

In the static process, at thermodynamic equilibrium, the vapour pressure established in a closed system is determined at a specified temperature. This method is suitable for one component and multicomponent solids and liquids.

Recommended range:

10 up to 10^5 Pa.

This method can also be used in the range 1 to 10 Pa, providing care is taken.

1.4.3. Isoteniscope

This standardized method is also a static method but is usually not suitable for multicomponent systems. Additional information is available in ASTM method D-2879-86.

Recommended range:

from 100 up to 10^5 Pa.

1.4.4. Effusion method: Vapour pressure balance

The quantity of substance leaving a cell per unit time through an aperture of known size is determined under vacuum conditions such that return of substance into the cell is negligible (e.g. by measurement of the pulse generated on a sensitive balance by a vapour jet or by measuring the weight loss).

Recommended range:

10^{-3} to 1 Pa.

1.4.5. Effusion method: By loss of weight or by trapping vaporisate

The method is based on the estimation of the mass of test substance flowing out per unit of time of a Knudsen cell (4) in the form of vapour, through a micro-orifice under ultra-vacuum conditions. The mass of effused vapour can be obtained either by determining the loss of mass of the cell or by condensing the vapour at low temperature and determining the amount of volatilized substance using chromatographic analysis. The vapour pressure is calculated by applying the Hertz-Knudsen relation.

Recommended range:

10^{-3} to 1 Pa.

1.4.6. Gas saturation method

A stream of inert carrier gas is passed over the substance in such a way that it becomes saturated with its vapour. The amount of material transported by a known amount of carrier gas is measurable either by collection in a suitable trap or by an intrain analytical technique. This is then used to calculate the vapour pressure at a given temperature.

Recommended range:

10^{-4} to 1 Pa.

This method can also be used in the range 1 to 10 Pa providing care is taken.

1.4.7. Spinning rotor

In the spinning rotor gauge, the actual measuring element is a small steel ball which is suspended in a magnetic field and rotates with high speed. The gas pressure is deduced from the pressure-dependent slow-down of the steel ball.

Recommended range:

10^{-4} to 0,5 Pa.

1.5. QUALITY CRITERIA

The various methods of determining the vapour pressure are compared as to application, repeatability, reproducibility, measuring range, existing standard. This is done in the following table.

Measuring Method	Substances		Estimated Repeatability ⁽¹⁾	Estimated Reproducibility ⁽¹⁾	Recommended Range	Existing Standard
	solid	liquid				
1.4.1. Dynamic method	Low melting	yes	Up to 25%	Up to 25%	10^3 Pa to 2×10^3 Pa	—
			1 to 5%	1 to 5%	2×10^3 Pa to 10^5 Pa	—
1.4.2. Static method	yes	yes	5 to 10%	5 to 10%	10 Pa to 10^5 Pa ⁽²⁾	NFT 20-048 (5)
1.4.3. Isoteniscope	yes	yes	5 to 10%	5 to 10%	10^2 Pa to 10^5 Pa	ASTM-D 2879-86
1.4.4. Effusion method Vap.Pres. balance	yes	yes	5 to 20%	Up to 50 %	10^{-3} Pa to 1 Pa	NFT 20-047(6)
1.4.5. Effusion method weight loss	yes	yes	10 to 30%	—	10^{-3} Pa to 1 Pa	—
1.4.6. Gas saturation method	yes	yes	10 to 30%	Up to 50 %	10^{-4} Pa to 1 Pa ⁽²⁾	—
1.4.7. Spinning rotor method	yes	yes	10 to 20%	—	10^{-4} Pa to 0,5 Pa	—

⁽¹⁾ Dependent of the degree of purity

⁽²⁾ These methods can also be used in the range 1 to 10 Pa providing care is taken.

1.6. DESCRIPTION OF THE METHODS

1.6.1. Dynamic measurement

1.6.1.1. Apparatus

The measuring apparatus typically consists of a boiling vessel with attached cooler made of glass or metal (figure 1), equipment for measuring the temperature, and equipment for regulating and measuring the pressure. A typical measuring apparatus shown in the drawing is made from heat-resistant glass and is composed of five parts:

The large, partially double-walled tube consists of a ground jacket joint, a cooler, a cooling vessel and an inlet.

The glass cylinder, with a Cottrell 'pump', is mounted in the boiling section of the tube and has a rough surface of crushed glass to avoid 'bumping' in the boiling process.

The temperature is measured with a suitable temperature sensor (e.g. resistance thermometer, jacket thermocouple) immersed in the apparatus to the point of measurement (No.5, figure 1) through a suitable inlet (e.g. male ground joint).

The necessary connections are made to the pressure regulation and measuring equipment.

The bulb, which acts as a buffer volume, is connected with the measuring apparatus by means of a capillary tube.

The boiling vessel is heated by a heating element (e.g. cartridge heater) inserted into the glass apparatus from below. The heating current required is set and regulated via a thermocouple.

The necessary vacuum of between 10^2 Pa and approximately 10^5 Pa is produced with a vacuum pump.

A suitable valve is used to meter air or nitrogen for pressure regulation (measuring range approximately 10^2 to 10^5 Pa) and ventilation.

Pressure is measured with a manometer.

1.6.1.2. Measurement procedure

The vapour pressure is measured by determining the boiling temperature of the sample at various specified pressures between roughly 10^3 and 10^5 Pa. A steady temperature under constant pressure indicates that the boiling temperature has been reached. Frothing substances cannot be measured using this method.

The substance is placed in the clean, dry sample vessel. Problems may be encountered with non-powder solids but these can sometimes be solved by heating the cooling jacket. Once the vessel has been filled the apparatus is sealed at the flange and the substance degassed. The lowest desired pressure is then set and the heating is switched on. At the same time, the temperature sensor is connected to a recorder.

Equilibrium is reached when a constant boiling temperature is recorded at constant pressure. Particular care must be taken to avoid bumping during boiling. In addition, complete condensation must occur on the cooler. When determining the vapour pressure of low melting solids, care should be taken to avoid the condenser blocking.

After recording this equilibrium point, a higher pressure is set. The process is continued in this manner until 10^5 Pa has been reached (approximately 5 to 10 measuring points in all). As a check, equilibrium points must be repeated at decreasing pressures.

1.6.2. Static measurement

1.6.2.1. Apparatus

The apparatus comprises a container for the sample, a heating and cooling system to regulate the temperature of the sample and measure the temperature. The apparatus also includes instruments to set and measure the pressure. Figures 2a and 2b illustrate the basic principles involved.

The sample chamber (figure 2a) is bounded on one side by a suitable high-vacuum valve. A U-tube containing a suitable manometer fluid is attached to the other side. One end of the U-tube branches off to the vacuum pump, the nitrogen cylinder or ventilation valve, and a manometer.

A pressure gauge with a pressure indicator can be used instead of a U-tube (figure 2b).

In order to regulate the temperature of the sample, the sample vessel together with valve and U-tube or pressure gauge is placed in a bath which is kept at a constant temperature of $\pm 0,2$ K. The temperature measurements are taken on the outside wall of the vessel containing the sample or in the vessel itself.

A vacuum pump with an upstream cooling trap is used to evacuate the apparatus.

In method 2a the vapour pressure of the substance is measured indirectly using a zero indicator. This takes into account the fact that the density of the fluid in the U-tube alters if the temperature changes greatly.

The following fluids are suitable for use as zero indicators for the U-tube, depending on the pressure range and the chemical behaviour of the test substance: silicone fluids, phthalates. The test substance must not dissolve noticeably in or react with the U-tube fluid.

For the manometer, mercury can be used in the range of normal air pressure to 10^2 Pa, while silicone fluids and phthalates are suitable for use below 10^2 Pa down to 10 Pa. Heatable membrane capacity manometers can even be used at below 10^{-1} Pa. There are also other pressure gauges which can be used below 10^2 Pa.

1.6.2.2. Measurement procedure

Before measuring, all components of the apparatus shown in figure 2 must be cleaned and dried thoroughly.

For method 2a, fill the U-tube with the chosen liquid, which must be degassed at an elevated temperature before readings are taken.

The test substance is placed in the apparatus, which is then closed and the temperature is reduced sufficiently for degassing. The temperature must be low enough to ensure that the air is sucked out, but -in the case of multiple component system- it must not alter the composition of the material. If required, equilibrium can be established more quickly by stirring.

The sample can be supercooled with e.g. liquid nitrogen (taking care to avoid condensation of air or pump fluid) or a mixture of ethanol and dry ice. For low-temperature measurements use a temperature-regulated bath connected to an ultra-cryomat.

With the valve over the sample vessel open, suction is applied for several minutes to remove the air. The valve is then closed and the temperature of the sample reduced to the lowest level desired. If necessary, the degassing operation must be repeated several times.

When the sample is heated the vapour pressure increases. This alters the equilibrium of the fluid in the U-tube. To compensate for this, nitrogen or air is admitted to the apparatus via a valve until the pressure indicator fluid is at zero again. The pressure required for this can be read off a precision manometer at room temperature. This pressure corresponds to the vapour pressure of the substance at that particular measuring temperature.

Method 2b is similar but the vapour pressure is read off directly.

The temperature-dependence of vapour pressure is determined at suitably small intervals (approximately 5 to 10 measuring points in all) up to the desired maximum. Low-temperature readings must be repeated as a check.

If the values obtained from the repeated readings do not coincide with the curve obtained for increasing temperature, this may be due to one of the following:

1. The sample still contains air (e.g. high-viscosity materials) or low-boiling substances, which is released during heating and can be removed by suction following further supercooling.
2. The cooling temperature is not low enough. In this case liquid nitrogen is used as the cooling agent.

If either 1 or 2 is the case, the measurements must be repeated.

3. The substance undergoes a chemical reaction in the temperature range investigated (e.g. decomposition, polymerization).

1.6.3. Isoteniscope

A complete description of this method can be found in reference 7. The principle of the measuring device is shown in figure 3. Similarly to the static method described in 1.6.2, the isoteniscope is appropriate for the investigation of solids or liquids.

In the case of liquids, the substance itself serves as the fluid in the auxiliary manometer. A quantity of the liquid, sufficient to fill the bulb and the short leg of the manometer section, is put in the isoteniscope. The isoteniscope is attached to a vacuum system and evacuated, then filled by nitrogen. The evacuation and purge of the system is repeated twice to remove residual oxygen. The filled isoteniscope is placed in an horizontal position so that the sample spreads out into a thin layer in the sample bulb and manometer section (U-part). The pressure of the system is reduced to 133 Pa and the sample gently warmed until it just boils (removal of dissolved fixed gases). The isoteniscope is then placed so that the sample returns to the bulb and short leg of the manometer, so that both are entirely filled with liquid. The pressure is maintained as for degassing; the drawn-out tip of the sample bulb is heated with a small flame until sample vapour released expands sufficiently to displace part of the sample from the upper part of the bulb and manometer arm into the manometer section of the isoteniscope, creating a vapour-filled, nitrogen-free space.

The isoteniscope is then placed in a constant temperature bath, and the pressure of nitrogen is adjusted until its pressure equals that of the sample. Pressure balance is indicated by the manometer section of the isoteniscope. At the equilibrium, the vapour pressure of nitrogen equals the vapour pressure of the substance.

In the case of solids, depending on the pressure and temperature range, the manometer liquids listed in 1.6.2.1 are used. The degassed manometer liquid is filled into a bulge on the long arm of the isoteniscope. Then the solid to be investigated is placed in the bulb and is degassed at elevated temperature. After that the isoteniscope is inclined so that the manometer liquid can flow into the U-tube. The measurement of vapour pressure as a function of temperature is done according to 1.6.2.

1.6.4. Effusion method: Vapour pressure balance

1.6.4.1. Apparatus

Various versions of the apparatus are described in the literature (1). The apparatus described here illustrates the general principle involved (figure 4). Figure 4 shows the main components of the apparatus, comprising a high-vacuum stainless steel or glass container, equipment to produce and measure a vacuum and built-in components to measure the vapour pressure on a balance. The following built-in components are included in the apparatus:

-an evaporator furnace with flange and rotary inlet. The evaporator furnace is a cylindrical vessel, made of e.g. copper or a chemically resistant alloy with good thermal conductivity. A glass vessel with a copper wall can also be used. The furnace has a diameter of approximately 3 to 5 cm and is 2 to 5 cm high. There are between one and three openings of different sizes for the vapour stream. The furnace is heated either by a heating spiral around the outside. To prevent heat being dissipated to the

base plate, the heater is attached to the base plate by a metal with low thermal conductivity (nickel-silver or chromium-nickel steel), e.g. a nickel-silver pipe attached to a rotary inlet if using a furnace with several openings. This arrangement has the advantage of allowing the introduction of a copper bar. This allows cooling from the outside using a cooling bath,

- if the copper furnace lid has three openings of different diameters at 90° to each other, various vapour pressure ranges within the overall measuring range can be covered (openings between approximately 0,30 and 4,50 mm diameter). Large openings are used for low vapour pressure and vice versa. By rotating the furnace the desired opening or an intermediate position in the vapour stream (furnace opening -shield - balance pan) can be set and the stream of molecules is released or deflected through the furnace opening onto the scale pan. In order to measure the temperature of the substance, a thermocouple or resistance thermometer is placed at a suitable point,
- above the shield is a balance pan belonging to a highly sensitive microbalance (see below). The balance pan is approximately 30 mm in diameter. Gold-plated aluminium is a suitable material,
- the balance pan is surrounded by a cylindrical brass or copper refrigeration box. Depending on the type of balance, it has openings for the balance beam and a shield opening for the stream of molecules and should guarantee complete condensation of the vapour on the balance pan. Heat dissipation to the outside is ensured e.g. by a copper bar connected to the refrigeration box. The bar is routed through the base plate and thermally insulated from it, e.g. with a chromium-nickel steel tube. The bar is immersed in a Dewar flask containing liquid nitrogen under the base plate or liquid nitrogen is circulated through the bar. The refrigeration box is thus kept at approximately -120 °C. The balance pan is cooled exclusively by radiation and is satisfactory for the pressure range under investigation (cooling approximately 1 hour before the start of measurement),
- the balance is positioned above the refrigeration box. Suitable balances are e.g. a highly sensitive 2-arm electronic microbalance (8) or a highly sensitive moving coil instrument (see OECD Test Guideline 104, Edition 12.05.81),
- the base plate also incorporates electrical connections for thermocouples (or resistance thermometers) and heating coils,
- a vacuum is produced in the vessel using a partial vacuum pump or high-vacuum pump (required vacuum approximately $1 \text{ to } 2 \cdot 10^{-3} \text{ Pa}$, obtained after 2 h pumping). The pressure is regulated with a suitable ionisation manometer.

1.6.4.2. Measurement procedure

The vessel is filled with the test substance and the lid is closed. The shield and refrigeration box are slid above the furnace. The apparatus is closed and the vacuum pumps are switched on. The final pressure before starting to take measurements should be approximately 10^{-4} Pa . Cooling of the refrigeration box starts at 10^{-2} Pa .

Once the required vacuum has been obtained, start the calibration series at the lowest temperature required. The corresponding opening in the lid is set, the vapour stream passes through the shield directly above the opening and strikes the cooled balance pan. The balance pan must be big enough to ensure that the entire stream guided through the shield strikes it. The momentum of the vapour stream acts as a force against the balance pan and the molecules condense on its cool surface.

The momentum and simultaneous condensation produce a signal on the recorder. Evaluation of the signals provides two pieces of information:

1. In the apparatus described here the vapour pressure is determined directly from the momentum on the balance pan (it is not necessary to know the molecular weight for this (2)). Geometrical factors such as the furnace opening and the angle of the molecular stream must be taken into account when evaluating the readings.
2. The mass of the condensate can be measured at the same time and the rate of evaporation can be calculated from this. The vapour pressure can also be calculated from the rate of evaporation and molecular weight using the Hertz equation (2).

$$p = G \sqrt{\frac{2\pi R T \times 10^3}{M}}$$

where

G = evaporation rate ($\text{kg s}^{-1} \text{m}^{-2}$)

M = molar mass (g mol^{-1})

T = temperature (K)

R = universal molar gas constant ($\text{Jmol}^{-1} \text{K}^{-1}$)

p = vapour pressure (Pa)

After the necessary vacuum is reached, the series of measurements is commenced at the lowest desired measuring temperature.

For further measurements, the temperature is increased by small intervals until the maximum desired temperature value is reached. The sample is then cooled again and a second curve of the vapour pressure may be recorded. If the second run fails to confirm the results of the first run, then it is possible that the substance may be decomposing in the temperature range being measured.

1.6.5. Effusion method -by loss of weight

1.6.5.1. Apparatus

The effusion apparatus consists of the following basic parts:

- a tank that can be thermostated and evacuated and in which the effusion cells are located,
- a high vacuum pump (e.g. diffusion pump or turbomolecular pump) with vacuum gauge,
- a trap, using liquefied nitrogen or dry ice.

An electrically heated, aluminium vacuum tank with 4 stainless steel effusion cells is shown in figure 5 for example. The stainless steel foil of about 0,3 mm thickness has an effusion orifice of 0,2 to 1,0 mm diameter and is attached to the effusion cell by a threaded lid.

1.6.5.2. Measurement procedure

The reference and test substances are filled into each effusion cell, the metal diaphragm with the orifice is secured by the threaded lid, and each cell is weighed to within an accuracy of 0,1 mg. The cell is placed in the thermostated apparatus, which is then evacuated to below one tenth of the expected pressure. At defined intervals of time ranging from 5 to 30 hours, air is admitted into the apparatus, and the loss in mass of the effusion cell is determined by reweighing.

In order to ensure that the results are not influenced by volatile impurities, the cell is reweighed at defined time intervals to check that the evaporation rate is constant over at least two such intervals of time.

The vapour pressure p in the effusion cell is given by:

$$p = \frac{m}{KA t} \sqrt{\frac{2\pi RT}{M}}$$

where

p = vapour pressure (Pa)

m = mass of the substance leaving the cell during time t (kg)

t = time (s)

A = area of the hole (m^2)

K = correction factor

R = universal gas constant ($\text{Jmol}^{-1} \text{K}^{-1}$)

T = temperature (K)

M = molecular mass (kg mol^{-1})

The correction factor K depends on the ratio of length to radius of the cylindrical orifice:

ratio:	0,1	0,2	0,6	1,0	2,0
K:	0,952	0,909	0,771	0,672	0,514

The above equation may be written:

$$p = E \frac{m}{t} \sqrt{\frac{T}{M}}$$

where $E = \frac{1}{KA} \sqrt{2\pi R}$ and is the effusion cell constant.

This effusion cell constant E may be determined with reference substances (2,9), using the following equation:

$$E = \frac{p(r)t}{m} \sqrt{\frac{M(r)}{T}}$$

where

$p(r)$ = vapour pressure of the reference substance (Pa)

$M(r)$ = molecular mass of the reference substance ($\text{kg}\cdot\text{mol}^{-1}$)

1.6.6. Gas saturation method

1.6.6.1. Apparatus

A typical apparatus used to perform this test comprises a number of components given in figure 6a and described below (1).

Inert gas:

The carrier gas must not react chemically with the test substance. Nitrogen is usually sufficient for this purpose but occasionally other gases may be required (10). The gas employed must be dry (see figure 6a, key 4: relative humidity sensor).

Flow control:

A suitable gas-control system is required to ensure a constant and selected flow through the saturator column.

Traps to collect vapour:

These are dependent on the particular sample characteristics and the chosen method of analysis. The vapour should be trapped quantitatively and in a form which permits subsequent analysis. For some test substances, traps containing liquids such as hexane or ethylene glycol will be suitable. For others, solid absorbents may be applicable.

As an alternative to vapour trapping and subsequent analysis, in-train analytical techniques, like chromatography, may be used to determine quantitatively the amount of material transported by a known amount of carrier gas. Furthermore, the loss of mass of the sample can be measured.

Heat exchanger:

For measurements at different temperatures it may be necessary to include a heat-exchanger in the assembly.

Saturator column:

The test substance is deposited from a solution onto a suitable inert support. The coated support is packed into the saturator column, the dimensions of which and the flow rate should be such that

complete saturation of the carrier gas is ensured. The saturator column must be thermostated. For measurements above room temperature, the region between the saturator column and the traps should be heated to prevent condensation of the test substance.

In order to lower the mass transport occurring by diffusion, a capillary may be placed after the saturator column (figure 6b).

1.6.6.2. Measurement procedure

Preparation of the saturator column:

A solution of the test substance in a highly volatile solvent is added to a suitable amount of support. Sufficient test substance should be added to maintain saturation for the duration of the test. The solvent is totally evaporated in air or in a rotary evaporator, and the thoroughly mixed material is added to the saturator column. After thermostating the sample, dry nitrogen is passed through the apparatus.

Measurement:

The traps or in-train detector are connected to the column effluent line and the time recorded. The flow rate is checked at the beginning and at regular intervals during the experiment, using a bubble meter (or continuously with a mass flow-meter).

The pressure at the outlet to the saturator must be measured. This may be done either:

- by including a pressure gauge between the saturator and traps (this may not be satisfactory because this increases the dead space and the adsorptive surface); or
- by determining the pressure drops across the particular trapping system used as a function of flow rate in a separate experiment (this may be not very satisfactory for liquid traps).

The time required for collecting the quantity of test substance that is necessary for the different methods of analysis is determined in preliminary runs or by estimates. As an alternative to collecting the substance for further analysis, in-train quantitative analytical technique may be used (e.g. chromatography). Before calculating the vapour pressure at a given temperature, preliminary runs are to be carried out to determine the maximum flow rate that will completely saturate the carrier gas with substance vapour. This is guaranteed if the carrier gas is passed through the saturator sufficiently slowly so that a lower rate gives no greater calculated vapour pressure.

The specific analytical method will be determined by the nature of the substance being tested (e.g. gas chromatography or gravimetry).

The quantity of substance transported by a known volume of carrier gas is determined.

1.6.6.3. Calculation of vapour pressure

Vapour pressure is calculated from the vapour density, W/V, through the equation:

$$p = \frac{W}{V} \times \frac{RT}{M}$$

where:

- p = vapour pressure (Pa)
W = mass of evaporated test substance (g)
V = volume of saturated gas (m³)
R = universal molar gas constant (Jmol⁻¹ K⁻¹)
T = temperature (K)
M = molar mass of test substance (g mol⁻¹)

Measured volumes must be corrected for pressure and temperature differences between the flow meter and the thermostated saturator. If the flow meter is located downstream from the vapour trap, corrections may be necessary to account for any vaporized trap ingredients (1).

1.6.7. Spinning rotor (8, 11, 13)

1.6.7.1. Apparatus

The spinning rotor technique can be carried out using a spinning rotor viscosity gauge as shown in figure 8. A schematic drawing of the experimental set-up is shown in figure 7.

The measuring apparatus typically consists of a spinning rotor measuring head, placed in a thermostated enclosure (regulated within 0,1 °C). The sample container is placed in a thermostated enclosure (regulated within 0,01 °C), and all other parts of the set-up are kept at a higher temperature to prevent condensation. A high-vacuum pump device is connected to the system by means of high-vacuum valves.

The spinning rotor measuring head consists of a steel ball (4 to 5 mm diameter) in a tube. The ball is suspended and stabilized in a magnetic field, generally using a combination of permanent magnets and control coils.

The ball is made to spin by rotating fields produced by coils. Pick-up coils, measuring the always present low lateral magnetization of the ball, allow its spinning rate to be measured.

1.6.7.2. Measurement procedure

When the ball has reached a given rotational speed $v(o)$ (usually about 400 revolutions per second), further energizing is stopped and deceleration takes place, due to gas friction.

The drop of rotational speed is measured as a function of time. As the friction caused by the magnetic suspension is negligible as compared with the gas friction, the gas pressure p is given by:

$$p = \frac{\pi \bar{c} r \rho}{\sigma l \sigma t} \times \ln \frac{v(t)}{v(0)}$$

where

\bar{c} = average speed of the gas molecules

r = radius of the ball

ρ = mass density of the ball

σ = coefficient of tangential momentum transfer ($\epsilon = 1$ for an ideal spherical surface of the ball)

t = time

$v(t)$ = rotational speed after time t

$v(o)$ = initial rotational speed

This equation may also be written:

$$p = \frac{\pi \bar{c} r \rho}{10 \sigma} \times \frac{t_n - t_{n-1}}{t_n \times t_{n-1}}$$

where t_n, t_{n-1} are the times required for a given number N of revolutions. These time intervals t_n and t_{n-1} succeed one another, and $t_n > t_{n-1}$.

The average speed of the gas molecule c is given by:

$$\bar{c} = \left(\frac{8RT}{\pi M} \right)^{\frac{1}{2}}$$

where:

T = temperature

R = universal molar gas constant

M = molar mass

2. DATA

The vapour pressure from any of the preceding methods should be determined for at least two temperatures. Three or more are preferred in the range 0 to 50 °C, in order to check the linearity of the vapour pressure curve.

3. REPORTING

The test report shall, if possible, include the following information:

- method used,
- precise specification of the substance (identity and impurities) and preliminary purification step, if any,
- at least two vapour pressure and temperature values, preferably in the range 0 to 50 °C,
- all of the raw data,
- a log p versus 1/ T curve,
- an estimate of the vapour pressure at 20 or 25 °C.

If a transition (change of state, decomposition) is observed, the following information should be noted:

- nature of the change,
- temperature at which the change occurs at atmospheric pressure,
- vapour pressure at 10 and 20 °C below the transition temperature and 10 and 20 °C above this temperature (unless the transition is from solid to gas).

All information and remarks relevant for the interpretation of results have to be reported, especially with regard to impurities and physical state of the substance.

4. REFERENCES

- (1) OECD, Paris, 1981, Test Guideline 104, Decision of the Council C(81) 30 final.
- (2) Ambrose, D. in B. Le Neindre, B. Vodar, (Eds.): Experimental Thermodynamics, Butterworths, London, 1975, VoII.
- (3) R. Weissberger ed.: Technique of Organic Chemistry, Physical Methods of Organic Chemistry, 3rd ed. Chapter IX, Interscience Publ., New York, 1959, Vol. I, Part I.
- (4) Knudsen, M. Ann. Phys. Lpz., 1909, vol. 29, 1979; 1911, vol. 34,593.
- (5) NF T 20-048 AFNOR (Sept. 85). Chemical products for industrial use -Determination of vapour pressure of solids and liquids within range from 10⁻¹ to 10⁵Pa -Static method.
- (6) NF T 20-047 AFNOR (Sept. 85). Chemical products for industrial use -Determination of vapour pressure of solids and liquids within range from 10⁻³ to 1 Pa -Vapour pressure balance method.
- (7) ASTM D 2879-86, Standard test method for vapour pressure- temperature relationship and initial decomposition temperature of liquids by isoteniscope.
- (8) G. Messer, P. Rohl, G. Grosse and W. Jitschin. J. Vac. Sci. Technol.(A), 1987, VoI. 5 (4),2440.
- (9) Ambrose, D.; Lawrenson, I.J.; Sprake, C.H.S. J. Chem. Thermodynamics 1975, vol. 7,1173.
- (10) B.F. Rordorf. Thermochemica Acta, 1985, vol. 85,435.
- (11) G. Comsa, J.K. Fremery and B. Lindenau. J. Vac. Sci. Technol., 1980, vol. 17 (2),642.

(12) G. Reich. J. Vac. Sci. Technol., 1982, vol. 20 (4),1148.

(13) J.K. Fremerey. J. Vac. Sci. Technol.(A), 1985, vol. 3 (3),1715.

Appendix 1

Estimation Method

INTRODUCTION

Calculated values of the vapour pressure can be used:

- for deciding which of the experimental methods is appropriate,
- for providing an estimate or limit value in cases where the experimental method cannot be applied due to technical reasons (including where the vapour pressure is very low),
- to help identify those cases where omitting experimental measurement is justified because the vapour pressure is likely to be $< 10^{-5}$ Pa at ambient temperature.

ESTIMATION METHOD

The vapour pressure of liquids and solids can be estimated by use of the modified Watson Correlation (a). The only experimental data required is the normal boiling point. The method is applicable over the pressure range from 10^5 Pa to 10^{-5} Pa.

Detailed information on the method is given in 'Handbook of Chemical Property Estimation Methods' (b).

CALCULATION PROCEDURE

According to (b) the vapour pressure is calculated as follows:

$$\ln P_{vp} \approx \frac{\Delta H_{vb}}{\Delta Z_b R T_b} \left[1 - \frac{\left(3 - 2 \frac{T}{T_b}\right)^m}{\frac{T}{T_b}} - 2m \left(3 - 2 \frac{T}{T_b}\right)^{m-1} \ln \frac{T}{T_b} \right]$$

where:

T = temperature of interest

T_b = normal boiling point

P_{vp} = vapour pressure at temperature T

ΔH_{vb} = heat of vaporization

ΔZ_b = compressibility factor (estimated at 0,97)

m = empirical factor depending on the physical state at the temperature of interest

Further

$$\frac{\Delta H_{vb}}{T_b} = K_F(8,75 + R \ln T_b)$$

where K_F is an empirical factor considering the polarity of the substance. For several compound types, K_F factors are listed in reference (b).

Quite often, data are available in which a boiling point at reduced pressure is given. In such a case, according to (b), the vapour pressure is calculated as follows:

$$\ln P_{vp} \approx \ln P_1 + \frac{\Delta H_{v1}}{\Delta Z_b R T_1} \left[1 - \left(3 - 2 \frac{T}{T_1}\right) m \frac{T_1}{T} - 2m \left(3 - 2 \frac{T}{T_1}\right)^{m-1} \ln \frac{T}{T_1} \right]$$

where T₁ is the boiling point at the reduced pressure P₁.

REPORT

When using the estimation method, the report shall include a comprehensive documentation of the calculation.

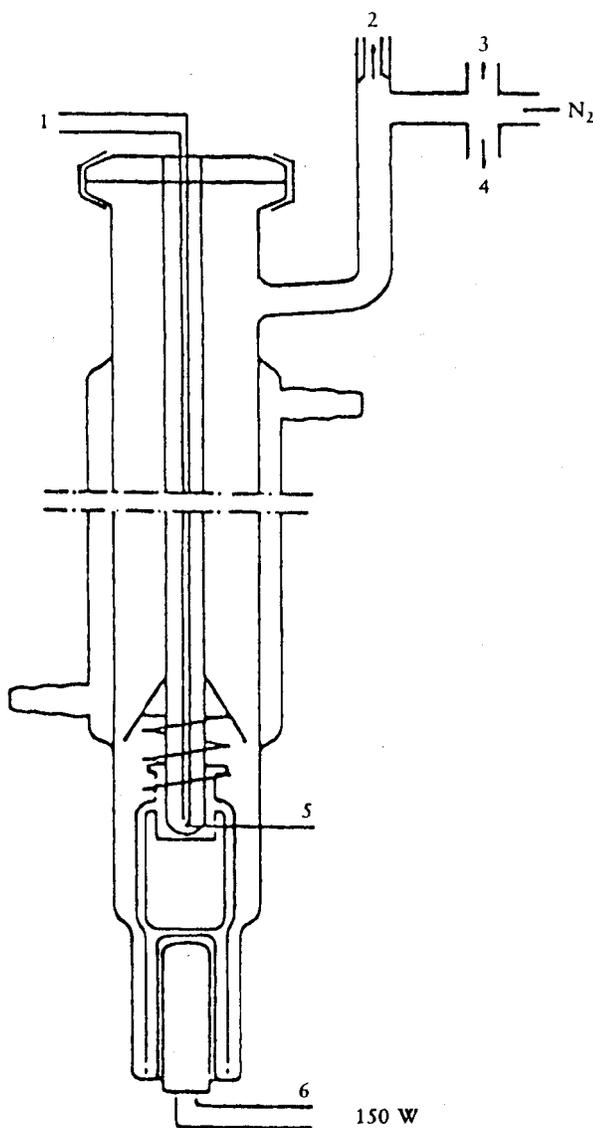
LITERATURE

- (a) K.M. Watson, Ind. Eng. Chem; 1943, vol. 35,398.
- (b) W.J. Lyman, W.F. Reehl, D.H. Rosenblatt. Handbook of Chemical Property Estimation Methods, Mc Graw-Hill, 1982.

Appendix 2

Figure 1

Apparatus for determining the vapour pressure curve according to the dynamic method



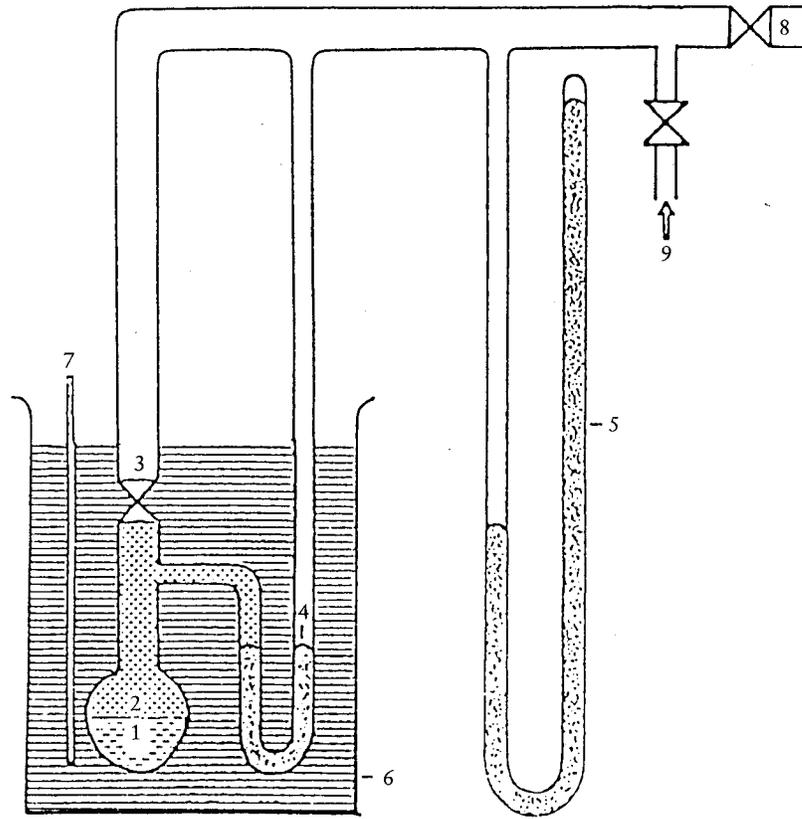
- 1 = Thermocouple
- 2 = Vacuum buffer volume
- 3 = Pressure gauge
- 4 = Vacuum
- 5 = Measuring point
- 6 = Heating element *circa* 150 W

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Figure 2a
 Apparatus for determining the vapour pressure curve according to the static method (using a U-tube manometer)



1. Test substance
2. Vapour phase
3. High vacuum valve
4. U-tube (auxiliary manometer)
5. Manometer

6. Temperature bath
7. Temperature measuring device
8. To vacuum pump
9. Ventilation

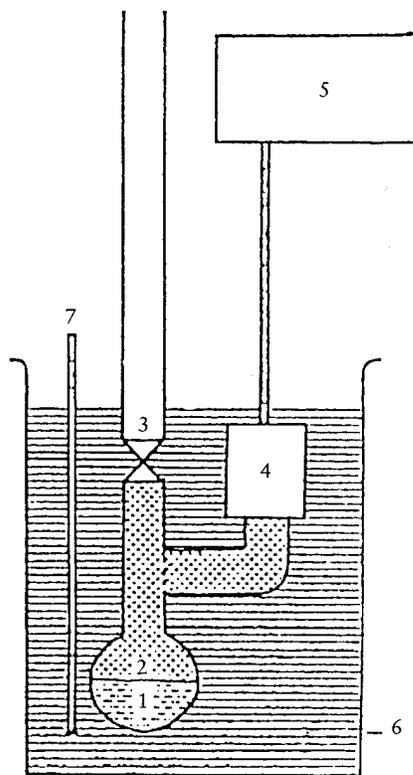
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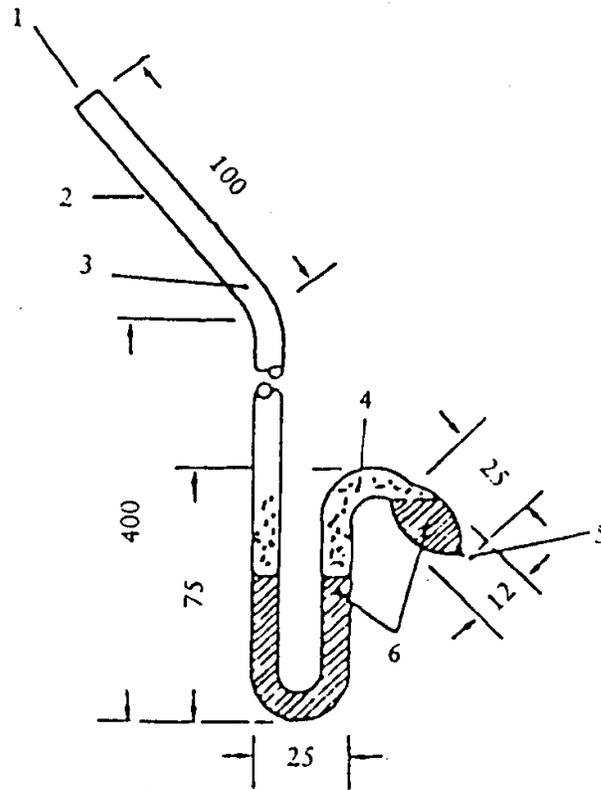
Figure 2b
Apparatus for determining the vapour pressure curve according to the static method (using a pressure indicator)



1. Test substance
2. Vapour phase
3. High vacuum valve
4. Pressure gauge

5. Pressure indicator
6. Temperature bath
7. Temperature measuring device

Figure 3
Isoteniscope (see reference 7)



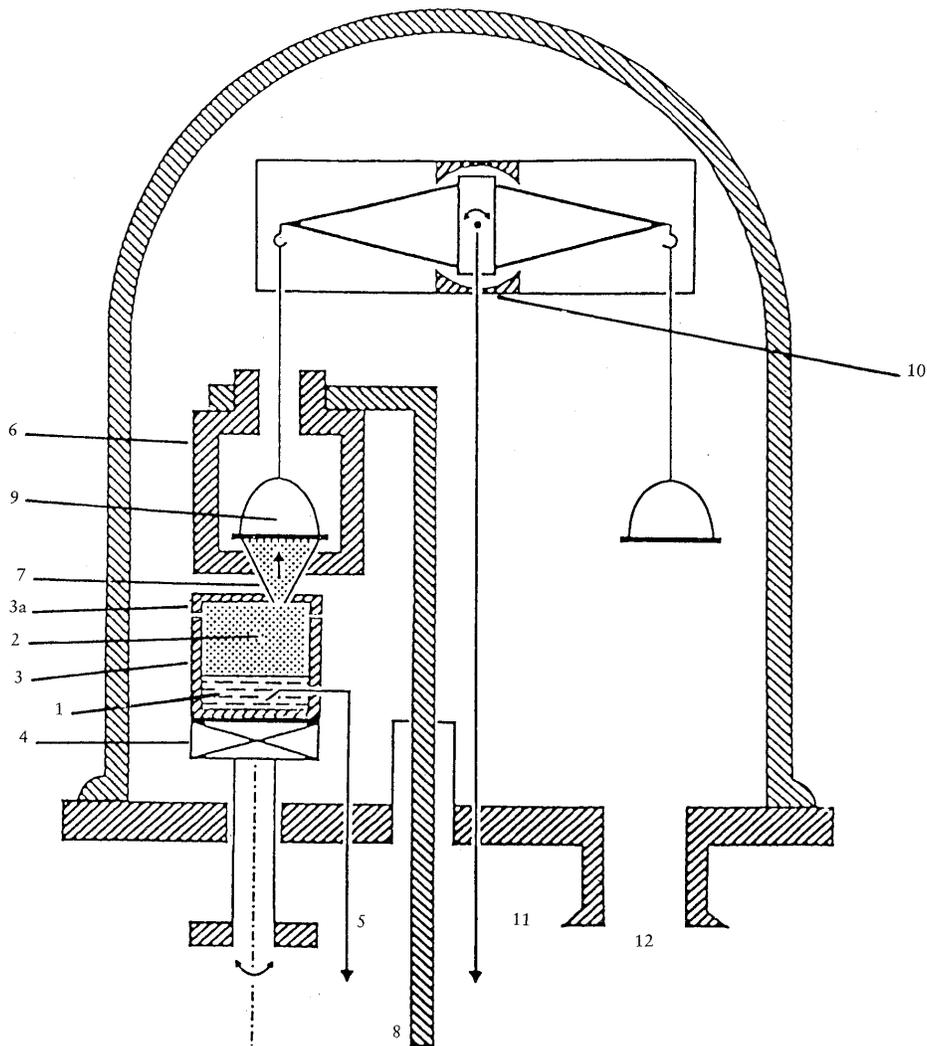
1. To pressure control and measurement system
2. 8 mm OD tube
3. Dry nitrogen in pressure system
4. Sample vapour
5. Small tip
6. Liquid sample

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Figure 4
Apparatus for determining the vapour pressure curve according to the vapour pressure balance method



- | | |
|--|--|
| 1. Test substance | 7. Shield |
| 2. Vapour phase with vapour stream | 8. Refrigeration bar for refrigeration box |
| 3. Evaporation furnace with rotary inlet | 9. Balance pan |
| 3a. Furnace lid with opening | 10. Microbalance |
| 4. Furnace heating (refrigeration) | 11. To recorder |
| 5. Measurement of temperature of sample | 12. To high-vacuum pump |
| 6. Refrigeration box | |

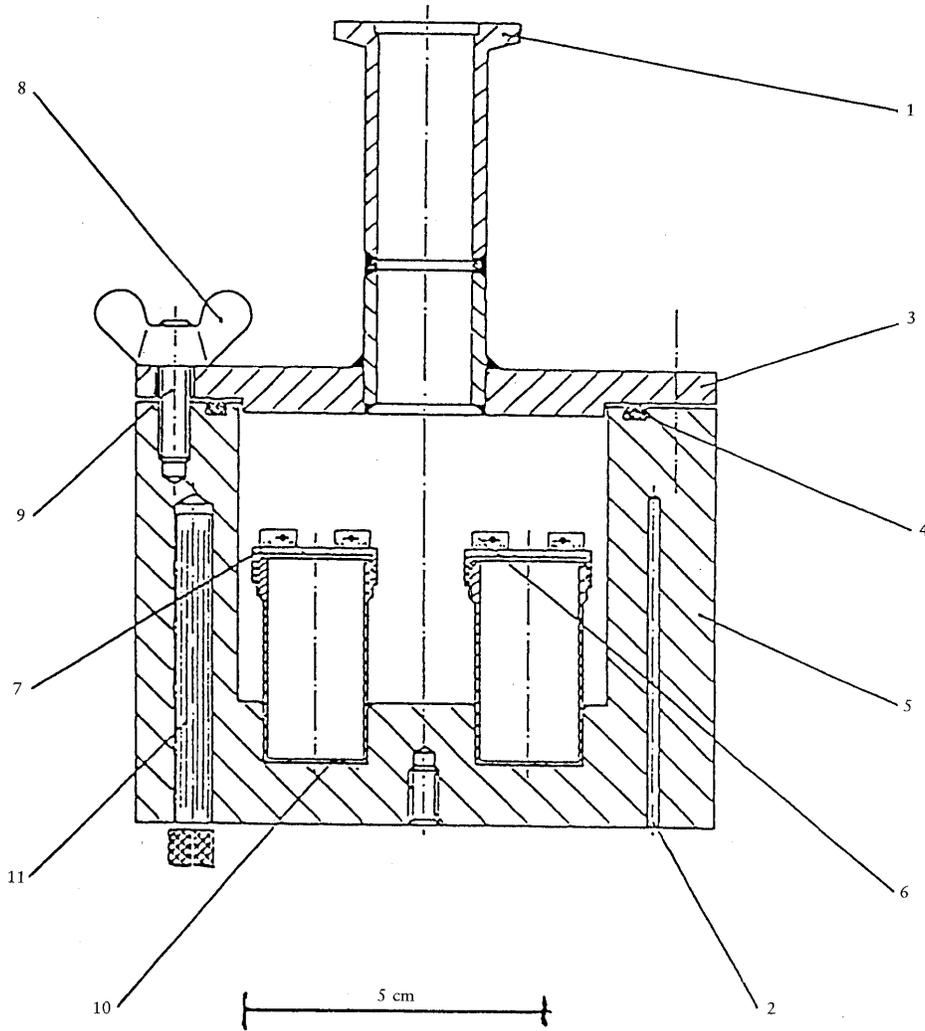
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Figure 5

Example of apparatus for evaporation at low pressure by effusion method, with an effusion cell volume of 8 cm^3



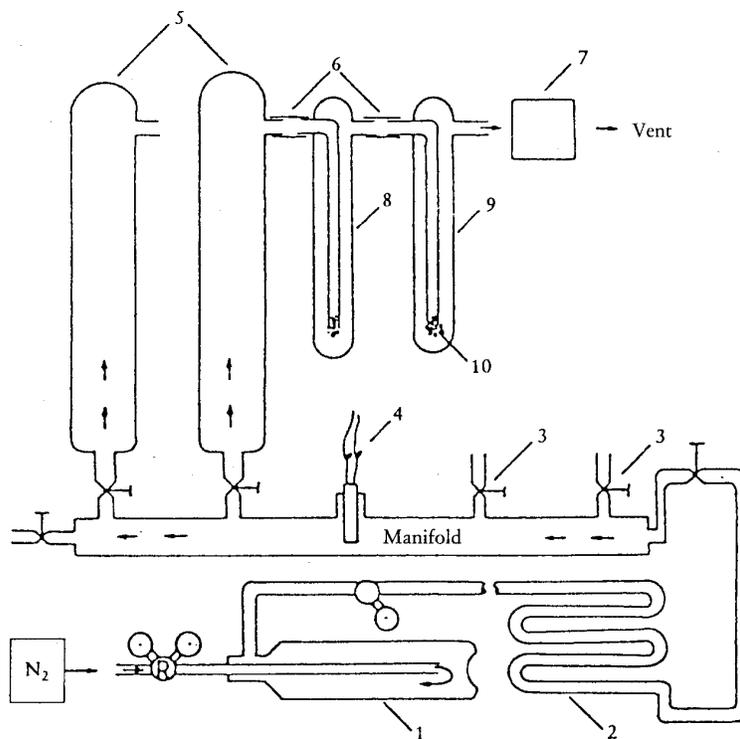
- 1 Connection to vacuum
- 2 Wells for platinum resistance thermometer or temperature measurement and control (2)
- 3 Lid for vacuum tank
- 4 O-ring
- 5 Aluminium vacuum tank
- 6 Device for installing and removing the effusion cells
- 7 Threaded lid
- 8 Butterfly nuts (6)
- 9 Bolts (6)
- 10 Stainless steel effusion cells
- 11 Heater cartridges (6)

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Figure 6a

An example of a flow system for the determination of vapour pressure by the gas saturation method



- 1 = Flow regulator
- 2 = Heat exchanger
- 3 = Needle valves
- 4 = Relative humidity sensor
- 5 = Saturation columns
- 6 = PTFE joints
- 7 = Flow meter
- 8 = Trap (absorber)
- 9 = Oil trap
- 10 = Fritted bubbler

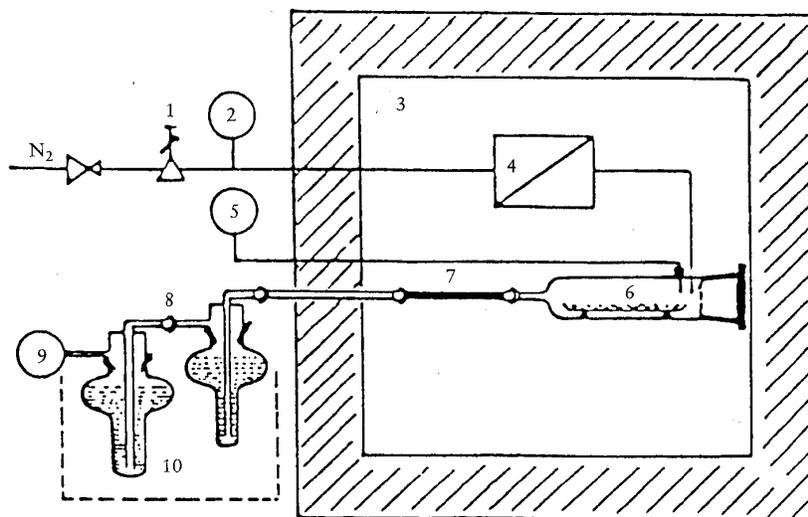
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Figure 6b

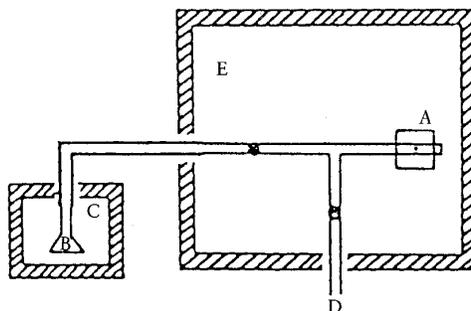
An example of a system for the determination of vapour pressure by the gas saturation method, with a capillary placed after the saturation chamber



- | | |
|---------------------------------------|---------------------------|
| 1. Thermal mass flowmeter | 6. Gas saturation chamber |
| 2. Manometer | 7. Capillary |
| 3. Temperature-controlled chamber | 8. Absorption vessels |
| 4. Thermostating coil for carrier gas | 9. Gas meter |
| 5. Thermometer (Pt 100) | 10. Cold trap |

Figure 7

Example of the experimental set-up for spinning rotor method



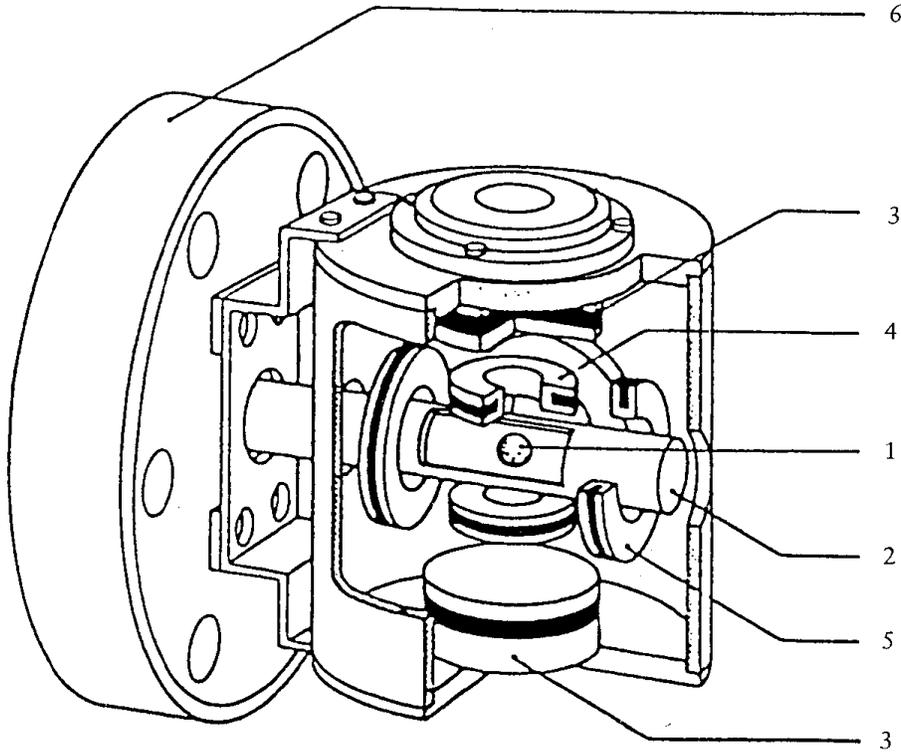
- Vapour pressure apparatus
- A. spinning rotor sensor head;
 - B. sample cell;
 - C. thermostat
 - D. vacuum line (turbo pump);
 - E. air thermostat.

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Figure 8

Example of spinning rotor measuring head



1. Ball;
2. Evacuated tubular extension of 6
3. Permanent magnets (2);
4. Coils (2) for vertical stabilization;
5. Driving coils (4)
6. Connection flange.

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