

New vapour pressure balance from Rubotherm

The vapour pressure is an important characteristic property of chemicals. For pure substances it depends only on temperature. It has to be determined for any new substance which should be placed on the market according to the European REACH regulation [EUR06]. In the OECD Guideline for the Testing of Chemicals different methods for measuring vapour pressure are proposed which can be applied in different vapour pressure ranges [OEC06]. The effusion method with a Knudsen cell covers a wide range of vapour pressures and provides comparable accurate data amongst the different measuring methods. This method is applied in an improved way using a magnetic suspension balance instrument. This setup allows highly accurate recording of the weight change of the Knudsen cell under ultra-high vacuum conditions. Additionally the special design of the instrument enables the reliable temperature control of the Knudsen cell in a wide temperature range. The new instrument design combines a high flexibility for performing vapour pressure measurements with different test substances (liquid or solid) in a wide vapour pressure range, ease of operation, and high reproducibility and accuracy.

The schematic setup of a magnetic suspension balance for weighing Knudsen cell in ultra-high vacuum conditions is shown in Figure 1.

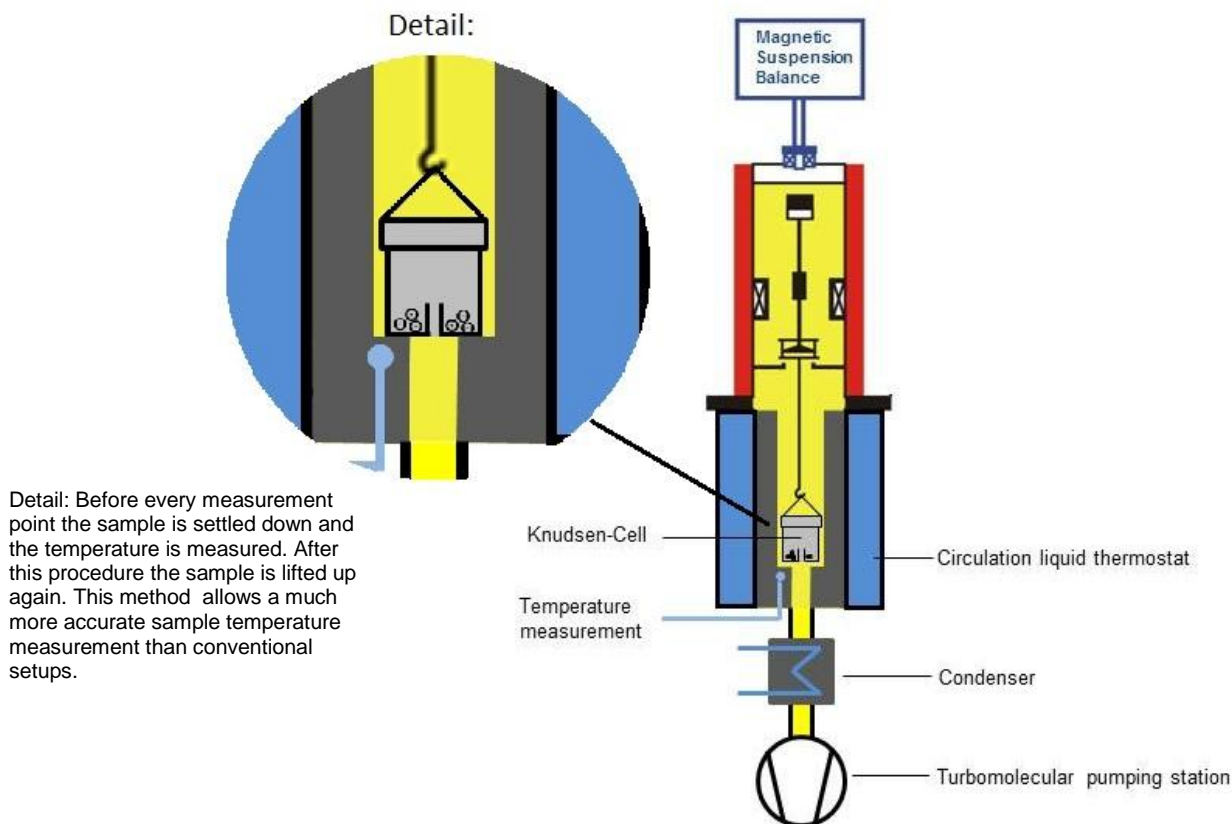


Figure 1: Schematic setup of magnetic suspension balance for vapour pressure measurement applying effusion method with Knudsen cell.

Table 1: Key specifications of the MSB instrument for vapour pressure measurement applying effusion method with Knudsen cell.

MSB, µg-LP version	Magnetic Suspension Balance	
	weighing range	0 g...20 g
	resolution	1×10^{-6} g
	accuracy & reproducibility	$\leq \pm(0.002\% + 3 \times 10^{-6} \text{ g})$
Pirani / cold cathode transmitter with display	Pressure Gauge	
	measuring range	5×10^{-9} mbar...1000 mbar
	repeatability	$\pm 5\%$ (10^{-8} mbar...100 mbar)
	accuracy	$\pm 30\%$ (10^{-8} mbar...100 mbar)
Thermo Sensor, 4-wire Pt100 in SS protection tube with display	Temperature Sensor	
	measuring range	100 K...870 K
	resolution	0.01 K
	accuracy & reproducibility	$\leq \pm 0.01\%$
Thermostat with double walled thermostatic jacket	Liquid Thermostat	
	controlling range	273 K...420 K
	controlling stability	$\leq \pm 0.02$ K
Hotset, Hotspring with controller	Electrical Heating	
	controlling range	370 K...670 K
	controlling stability	$\leq \pm 0.03$ K
Pfeiffer Vacuum, HiCube 80	Turbo Molecular Pump	
	pumping speed	67 l/s
	end vacuum	$< 1 \times 10^{-6}$ mbar

For vapour pressure measurements additionally to the correction of the baseline drift the regular change between Measuring Position (MP) and Zero Position (ZP) is used to thermostat the Knudsen cell. In order to make sure that the Knudsen cell has the same temperature than the reactor wall it is set down on the inner surface of the reactor while the instrument is in ZP.

Under these conditions direct contact between the (metallic) reactor wall and the (also metallic) Knudsen cell is established. This allows heat exchange by conductivity which is an important feature in this case, since in high vacuum the convective heat exchange is reduced. The procedure of measurement is so, that the Knudsen cell is mostly resting on the reactor wall and only picked up from time to time for measuring the mass change due to vapour effusion. The time intervals can be freely chosen depending on the vapour pressure and resulting mass change rate of the Knudsen cell. By this measuring principle the temperature of the Knudsen cell is exactly controlled and known from the temperature measurement in the reactor wall.

The efficiency of this technique was proven in test measurements with water as substance with an extra temperature sensor installed in a Knudsen cell. This sensor monitored the temperature difference between the Knudsen cell and the reactor wall during a vapour pressure measurement. No systematic temperature difference between the Knudsen cell and the reactor wall could be measured within the accuracy of the used Pt100 thermometers.

Measuring results

Dibutyl phthalate ($C_{16}H_{22}O_4$) was chosen as reference substance for testing the vapour pressure balance. The above described Knudsen cells were filled with ca. 0.2 g to 0.3 g liquid Dibutyl phthalate and then located in the vapour pressure balance. After evacuating the balance and equilibrating the temperature for at least one hour the weight change of the Knudsen cell was measured. Measurements were performed at 293.15 K, 303.15 K and 323.15 K.

The software was set in a way that the Knudsen cell was lifted from the support for 180 seconds. During this time 10 weight data points were recorded. After the 180 seconds the Knudsen cell was set down on the thermostated support for 420 seconds in order to establish temperature equilibrium between the cell and the wall. This procedure was repeated 20 times for each temperature.

An example for the resulting experimental data is shown in the next diagram (Figure 2). Here the recorded weight changes of the Knudsen cell are provided as function of time for three measuring / thermostating sequences. The weight change data can be represented by a linear fit with a quality of better than 0.9996. This proper linearity of the weight change data could be obtained for all three temperatures after an equilibration period of approximately 1 hour.

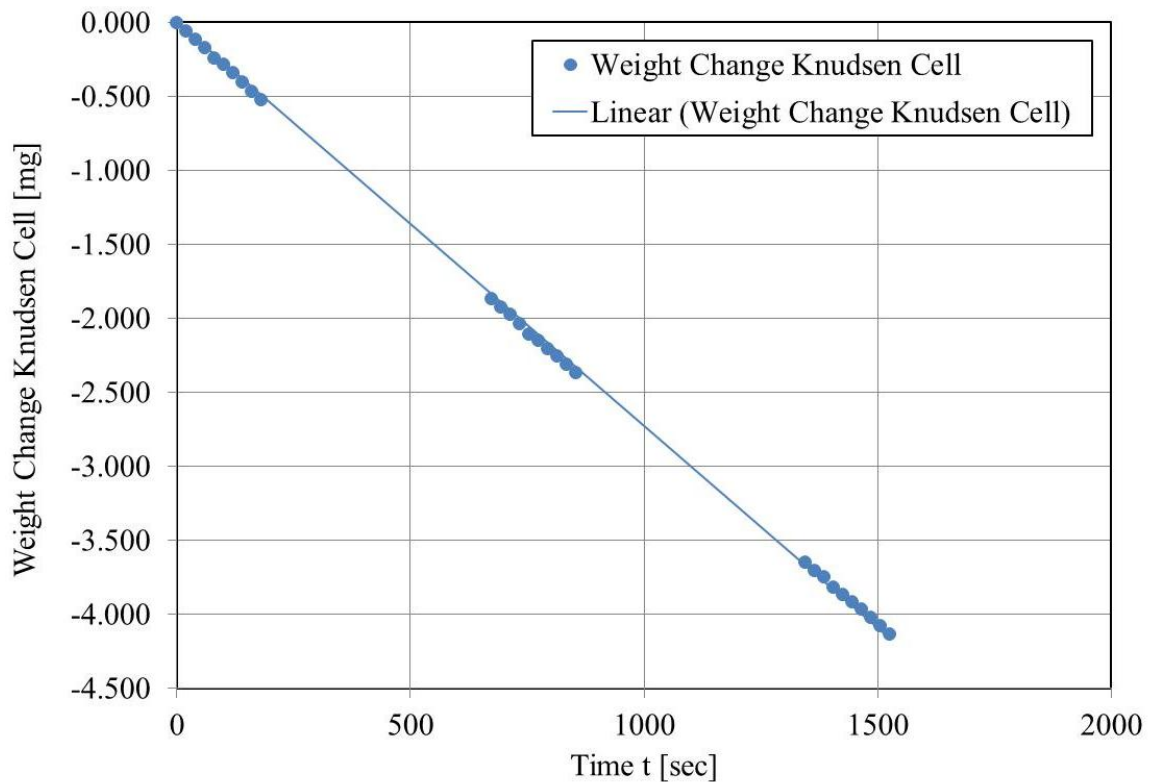


Figure 2: Measured weight change of a Knudsen cell with Dibutyl phthalate ($C_{16}H_{22}O_4$) at 323.15 K as function of time. Linear regression of experimental data.

The slope determined by the linear regression is the evaporation rate \dot{m} of the Dibutyl phthalate at this temperature. Equation 1 was used with this evaporation rate and the geometrical parameters of the Knudsen cell for calculation of the vapour pressure. The resulting vapour pressures were compared with literature reference data. A proportional deviation between the measured and literature data was found, which was taken into account by introducing a “shape factor” K into equation 1:

$$p(T) = K \cdot \frac{\dot{m}}{A} \cdot \sqrt{\frac{2 \pi \cdot R \cdot T \cdot 10^3}{M}} \quad \text{Equation 1}$$

This shape factor is an instrument characteristic constant and takes into account all the effects caused by the Knudsen cell and the balance on the evaporation. For the three measuring temperatures the same factor of $K = 0.8645 \pm 0.0002$ was determined. Using these data an excellent agreement between experimental and literature values was obtained. The resulting experimental vapour pressures are compared in the next diagram (Figure 3) with the literature data.

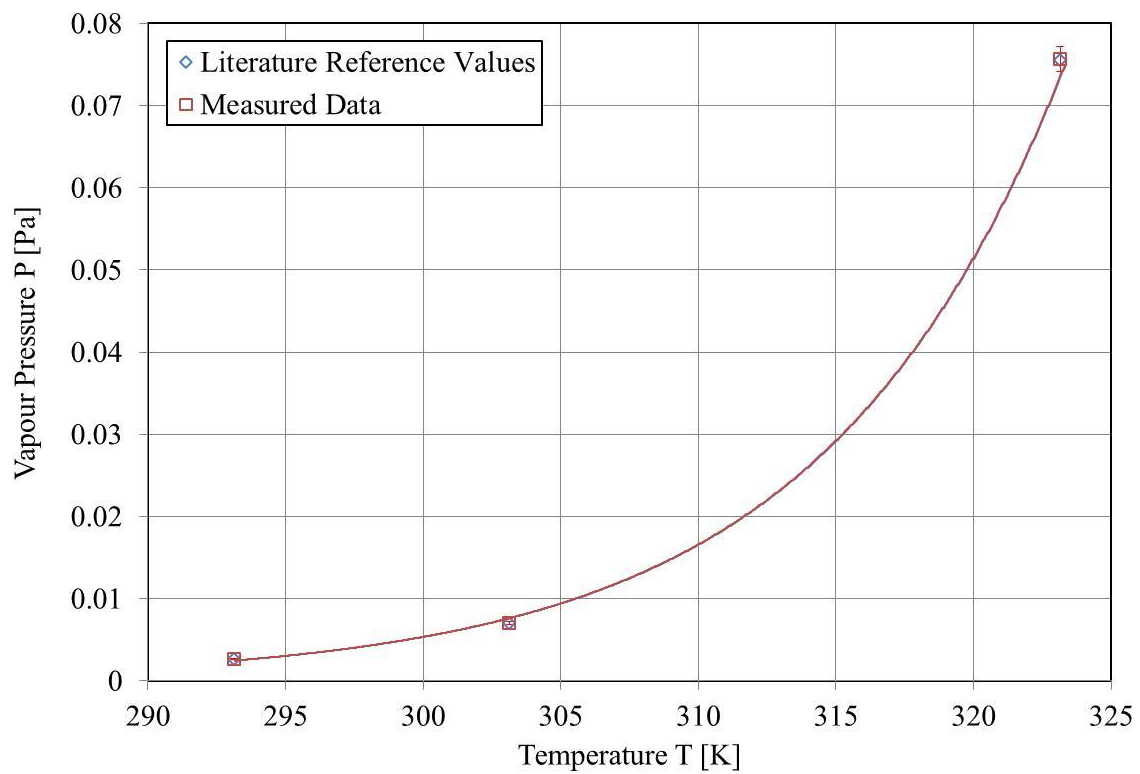


Figure 3: Measured vapour pressure data of Dibutyl phthalate (C₁₆H₂₂O₄) at 293.15 K, 303.15 K, and 323.15 K compared with literature reference data.