MEASUREMENT OF LOW VAPOUR PRESSURES ACCORDING TO THE KNUDSEN EFFUSION METHOD

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ABSTRACT

The exact measurement of low vapour pressures during recent years has be-
come increasingly important, particularly for environmental problems caused
by organic chemicals. Not only for this but for many other fields information
about the phase transition solid - gas and liquid - gas is of great scienti-
fic interest. In this work a brief survey of the determination of vapour
pressures with thermo-analytical methods is made. In particular the thermo-
gravimetric vapour pressure measurements by means of a Knudsen cell and a
newly developed vapour pressure balance for exact measurement of very low
vapour pressures are described. Applications for organic materials (fungi-
cides, benzoic acid, oils) are discussed.

INTRODUCTION

The determination of the vapour pressure of a substance is necessary for
the characterization of the material, for physico-chemical, toxicological
and eco-toxicological tests as well as for a calculation of the distribution
in the environment.

The vapour pressure of a substance is the equilibrium pressure above the
solid or liquid material at a certain temperature. The vapour pressure curve
shows its temperature dependence and is the continuation of the sublimation
curve for the temperature range between the triple point and the critical
temperature. The various effusion methods to determine the vapour pressure
are based on the effusion of the vaporized substance from the surface or
through an orifice. Either the mass change of the vaporizing sample or the
mass increase of a target, where the vapour is condensed, are measured with
effusion methods.

In the Knudsen effusion method, first described as early as 1909 /Ref. 1/
the substance contained in a capsule effuses through a small hole of known
cross section. When this orifice is very short and round and the capsule con-
taining the condensed sample is in an evacuated chamber, the equilibrium
pressure at temperature T is determined from the mass change against time,
the orifice area, the gas constant and the molecular weight of the vapour.

$$p = 2285,61 \; \frac{m}{A \cdot t} \sqrt{\frac{T}{M}}$$

(SI-units)

p equilibrium pressure
m mass of vapour
t time
A cross section
T temperature
M molecular weight

This Knudsen effusion method works in a low pressure range, down to about 10^{-5} Pa and found wide application for metals, inorganic and organic chemicals. The main problem here is to detect the effusion rate, without breaking the vacuum.
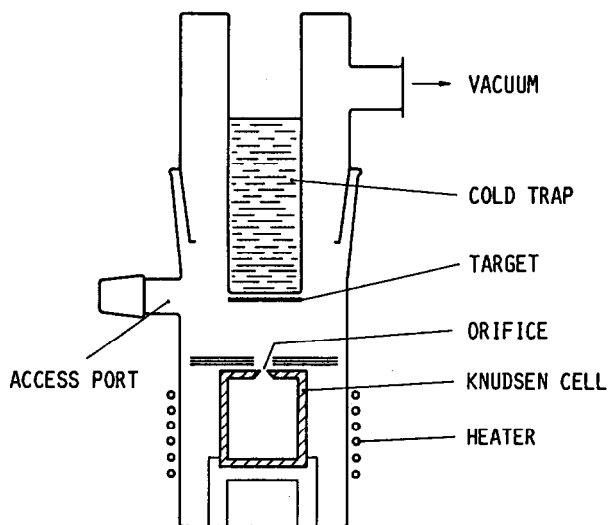

Fig. 1. An early Knudsen Effusion Apparatus

Vapour pressure measurement with TG

The use of a TG unit with high vacuum capability allows the measurement of the effusion rate. The effusion cell is placed on the TG sample holder, a thermocouple in direct contact with the cell or the sample itself provides an exact temperature measurement.
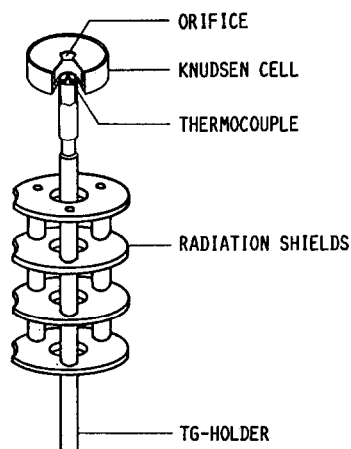
Fig. 2. Thermogravimetry with Knudsen cell

The pressure range depends on the vacuum level which can be achieved for the corresponding isothermal step and with the continuously evaporating sample, and also on the sensitivity of the balance to detect small mass changes against time. Good results are reported in the range 10^{-4} to 1 Pascal for diffusion pump oils, for metals /Ref. 2/ and organic chemicals /Ref. 3/.
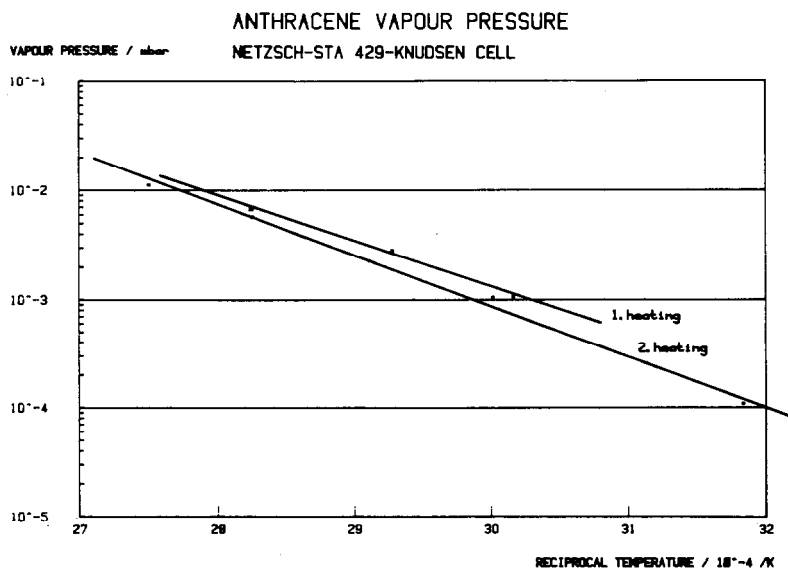

Fig. 3. TG result for anthracene vapour pressure

The limitation of this arrangement is the capacity, long term stability and sensitivity of the balance, and the stability of vacuum. All the effusion rate methods suffer from the limitation that the molecular weight must be known. The selection of orifice diameter is a compromise between the ideal ratio of 1 : 100 X and an orifice large enough for sufficient material to effuse which is necessary for equilibrium inside the cell. With some TG units an identification of the vapour phase is easily possible with coupled MS.

Vapour pressure balance

With a newly developed vapour pressure balance many of the limitations of effusion methods have been overcome. The measuring principle is based on an homogeneously heated Knudsen cell with different effusion orifices in line with a cooled target which is connected to a sensitive microbalance. The whole system is mounted in a special high vacuum chamber with a built in cold trap.

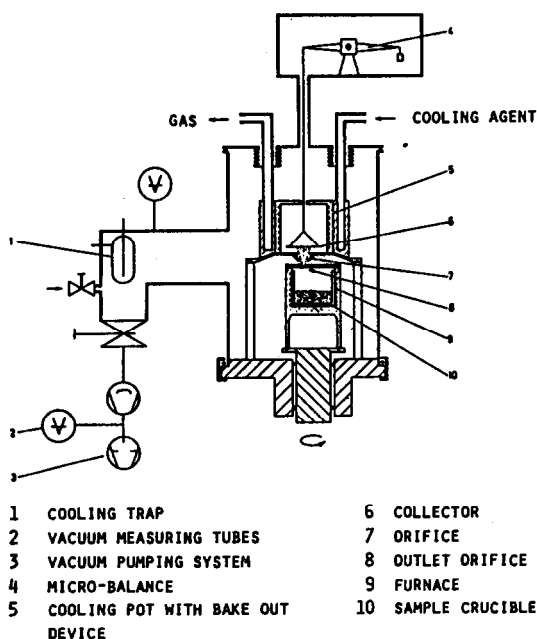|			
1	COOLING TRAP	6	COLLECTOR
2	VACUUM MEASURING TUBES	7	ORIFICE
3	VACUUM PUMPING SYSTEM	8	OUTLET ORIFICE
4	MICRO-BALANCE	9	FURNACE
5	COOLING POT WITH BAKE OUT DEVICE	10	SAMPLE CRUCIBLE

Fig. 4. Scheme of vapour pressure balance

The Knudsen cell is heated to a preselectable test temperature within the temperature range -50 to 300°C, controlled by a microprocessor programmer. When an orifice is opened, the impulse of the molecular beam of defined geometry is detected by the microbalance as a weight loss step. The vapour immediately condenses on the cooled target producing a weight increase against time, pro-
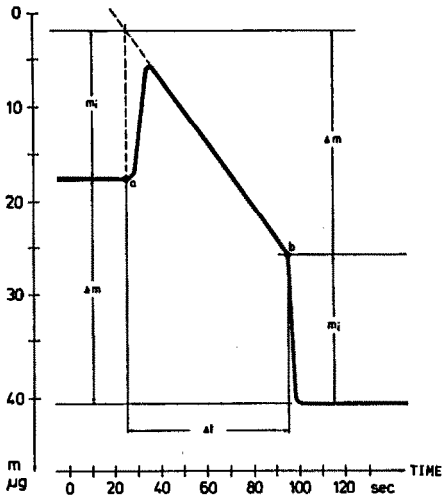
portional to the effusion rate.

Fig. 5. Typical weight curve

In the pressure range 10^{-3} to 1 Pascal there are two possibilities for the calculation of vapour pressure values: - The impulse method gives the vapour pressure without knowing the molecular weight of the vapour. The combination with the effusion rate value for the vapour pressure allows the determination of the molecular weight, using the Hertz equation

$$p = \frac{m}{A \cdot t} \sqrt{\frac{2\;RT}{M}} \quad \text{so} \quad M = \frac{2}{A^2} \frac{RT}{t^2} \frac{m^2}{p^2} \; ; \quad R = \text{gas constant}$$

(Formula simplified by omission of some geometry factors of the molecular beam)

This molecular weight determination is precise enough to decide between monomeric, dimeric, trimeric ... vapours. More precise molecular weight value is obtained by coupling a MS analyzer to the system. Below 10^{-3} Pa the impulse values (weight signals) are too small for an exact calculation. With oil diffusion or turbo molecular pumping systems one can achieve a high enough vacuum level to ensure that for all orifice cross sections the mean free path of the vapour is 10 times greater than the orifice diameter (s. Knudsen /Ref. [1]/) and that the residual gas pressure is approximately 10 times lower than the vapour pressure to be measured.

RESULTS AND DISCUSSION

Typical applications for this new vapour pressure balance are organic chem-
istry in conjunction with environmental protection. In the following results
for benzoic acid and known vapour pressure reference materials are shown.
The log of the vapour pressure is plotted against the reciprocal of temperature,
the slope of the line is a measure of the sublimation or evaporation enthalpy.
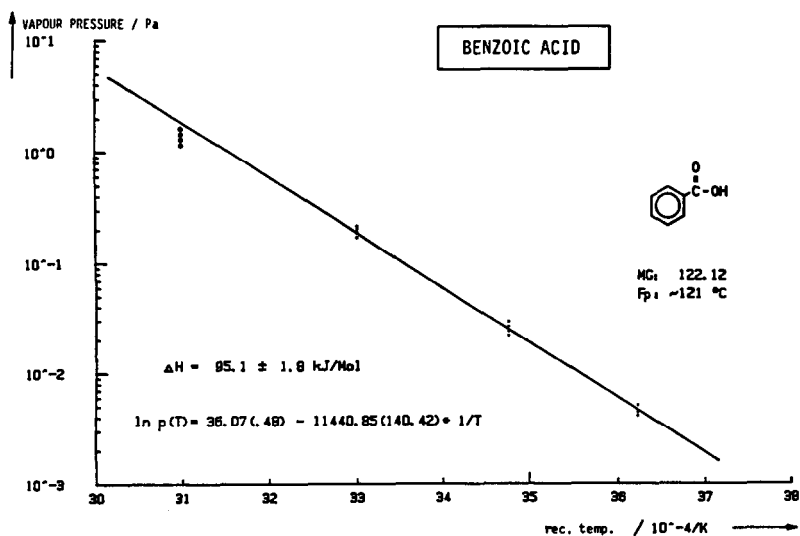

Fig. 6. Benzoic acid

CONCLUSION

For the determination of low vapour pressure a semiautomatic instrument was
developed. An exact determination of a vapour pressure curve takes 1 - 2 days,
with repeated determinations at several isothermal steps. The equilibrium va-
pour pressure is achieved with pure chemicals, whereas for mixtures the vapour
pressure determination can be used as an analytical tool.

ACKNOWLEDGEMENT

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