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# The design, construction, and testing of a new Knudsen effusion apparatus

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**Abstract**

A new Knudsen effusion apparatus, enabling the simultaneous operation of nine effusion cells at three different temperatures, is fully described. The performance of the new apparatus was checked by measuring the vapour pressures, between 0.1 Pa and 1 Pa, over *ca.* 20 K temperature intervals of benzoic acid, phenanthrene, anthracene, benzanthrone, and 1,3,5-triphenylbenzene. The derived standard molar enthalpies of sublimation are in excellent agreement with the mean of the literature values available for these five compounds and with the recommended values for four of them.


*Keywords:* Effusion apparatus; Knudsen effusion; Vapour pressures; Enthalpy of sublimation; Entropy of sublimation; Benzoic acid; Phenanthrene; Anthracene; Benzanthrone; 1,3,5-Triphenylbenzene

## 1. Introduction

The Knudsen effusion method [1–3] is one of the most widely used methods for measuring the vapour pressures of crystalline organic compounds for pressures less than 1 Pa. In a typical effusion experiment, the crystalline sample is placed at the bottom of a cylindrical cell kept at a constant temperature and the vapour (assumed to be in equilibrium with the crystalline phase) is allowed to effuse through a small orifice located at the top of the cell into an evacuated space. At the temperature $T$, the mass $m$ of the sample sublimed from the effusion cell, during the time period $t$, is related to the vapour pressure of the crystalline compound by the following equation:

$$p = (m/A_o w_o t) \cdot (2\pi RT/M)^{1/2}, \quad (1)$$

where $M$ is the molar mass of the effusing vapour, $R$ is the gas constant, $A_o$ is the area of the effusion orifice and $w_o$ is the transmission probability factor which is usually calculated by means of equation (2) or of equation (3) where $l$ is the length of the effusion orifice and $r$ its radius:

$$w_o = \{1 + (3l/8r)\}^{-1}, \quad (2)$$

$$w_o = \{1 + (l/2r)\}^{-1}. \quad (3)$$

This method has been widely used by our Research Group for measuring the vapour pressures of several organic compounds using an effusion apparatus enabling the simultaneous operation of three effusion cells at each experimental temperature [4]. As each effusion cell has a different effusion orifice area, the obtained results may be checked for deviations from the equilibrium pressure. If the areas of the effusion orifices are not very different, the pressures calculated at each temperature for each effusion cell are usually equal to within experimental error. For some compounds, however, the calculated pressures systematically decrease with the increasing size of the effusion orifice indicating that the results may be affected by a low condensation coefficient value or by a self cooling effect [5,6]. In this case, according to the equation developed by

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Whitman [7] and Motzfeldt [8], the equilibrium pressure at each temperature may be derived by plotting $p$ against $(pw_oA_o)$, to obtain the intercepts of the derived straight lines at zero area as the equilibrium pressures.

The new apparatus presented in this work enables the simultaneous operation of nine effusion cells, which may be controlled at three different temperatures, during one effusion experiment. By keeping the same temperature for each group of three effusion cells with different orifice areas, deviation of results from the equilibrium pressures at three different temperatures may be checked, simultaneously. So in one experimental run the equilibrium pressures at three different temperatures are determined.

## 2. The experimental apparatus and procedure

Besides the possibility of the simultaneous operation of nine effusion cells instead of only three, the main differences between the new effusion apparatus and the previous one are related to the control and measurement of the effusion temperature. The previous thermostatic oil or water bath has been replaced by temperature controlled aluminium blocks enabling experimental measurements between ambient temperature and *ca.* 480 K. The temperatures are measured using platinum resistance probes instead of mercury thermometers. A schematic representation of the apparatus is presented in figure 1.

### 2.1. The pumping system

The main components of the pumping system are the rotary pump (Edwards model RV12) which is used for preevacuating the system and for backing the oil diffusion pump (Edwards cryo-cooled diffstack model CR160). The pumping system enables the achievement of a pressure lower then $5 \cdot 10^{-4}$ Pa in less than one minute and an ultimate pressure of $5 \cdot 10^{-5}$ Pa.

### 2.2. The sublimation chamber

Each effusion cell is contained in one of the three cylindrical holes inside the aluminium blocks. The three aluminium blocks are contained inside the sublimation chamber, represented in figure 2, consisting of a glass bell jar ($\phi_i =$ 296 mm, $h = 360$ mm, $l = 5$ mm) with a cylindrical aluminium lid. Each block contains three cylindrical holes of dimensions similar to the effusion cells and is connected to a sliding aluminium platform by three ceramic elements. To prevent sample contamination of the pumps, the glass connection between the pumping system and the sublimation chamber includes a glass cold finger for liquid nitrogen connected to the lid of the sublimation chamber.

### 2.3. Temperature measurement and control

Each aluminium block may be heated to the desired temperature by two circular heating elements – fast response 115 Ω electrical resistances from Ari, model Aerorod BXX – connected in parallel to a power supply of 40 or 60 V, ac, depending on the controlled temperature. The temperature of each block is kept constant by a PID (proportional, integral and differential) controller receiving information of a Pt-100 sensor located near the heating element as shown in figure 3. The temperature of each block is measured by

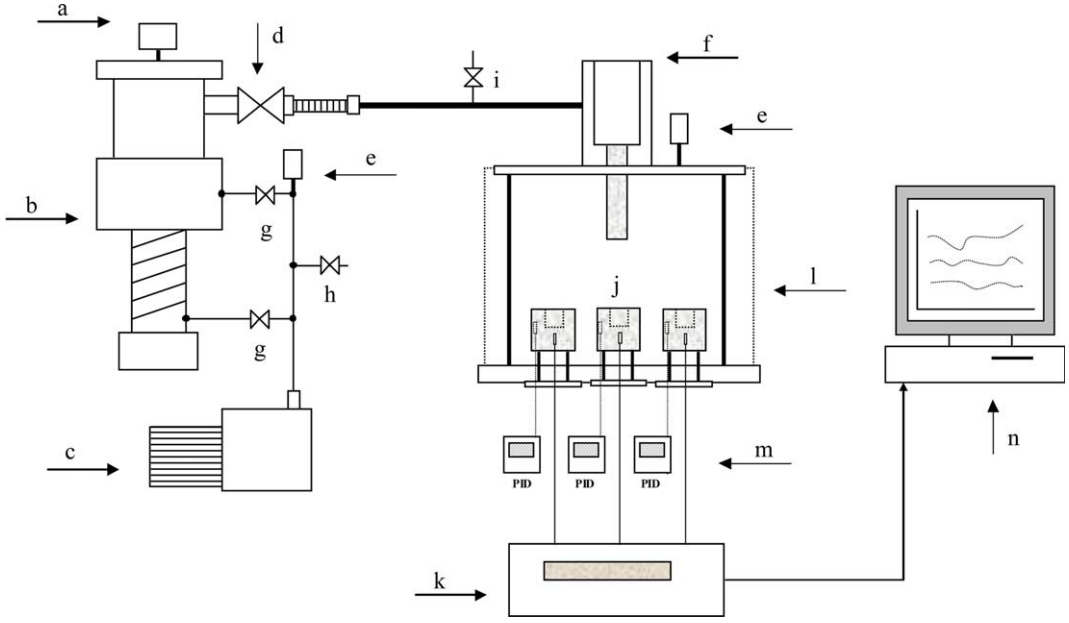


FIGURE 1. Schematic representation of the new effusion apparatus: a, inverted magnetron gauge Edwards AIM-S; b, oil diffusion pump Edwards cryo-cooled diffstak CR160; c, Rotary pump Edwards RV12; d, isolation valve Edwards IPV40 MKS; e, Pirani gauges Edwards APG-M; f, glass cold finger for liquid nitrogen; g, Speedivalves Edwards SP25K; h, air admittance valve AV10K; i, teflon greaseless gas admittance valve J. Young ALS1; j, aluminium blocks (ovens); k, data logger Agilent 34970A; l, glass bell jar; m, PID temperature controllers Omron E5CN; n, computer.