Vapor Pressure of Low Volatile Chemicals from a Knudsen Effusion Technique

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Abstract

Vapor pressure data are vital to understanding impacts that substances, specifically pesticides and other agrochemicals, may exert on the environment. They enter into atmospheric deposition models for such chemicals which determine the fate and transport of these species in the environment. At normal application temperatures (i.e. room temperature) the vapor pressures of many of these chemicals are too low to be determined by conventional means. An isothermal Knudsen effusion technique was designed and developed in our laboratory for such measurements. The effusion mass as a function of time is measured in our technique using a thickness shear mode (TSM) acoustic wave sensor, which allows for extremely high (few nanograms) sensitivity. This sensitivity allows for much more rapid determination of low vapor pressures (10^{-1} to 10^{-5} Pa) than is possible by other Knudsen effusion techniques. Basing the effusion mass measurement on the TSM sensor as in our apparatus eliminates the typically seen dependence on vibration in conventional microbalance-based effusion techniques. Full design details of our apparatus and specifically the Knudsen cell, based on original equations derived by Knudsen, and many corrections that have been noted in the literature for cell and effusion-hole dimensions, are presented. The accuracy of our method was validated by a comparison of published vapor pressure data to vapor pressure data acquired in our laboratory with measurements on naphthalene (320-350 K). Vapor pressure data of catechol (290-310 K), hydroquinone (320-340 K), anthracene (320-360 K), caffeic acid (410-430 K), ferulic acid (360-390 K), gentisic acid (360-380 K), and myoinositol (440-460 K) will follow to compare with results from other techniques to further validate and understand the technique before proceeding with measurements on chemicals with unknown vapor pressure data.

Introduction

Agrochemicals, such as pesticides, are very useful in the protection of foods that are threatened by insects during growth. Pesticide sales in the United States is a multi-billion dollar business, and companies work to develop new pesticides each year that are made to fit the needs of their consumers. The Environmental Protection Agency (EPA) reported that in 2001 $11.1 billion was spent on pesticides in the United States alone, accounting for 35% of the World market [1]. The majority of the money is spent for agricultural purposes.

While the agrochemical business is vast, the potential dangers that pesticides pose to humans and other living things are also substantial and must not be overlooked. Certain properties of every pesticide must be known and submitted to the EPA before it can be used legally in the United States due to the potential threats they pose to humans and the environment in general [2]. One of the properties of each pesticide that must be submitted in order to pass EPA certification is its vapor pressure, the pressure at a given temperature at which the liquid or solid substance will turn into a vapor. This property is vital to understanding the potential harmful impacts pesticides pose to the environment.

It has been estimated that of the pesticide applied, only 0.1% impacts the insects, leaving 99.9% lost to the environment [3]. This research focuses on low-vapor pressure pesticides. With a lower vapor pressure and subsequent relative volatility the chemical will tend not to vaporize and in turn will display properties of higher solubility in water and higher absorptivity onto the land. This creates a hazard for the environment and can negatively influence water and crops. By knowing the vapor pressures, the EPA can regulate the amount of pollution created by controlling the use of these contaminants.

Vapor pressure determination may be accomplished by a variety of methods. The method chosen for this research was the Knudsen Effusion method [4] because of temperature control and time constraint advantages over other methods. The Knudsen Effusion method utilizes an isothermal cell (K-cell) with a very small orifice (0.1-1.0mm.) out of which the chemical effuses (flows under pressure). The measured mass loss over time is proportional to the vapor pressure. The mass effusion rate was measured using a quartz crystal microbalance (QCM). A QCM is an extremely sensitive mass senor able to sense mass changes in the nanogram (10^{-9} g.) level. This makes it extremely attractive for use in a small application like this. The QCM consists of a piezoelectric device on a thin quartz plate with two electrodes attached to the plate. Vibrations from mass collection change the frequency of the QCM. The frequency change is directly proportional to the mass accumulation rate. The sensitivity and subsequent accuracy of the QCM makes it a very attractive option for the mass change measurement.

Experimental Apparatus

The apparatus was constructed with the QCM and K-Cell serving as the basis of design. Goodman [4] constructed an apparatus utilizing both a Knudsen Effusion method and a QCM. As with Goodman's design, Conflat components comprise the base structure for the apparatus. The Conflat components are comprised of a stainless steel frame with flanges designed for a tight seal for all connections using copper or viton rubber gaskets and bolts and nuts for tension. The structure and seals are designed to withstand the low vacuum associated with the objectives of this research.

The apparatus includes a vacuum to reduce pressure, a QCM with temperature control, a K-Cell with temperature control, a pressure gauge to for chamber pressure estimation, and a thermocouple to determine an accurate temperature of the cell enclosed in a 5-way cross.

The K-Cell requires temperature control because of the strict isothermal conditions required for vapor pressure data collection and calculations. Temperature control is obtained using a water chamber fed through and welded to the bottom of a blind flange. Two stainless steel tubes are fed into the chamber and connected to a temperature controlled water bath. The base of the K-cell is machined directly on top of the chamber to provide good heat transfer. A notch is formed around the top of the base so an o-ring may be placed to provide a seal between the base and a lid. Another notch is formed around the circumference of the base below the top to ensure compression between the other o-ring and the lid. Thin (0.1 mm) stainless steel plates were constructed to fit on top of the o-ring. Small (0.1 – 1.0 mm. diameter) orifices were laser drilled in the center of each plate. A stainless steel lid fits directly over the orifice plate and along the side of the base. A graphical representation of the K-Cell is shown in Figure 1.

The QCM holder is fed into the side of the 5-way cross so that it is parallel to the K-Cell, with the sensor directly above the orifice. The QCM is housed in a chamber through which refrigerated liquid passes, keeping the QCM at its desired temperature. It must be at a

temperature significantly below what the K-Cell temperature is so that the molecules recrystalize after effusion. The QCM holder was purchased from and fabricated by Maxtek, Inc. The QCM electrode itself is connected to an oscillator, which transmits the frequency of the sensor at any given time to a counter, from which data is transmitted to a computer. The computer is equipped with a LabView program which is programmed to display and store the frequency change of the crystal over time.

The experimental vapor pressures that are deemed accessible to this appartus are in the range of 10^{-5} -10^{-1} Pa. Pressures that are at least two orders of magnitude lower should be maintained outside the Knudsen cell. To achieve this a turbomolecular vacuum pump from Leybold (model BMH-70, which includes the roughing pump) was utilized. A flexible hose connects the vacuum to the side of the 5-way cross. A pressure gauge (Leybold model ITR 90) was utilized to monitor the chamber pressure.

A thermocouple is fed through the top of the apparatus. Connected to this are wires that transmit a temperature reading to a LED readout so that the temperature of the Knudsen cell may be read during runs. The thermocouple wires are attached via an adhesive to the side of the K-Cell. The thermocouple was calibrated using a NIST traceable mercury-in-glass thermometer.

Two Thermo (NESLAB RTE 17 AND 740) temperature contolled water baths are connected by Tygon rubber hose to the K-Cell water bath and the crystal holder, respectively. A mixture of commercial antifreeze and deionized water is used as the control liquid in each bath.

A graphical representation of the entire apparatus configuration is shown in Figure 2.

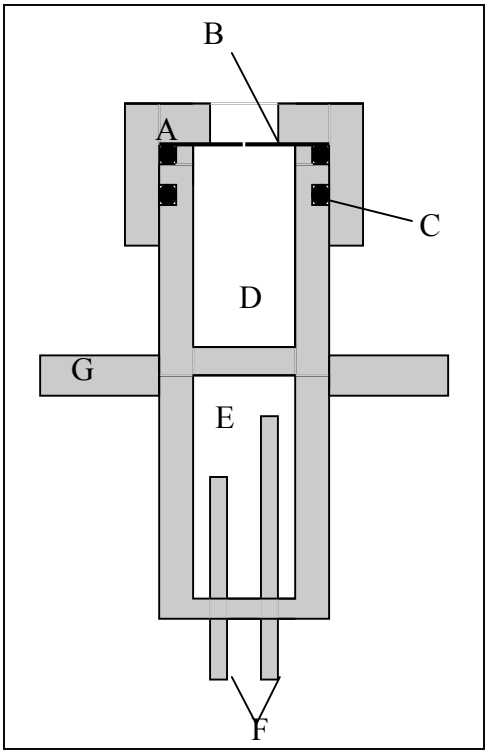

Figure 1. Knudsen effusion cell and liquid temperature control feedthrough: A. Cell lid; B. Orifice plate; C. Sealing O-rings; D. Cell chamber; E. Liquid temperature control chamber; F. Liquid feedthrough tubes; G. Conflat flange.

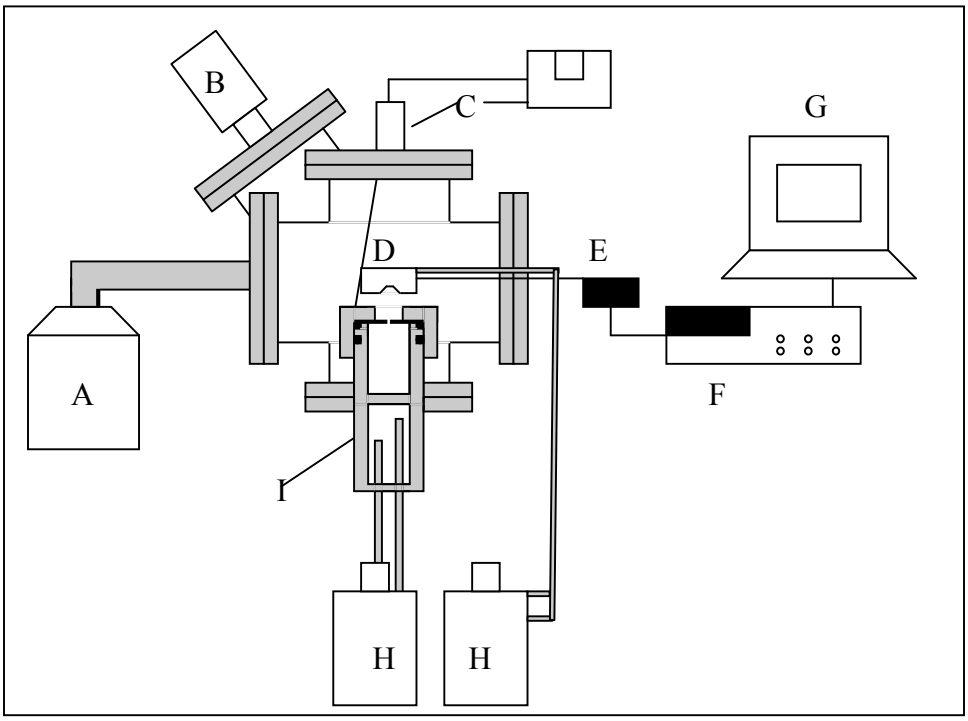

Figure 2. Overall Knudsen effusion apparatus: A. Turbomolecular vacuum pump; B. Pressure gauge; C. Thermocouple feedthrough and temperature readout; D. QCM in holder; E. Oscillator; F. Frequency counter; G. Computer; H. Liquid recirculating baths; I. K-cell/ liquid feedthrough.

Procedure

A small amount of the chemical of which vapor pressure data is desired is placed in the base of the K-Cell. The o-rings, orifice plate, and lid are then placed on the base. The K-Cell/temperature control feedthrough is fed into the bottom of the apparatus and sealed. The thermocouple readout, oscillator, counter, and computer are all turned on. Assuming all connections are sealed properly and a properly functioning crystal is placed in the holder, the vacuum pump is initiated. The water bath controlling the temperature of the K-Cell is then initiated, followed by the water bath controlling the temperature of the crystal. Once the thermocouple readout and frequency shift are stable, the initial frequency is recorded and the LabView program is initiated and run for approximately 10 minutes. The temperature of the water bath controlling the K-Cell temperature is then changed, and all subsequent procedure steps are repeated. This process is repeated for each desired temperature.

Calculations

The vapor pressure at each temperature was calculated from the measured frequency shift data by applying several corrections to the equation given below, which applies to substances under Knusden Effusion conditions **[4]**:

$$p = \frac{1}{A_o}\frac{dM_e}{dt}\left[\frac{2\pi RT}{M_W}\right]^{\frac{1}{2}} \tag{1.1}$$

Where p is the pressure (Pa), A_o is the cross-sectional area of the orifice (m^2), $\frac{dM_e}{dt}$ is the mass effusion rate (kg/s), R is the universal gas constant (J/(mol*K)), T is the temperature of the K-Cell (K), and M_W is molecular weight (kg/mol).

The mass effusion rate is obtained using the measured frequency shift $\frac{d(\Delta f)}{dt}$ (Hz/s) with the following equation, which additionally corrects for the distance between the orifice hole and the QCM **[5]**:

$$\frac{dM_e}{dt} = \frac{\pi r_q^2}{\cos\phi\cos\psi}\frac{1}{C_f}\frac{d(\Delta f)}{dt} \tag{2.1}$$

Where r_q is the radius of the active area of the QCM sensor (m), ϕ and ψ are angles between the QCM and the orifice hole as shown in Fig. 3, and C_f is a conversion factor found using the following equation:

$$C_f = \frac{2f_q^2}{\rho_q \nu_q} \tag{2.2}$$

Where f_q is the frequency of the crystal without any deposited material (Hz), ρ_q is the density of the quartz (kg/m^3), and ν_q is the shear wave velocity of the crystal (m/s).

To correct for the length of the orifice and the effect of the orifice on the equilibrium pressure of the K-Cell, the following equation is derived **[6]**:

$$p_s = p_o\left(1 + \frac{K_{Clausing} A_o}{A_s}\left(\frac{1}{\alpha} + \frac{1}{W} - 2\right)\right) \tag{3.1}$$

Where p_s is the equilibrium vapor pressure in K-Cell (Pa), p_o is the pressure near the orifice (Pa), A_s is the cross sectional area of K-Cell (m^2), a is the vaporization coefficient ($\approx$1 for loosely-packed solids), and the constants $K_{Clausing}$ and W are found using the following equations:

$$K_{Clausing} = \frac{1}{1 + \frac{3L}{8r_o}} \tag{3.2}$$

and

$$W = \frac{r_c}{h_c} \tag{3.3}$$

Where L is the length of the orifice (m), r_o is the radius of the orifice (m), r_c is the radius of inside of the K-Cell (m), and h_c is the height of K-Cell (m).

When all of the equations and correction factors are combined, the following equation results and is used in the determination of vapor pressures for various temperatures.

$$p_s = \left(\frac{1}{K_{Clausing}} \left(\frac{1}{A_o} \frac{\pi r_q^2}{\cos\phi \cos\psi} \frac{1}{C_f} \frac{d(\Delta f)}{dt} \left[\frac{2\pi RT}{M_W} \right]^{\frac{1}{2}} \right) \right) \left(1 + \frac{K_{Clausing} A_o}{A_s} \left(\frac{1}{\alpha} + \frac{1}{W} - 2 \right) \right) \tag{4.0}$$

Results

Vapor pressure data were measured for Naphthalene from 307-334 K. These data were compared to published data by Reid, et. al. [7] and is presented in Table 1 and Figure 3.

Table 1 – Vapor Pressure of Naphthalene

Temperature (K)	Experimental V.P. (Pa)	Published V.P. (Pa) [7]
307	7.98E-4	5.33E-3
311	1.01E-3	7.12E-3
318	2.29E-3	1.15E-2
322	8.08E-3	1.52E-2
328	1.12E-2	2.20E-2
334	2.96E-2	3.16E-2

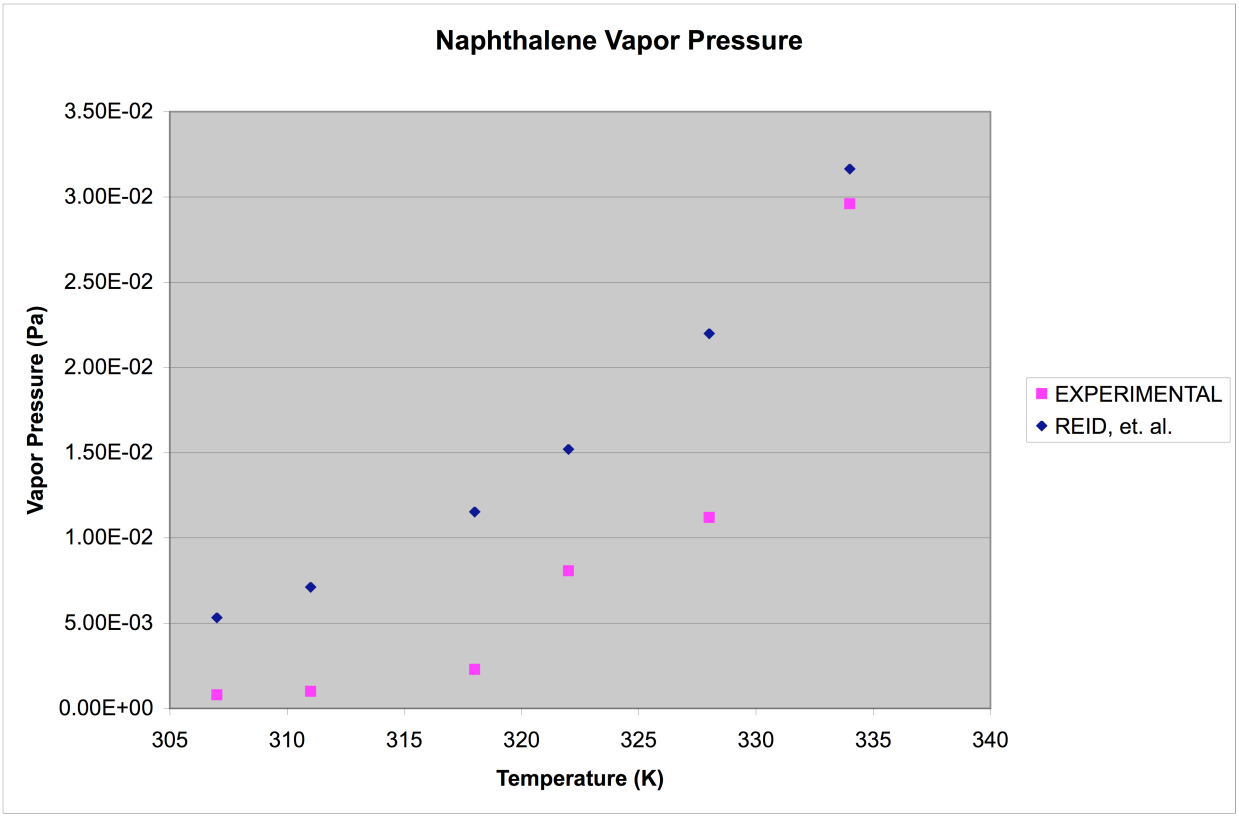

Figure 3. Comparison of experimental and published vapor pressure data for Naphthalene.

Discussion/Conclusion

While these data resemble the general trend of the published data, the variance between the two sets is too large to consider the current apparatus error-free. Factors including inadequate sealing of the K-cell, optimal orifice size and plate thickness, and optimal distance between the K-cell and sensor are possible contributors to this variance in data. While correction factors have been presented to correct for the hole size, plate thickness, and distance, these should be minimized to lessen the need for correction to the data. The inadequate sealing issue is currently being investigated. These issues are currently being addressed and vapor pressure data will be collected on catechol (290-310 K), hydroquinone (320-340 K), anthracene (320-360 K), caffeic acid (410-430 K), ferulic acid (360-390 K), gentisic acid (360-380 K), and myoinositol (440-460 K). These data will be compared to published data [6] for further validation of the technique.

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