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Correcting “static” measurements of vapor pressure for time dependence due to diffusion and decomposition

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Abstract

The static method for measuring vapor pressure assumes that the sample is pure and that its temperature is steady and uniform. In practice, the measured pressure may be time dependent due to evaporative cooling after pumping on the sample, transpiration of the sample in a temperature gradient, or diffusion of an impurity out of the sample. An impurity cannot be avoided if the sample is decomposing. This article identifies and quantifies various causes of time dependence, and it includes an analysis that can obtain the vapor pressure from the time-dependent pressure of a decomposing sample. The analysis was applied to measurements of TEMAH (tetrakisethylmethylaminohafnium), whose decomposition continuously generated a volatile impurity. The corrected vapor pressures obtained for three TEMAH samples at 39 °C agreed to within ± 1 %, even though the partial pressure of the impurity was as much as 7 times larger.

Graphical abstract

1. Introduction

Figure 1 shows an example of time dependence that was seen while using the “static” method to measure vapor pressure [1]. The measurements of pressure $P(t)$ began immediately after pumping on a sample of TEMAH (tetrakisethylmethylaminohafnium), and $P(t)$ was dominated by the sample’s recovery from evaporative cooling during the first few minutes. At later times $P(t)$ was dominated by diffusion of a volatile impurity out of the liquid. The pressure continued to increase for more than 6 h because decomposition of the TEMAH continuously generated more of the impurity.

The data in Figure 1 were acquired by the common practice of pumping briefly on the sample and then measuring the subsequent pressure $P(t)$, which may depend on time t . Ideally, $P(t)$ becomes steady within seconds, and inferring the equilibrium vapor pressure $P_v(T)$ from $P(t)$ is easy. In practice, slow equilibration of temperature or impurity concentration sometimes can cause an error. If the sample is pure and the pumping causes substantial cooling, the time dependent pressure $P(t)$ will approach $P_v(T)$ as the temperature equilibrates. However, if the sample contains a more volatile impurity, the pressure will continue to increase as the impurity diffuses into the vapor, and $P(t)$ will exceed $P_v(T)$. Thus, the time at which $P(t) = P_v(T)$ may be unclear. This is especially true if the sample is decomposing.

This article identifies and quantifies various causes of time-dependent pressure in static vapor pressure measurements; such understanding can help one avoid an error in the value of $P_v(T)$ derived from the measurements of $P(t)$. After a brief description of the apparatus, Sections 3, 4, and 5 discuss respectively temperature equilibration, outgassing of an impurity from a stable sample, and outgassing from a decomposing sample.

2. Apparatus

Figure 2 shows the relevant features of the apparatus that was used to acquire the TEMAH data, and Table 1 lists its dimensions. The sample tube, cold trap, pressure gauges, and pneumatic valves were contained in a convection oven that held the air temperature at T_{air} , while the temperature of the sample tube was held 1 K below T_{air} . The total volume of the hot manifold, including the sample tube, the pressure gauges, and the connecting tubing, was only $V_1 + V_2 = 29 \text{ cm}^3$, which allowed the vapor to be pumped out many times before depleting the sample. Such pumping was used when the sample was degassed by cyclic pumping. Such *in situ* degassing is especially useful for a decomposing sample because the more volatile decomposition products can be removed between sets of vapor pressure measurements. The companion article [1] gives a complete description of the apparatus and its operation.

3. Temperature equilibration

Pumping on the sample cools the sample surface, and its return to temperature equilibrium is affected by thermal diffusion, boiling, and transpiration. This section discusses those phenomena and calculates examples based on the apparatus with the dimensions in Table 1 and the properties of naphthalene in Table 2. Mass diffusion is ignored. The pumping is defined here as a single event: the sample container, of volume V_1 , is opened to the full manifold, of volume $V_1 + V_2$, so that the pressure in the sample tube drops by the ratio $V_1/(V_1 + V_2)$.

3.1 Initial drop of temperature and pressure

Just before opening the sample container, the sample surface temperature T_{surface} is the same as the temperature T_0 of the sample container, namely $T_{\text{surface}} = T_0$. Just after the initial pressure drop, evaporation increases the pressure and cools the sample surface until $P(t) \approx P_v(T_{\text{surface}})$. This process occurs quickly because it is limited only by molecular speeds and

not by diffusion. Let us temporarily ignore the slower processes of convection and heat flow from the container wall, which will be considered in later sections. Then, one can estimate the maximum possible temperature decrease, $T = T_0 - T_{\text{surface}}$, by equating two expressions for the heat Q removed from the sample surface. The first expression multiplies the amount of evaporated sample times the heat of evaporation (or sublimation) H to obtain

$$Q_{PV} \simeq \frac{P_V(T_0) V_2}{RT_0} \Delta H = K_{PT} P_V(T_0) V_2, \quad (1)$$

where R is the universal gas constant, and

$$K_{PT} \equiv \left(\frac{T}{P_V} \frac{dP_V}{dT} \right)_{T_0} \quad (2)$$

is the dimensionless slope of the vapor pressure curve at T_0 . The second expression assumes that the cooling occurs in a short time δt and is limited to a thin layer of thickness $\delta z = (4D_T \delta t)^{1/2}$ [5], where D_T is the thermal diffusivity:

$$Q_{cP} \simeq A c_P \Delta T \delta z \simeq A c_P \Delta T (4D_T \delta t)^{1/2}. \quad (3)$$

Here A is the sample surface area and c_P is the volumetric heat capacity of the liquid ($\text{J m}^{-3} \text{K}^{-1}$). Equating these two expressions yields

$$\Delta T \simeq \frac{K_{PT} P_V(T_0) V_2}{A c_P (4D_T \delta t)^{1/2}}. \quad (4)$$

Using $\delta t = 1$ s and the values for naphthalene at 80°C (Table 2) gives a surface cooling of $T = 2.5$ K. The associated relative pressure drop,

$$\frac{P_V(T_0) - P(T_0 - \Delta T)}{P_V(T_0)} \simeq K_{PT} \frac{\Delta T}{T_0} = 0.13, \quad (5)$$

is large. The next three subsections discuss how thermal diffusion, boiling, and transpiration affect the return of the sample temperature to the container temperature.

3.2 Thermal diffusion

Boiling and transpiration can dominate the thermal relaxation at pressures above 1 Pa. To appreciate the importance of these phenomena, which are discussed in the following two subsections, it is useful to ignore them temporarily and consider only thermal diffusion.

Just after the initial cooling, the temperature distribution will not depend on the sample geometry due to the slow speed of thermal diffusion, so its dependence on time t and depth z below the surface will be a solution of the heat diffusion equation in a semi-infinite sample. (See Eq. 2.1(2) of [5].) The “source” solution is:

$$\frac{T(z, t)}{T_0} = 1 - \left(\frac{\tau}{t}\right)^{1/2} \exp \left[-\left(\frac{z}{z_0}\right)^2 \left(\frac{\tau}{t}\right) \right]. \quad (6)$$

This corresponds to the release of heat Q at the surface at time $t = 0$. The characteristic length z_0 is related to the as-yet undetermined time constant τ by the definition $z_0 = (4D_T\tau)^{1/2}$. To obtain the heat removed from the sample, Eq. (6) is integrated:

$$Q = Ac_P \int_0^\infty [T_0 - T(z, t)] dz = (\sqrt{\pi}/2) Ac_P T_0 z_0. \quad (7)$$

Equating this result with Eq. (1) leads to the time-dependent surface temperature,

$$T(0, t) = T_0 \left[1 - \left(\frac{\tau}{t}\right)^{1/2} \right], \quad (8)$$

where the time constant that characterizes the square-root decay is

$$\tau = \left[\frac{K_{PT} P_V(T_0) V_2}{AT_0 (\pi \lambda c_P)^{1/2}} \right]^2. \quad (9)$$

Note that the time constant τ determines both the amplitude and the speed of the temperature relaxation, and that it depends on the amount of vapor per unit area, $P_V V_2/A$, that is removed from the sample. An apparatus with a small evacuated volume V_2 and a large sample surface area A will have a small time constant.

Using the example values in Table 2 gives $\tau = 65 \mu\text{s}$, which is consistent with the assumption that the initial cooling of the surface was instantaneous. (Equation (8) is unphysical for $t < \tau$.) The corresponding value of the thermal penetration length is $z_0 = 4 \mu\text{m}$, which is consistent with the assumption that the sample depth is infinite.

Using Eq. (8), the associated return of the pressure to the equilibrium value is given by

$$\frac{\Delta P(t)}{P_V} \equiv \frac{P_V(T_0) - P(t)}{P_V(T_0)} = K_{PT} \left(\frac{\tau}{t}\right)^{1/2}. \quad (10)$$

Table 3 gives values of P predicted for naphthalene at 80 °C (Table 2). After 100 s, the pressure is still 1.4 % below the equilibrium value. At later times, δz is larger than the

sample radius, so by then the relaxation will instead become proportional to $\exp(-t/\tau)$, where the time constant τ depends on the shape of the sample. See, for example, Eq. 8.4(6) of [5], which gives the general solution for a cylinder of diameter $2a$ and depth L . The slowest time constant is

$$\frac{1}{\tau} = D_T \left[\left(\frac{j_{01}}{a} \right)^2 + \left(\frac{\pi}{2L} \right)^2 \right], \quad (11)$$

where $j_{01} = 2.405$ is the first zero of the Bessel function J_0 . For the dimensions in Table 1 and naphthalene at 80 °C (Table 2), $\tau = 98$ s.

Equation (11) assumes that the sample is in good contact with the container wall. This may not be true for a solid because, when the sample is pumped, the warm layer close to the wall is preferentially evaporated. The resulting gap will have a low thermal conductance; for example, for naphthalene at 80 °C (Table 2), the thermal conductivity of the vapor is 30 times smaller than that of the solid. The gap will make the thermal time constant larger than given by Eq. (11).

3.3 Boiling

If the sample is liquid, vapor bubbles will form on the wall at depths less than

$$z_{\text{boil}} = \frac{P_v(T_0) - P(t)}{\rho g}, \quad (12)$$

where ρ is the sample density and g is the acceleration of gravity. If the bubbles detach and rise, they will stir the sample and speed the return to equilibrium, especially if the pressure difference $P_v(T_0) - P(t)$ exceeds 100 Pa, which corresponds to a sample depth of 1 mm. Figure 3 supports this idea by showing the time dependent pressures that were measured for diethyl phthalate after opening the sample tube to the evacuated hot manifold. Below 70 °C, where z_{boil} is less than 1 mm, the initial pressure difference was larger and the return to equilibrium was slower.

The pressure differences for the three coldest temperatures in Figure 3 are roughly 0.3 Pa at the first recorded time $t = 20$ s. This suggests that boiling became negligible when the pressure difference reached 0.3 Pa, which corresponds to the small depth $z_{\text{boil}} = 0.03$ mm. In contrast, the pressure difference for the three warmest temperatures at $t = 20$ s is only 0.06 Pa. Transpiration may have caused the faster equilibration at the higher temperatures, especially if vigorous boiling splashed a thin layer of liquid onto the container wall.

3.4 Transpiration

A temperature difference will drive a mass flux in the vapor; this phenomenon, which here is called transpiration, is the reason for the large thermal conductivity of heat pipes [6]. Figure 4 illustrates the phenomenon by dividing the sample into Parts 1 and 2 with surface temperatures T_1 and T_2 and surface areas A_1 and A_2 . (The sides are ignored.) Most of the

sample is in Part 2. The temperature below Part 2 is the nominal wall temperature T_0 , but below Part 1 it is warmer by the difference $T_1 - T_0$, so transpiration will slowly move Part 1 to Part 2. Section 6.1 of the appendix derives formulas for the following transpiration effects, which are estimated in terms of the container's underlying temperature difference $T_1 - T_0$:

1. The pressure difference $P - P_0$, where $P_0 \equiv P_V(T_0)$.
2. The temperature difference $T_1 - T_2$.
3. The molar flux $A_1 \dot{n}_1$.
4. The time interval t during which Part 1 moves to Part 2.

This subsection uses those formulas to discuss how transpiration affects the equilibration of a sample. The two main effects are (1) near uniformity of the sample surface temperature and (2) a small but persistent pressure error.

Surface temperature differences are small—Equation (41) of the appendix gives the relative temperature difference between the surfaces of Part 1 and Part 2. In the limit where the two parts have similar areas, $A_1 \approx A_2$, but Part 1 is much thinner than Part 2, $L_1 \ll L_2$ it becomes

$$\frac{T_1 - T_2}{\Delta T_0} = \frac{g_{ct}}{(1 + g_{12} + g_{ct})} \simeq g_0 = 2.3 \times 10^{-4}. \quad (13)$$

The value of g_0 was calculated for naphthalene at 80 °C (Table 2).

Equation (13) applies also to the evaporative cooling of a liquid sample, which is illustrated in Figure 5. A short time δt after the evacuation, most of the surface has cooled to T_2 to a depth of $\delta z = \sqrt{4D_T \delta t}$. However, close to the wall, within the radial distance δr , thermal conduction through the liquid causes the surface temperature T_1 to be warmer. Using $\delta t = 1$ s and the values for naphthalene at 80 °C (Table 2) gives the short length $\delta r \approx \delta z = 0.5$ mm. The calculation is similar to that in the appendix except that $A_1 = 2\pi a \delta r$, $A_2 = \pi a^2$, and $L_1 = L_2 = \delta r$.

Transpiration causes a pressure error—Equation (43) of the appendix gives the difference between the pressure P and the reference pressure $P_0 \equiv P_V(T_0)$:

$$\frac{P - P_0}{P_0} = K_{PT} \frac{\Delta T_0}{T_0} \left[\frac{g + d_1 A_1 / (A_1 + A_2)}{1 + g + d_1} \right]. \quad (14)$$

This difference will persist while Part 1 moves to Part 2, and the characteristic time for that movement is

$$\begin{aligned}\Delta t &= \frac{(\text{moles in Part 1})}{(\text{molar flux leaving Part 1})} \\ &= \frac{A_1 L_1 (\rho/M)}{A_1 \dot{n}_1}, \\ &= \frac{\rho \Delta H L_1^2}{M \lambda \Delta T_0} (1 + g_{12} + g_{ct})\end{aligned}\quad (15)$$

where H is the heat of evaporation. Equations (14) and (15) can be simplified by making two approximations, $g_{12} \gg 1$ and $g_{ct} \ll 1$. The first approximation comes from the assumptions used previously, namely $A_1 \approx A_2$ and $L_1 \ll L_2$, and the second holds for naphthalene at 80 °C (Table 2) and a reference depth of $L = 10$ mm. (The assumptions about the sample dimensions could apply, for example, if a thin layer of the sample was splashed onto the upper portion of the container's wall.) With these approximations, the relative pressure difference and the persistence time are simply:

$$\frac{P - P_0}{P_0} \simeq K_{PT} \frac{\Delta T_0}{T_0} \quad (16)$$

$$\Delta t \simeq \frac{\rho \Delta H L_1 L_2}{M \lambda \Delta T_0} \quad (17)$$

Note that the pressure difference is proportional to the underlying temperature difference T_0 , but the persistence time is inversely proportional to T_0 .

Table 4 lists example values of $P - P_0$ and t that were calculated for naphthalene at 80 °C and plausible dimensions of Parts 1 and 2. The pressure error can be reduced to 0.15 % by reducing the temperature difference to $T_0 = 0.03$ K. Creating a temperature uniformity of 0.03 K in the sample container may be easy, but the container must have a connection to a pressure gauge at a higher temperature. Thus, it is important to prevent any of the sample from condensing or splashing into the connection. Note also that reducing the area of Part 1 relative to that of Part 2 reduces the persistence time t but not the pressure error.

4. Outgassing from a stable sample

4.1 Raoult's law

Raoult's law gives a general understanding of the error caused by an impurity, which is useful when the impurity is a hydrocarbon with only a moderate vapor pressure. Although Henry's law is more general, the value of Henry's constant k_H is often not available. This subsection defines the relative volatility ratio α , and it calculates the pressure error for two example impurities.

Raoult's law assumes that the pressure P measured over a solution of compound A and impurity B is the sum of the components' respective vapor pressures, P_{VA} and P_{VB} , weighted by their mole fractions x_A and x_B in the condensed sample [7]:

$$P = x_A P_{VA} + x_B P_{VB}. \quad (18)$$

The relative error caused by the impurity is,

$$\frac{P - P_{VA}}{P_{VA}} = \left(\frac{P_{VB} - P_{VA}}{P_{VA}} \right) x_B = (\alpha - 1) x_B. \quad (19)$$

Here α is the relative volatility ratio defined by

$$\alpha \equiv \frac{y_B/x_B}{y_A/x_A} \cong \frac{k_H/P_{VA}}{1/1} \approx \frac{P_{VB}}{P_{VA}}, \quad (20)$$

where y_A and y_B are the equilibrium mole fractions in the vapor, and Henry's constant was approximated by P_{VB} . The relative error can be either positive or negative [8]; only positive (more volatile) impurities are considered here.

As an example, consider nitrogen dissolved in naphthalene just above its melting temperature of 80 °C. Using Raoult's law for nitrogen requires an estimate of the impurity "vapor pressure", even though at 353 K it is a gas far above its critical temperature T_c . The estimate can be obtained by extrapolating the impurity's vapor pressure curve to temperatures $T > T_c$ [7]. Air is a common impurity, so it is useful to state the extrapolation for nitrogen that was used here:

$$P_{\text{N}_2}(T) = (3.5 \text{ GPa}) \exp(-801\text{K}/T) = 0.36 \text{ GPa at } 80^\circ\text{C}. \quad (21)$$

(The coefficients in Eq. (21) were fit to values from the REFPROP database [10].) Raoult's law says that dissolving only 3×10^{-6} mole fraction nitrogen in the naphthalene will double the observed pressure.

Raoult's law assumes that the mixture is an ideal solution with no energy of mixing. To understand the error caused by that assumption and by the extrapolation of P_{VB} one can compare the above estimate to the measurements made by Gao et al [11]. A quadratic extrapolation of their high pressure measurements of nitrogen plus naphthalene gives a low pressure solubility that exceeds that predicted by Raoult's law by a factor of only 1.6. Thus, Raoult's law seems adequate for understanding vapor pressure errors caused by inadequate degassing.

As a second example, consider naphthalene containing the impurity indane, which has a vapor pressure of 4 kPa at 80 °C [12,13]. Raoult's law says that a 0.1 % concentration will cause only a 0.4 % error in the measured vapor pressure, which is much smaller than caused by the same concentration of nitrogen. However, the similarity between the vapor pressures of indane and naphthalene makes removing indane more difficult than removing nitrogen.

4.2 Diffusion time constant

In equilibrium, Raoult's law says that the pressure measured above a sample composed of compound A and a volatile impurity B will be greater than the pure compound's vapor pressure P_{VA} . Pumping on the sample removes the equilibrium vapor and replaces it temporarily with a nonequilibrium vapor that has a lower concentration of the impurity. Afterwards, more impurity diffuses out of the sample until its partial pressure in the vapor has again reached equilibrium. Figure 6 shows the evolution of the impurity concentration $\alpha(z,t)$ as function of normalized position z/L and time t/τ_D , where L is the sample height and the characteristic diffusion time constant is

$$\tau_D = \frac{L^2}{\pi^2 D}. \quad (22)$$

The surface is at $z = L$, and the concentration is c_0 at $t < 0$. After the brief time $t = 0.01 \tau_D$, the concentration at the surface has recovered to within 2 % of its initial value, and at $t = \tau_D$, the concentration has changed throughout the sample.

Figure 7 shows the evolution of the surface concentration $\alpha(L,t)$ of the impurity, which is proportional to the impurity's partial pressure. It asymptotically reaches the value $c_0/(1 + \gamma)$, where γ is the partition parameter defined by Eq. (45). See the appendix (Section 6.2) for details. Table 5 gives example values of D and τ_D for various liquid mixtures. The Wilke-Chang correlation [14,3] was used to estimate the diffusivity of impurity A in liquid compound B as

$$D = \left(7.4 \times 10^{-12} \text{ m}^2 \text{ s}^{-1}\right) \frac{\left(M_A / \text{g mol}^{-1}\right)^{1/2} (T/\text{K})}{\left(\eta_A / \text{cP}\right) \left(V_B / \text{cm}^3 \text{ mol}^{-1}\right)^{0.6}}, \quad (23)$$

where M_A and η_A are the molar mass and viscosity of the liquid, and V_B is the molar volume of the impurity. (Note the non-SI units.)

An estimated bound on the impurity concentration can be obtained from the time dependence of the pressure $P(t)$ observed after pumping on the sample. At the time $t = 0.01 \tau_D$, the slope of the curve in Figure 7 is approximately 1. If the temperature equilibration has finished by then, the partial pressure of the impurity will be approximately

$$\frac{P_B(t)}{P_{VA}} \approx \left(\frac{1}{P} \frac{dP}{dt}\right) \tau_D. \quad (24)$$

5. Outgassing from a decomposing sample

If the sample decomposes at the temperature of interest, its pressure can never be stable. This complication affected the measurements of TEMAH shown in Figure 8 (39 °C) and

Figure 9 (119 °C). The samples were partially purified by cyclic pumping, after which the time-dependent pressure $P(t)$ was measured for 6 h. The pressure histories $P(t)$ differed because the samples had different initial impurity concentrations or the pumping cycles were longer than the nominal cycle.

Five processes contributed to the time dependence during the 6 h period:

1. Evaporative cooling at $t = 0$.
2. Temperature equilibration.
3. Generation of a volatile impurity by decomposition with reaction rate k_A .
4. Removal of the impurity with reaction rate k_B .
5. Diffusion of the impurity from the liquid to the vapor, characterized by the rate k_D .

Temperature equilibration was assumed to be finished after $t_{\text{first}} = 400$ s [1], and the following equation, which was fit to the data at times $t > t_{\text{first}}$, accounted for the other processes:

$$P_{\text{fit}}(t) = P_{\text{fit}}(0) + P_B(\infty) \left(1 - e^{-t/\tau_B}\right) + P_1 \left(\frac{1}{1+\gamma}\right) e^{-t/\tau_B} \left(1 - e^{-t/\tau_D}\right) \quad (25)$$

Here

$$\begin{aligned} P_{\text{fit}}(0) &= \text{fitted pressure at } t=0 \\ P_B(\infty) &= \text{final, equilibrium pressure of the impurity B} \\ P_1 &= \text{disequilibrium pressure of the impurity at } t=0 \\ \tau_B &= \text{time constant for removal of impurity B} \\ \tau_D &= \text{time constant for diffusive equilibration of the impurity} \end{aligned} \quad (26)$$

Equation (45) of the appendix (Section 6.2) defines the partition parameter γ , and Section 6.3 of the appendix derives Eq. (25).

The five fitted parameters in Eq. (25) are the pressures $P_{\text{fit}}(0)$ and P_1 (units Pa) and the rates k_A , k_B , and k_D (s^{-1}). The most important is

$$P_{\text{fit}}(0) = P_{V,A} + P_B(0), \quad (27)$$

which is the sum of $P_{V,A}$, the vapor pressure of the compound of interest, and $P_B(0)$, the partial pressure of the impurity at $t = 0$.

In general, the fitted pressure $P_{\text{fit}}(0)$ is larger than the desired vapor pressure value $P_{V,A}$ because $P_{\text{fit}}(0)$ includes the initial pressure of the impurity as well as $P_{V,A}$. The uppermost curve of Figure 8 is an example where the initial total pressure was 8 times larger than $P_{V,A}$. Even so, $P_{V,A}$ can be obtained from $P_{\text{fit}}(t)$ if the measurements of $P(t)$ were preceded by

cyclic pumping. As described in Section 6.4 of the appendix, during each cycle the sample tube (volume V_1) was opened at $t = t_0$ to the total volume ($V_1 + V_2$). At $t = t_1$ the sample tube was closed while the volume V_2 was evacuated, and at $t = t_2$ the sample tube was re-opened. The value of P_{VA} was then

$$P_{VA} = \frac{P_{\text{fit}}(0)}{(1 - V_{12})} + P_{\text{fit}}(t_1) - \frac{P_{\text{fit}}(t_2)}{(1 - V_{12})}, \quad (28)$$

where $V_{12} \equiv V_1/(V_1 + V_2)$.

Figures 8 and 9 show examples of the successful use of the model represented by Eqs. (25) and (28). Even in the extreme case where the initial total pressure was 8 times larger than the vapor pressure of the pure compound, the fitted value of P_{VA} agreed to within 2 % with the values fit to other runs with less impurity. The figures also show that a simple linear extrapolation of the time-dependent pressure $P(t)$ to $t = 0$ can yield an incorrectly large value for P_{VA} . Also, depending on the initial evaporative cooling and impurity concentration, simply using the first measurement of $P(t)$ can yield a value of P_{VA} that is either too small or too large.

The values of vapor pressure obtained for TEMAH with this model are listed and compared with previous measurements by others in the companion article [1]. Depending on the source and the temperature, the previous values are 1 % to 29 % larger, which is consistent with an insufficient correction for a volatile impurity.

6. Conclusion

The pressure measured in a static vapor pressure apparatus can be time-dependent for various reasons. When the sample is pure, evaporative cooling, boiling, thermal diffusion, and transpiration through the vapor will affect the temperature of the sample's surface and cause the measured pressure to depend on time. The time for equilibration can be hours if the sample container has a temperature gradient as small as 0.03 K. When the sample is impure, diffusion of the impurity within the condensed sample will add further time dependence that is even slower. An impurity cannot be avoided if the sample is decomposing during the measurement, and the decomposition rate is another cause of time dependence. This article addressed these causes of time dependence, and it included a model that allows the vapor pressure of a decomposing compound to be obtained from the measured time-dependent pressure.

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7. Appendix

7.1 Details: Transpiration

Figure 4 shows a sample container with a wall temperature that varies by T_0 . The sample is divided into two parts, most of which is in Part 2. Below Part 2 the wall temperature is T_0 , and below Part 1 it is $T_0 + T_0$. Transpiration will slowly evaporate Part 1 and move it to Part 2. This appendix estimates the following effects due to transpiration:

1. The pressure difference $P - P_0$, where $P_0 \equiv P_V(T_0)$.
2. The temperature difference $T_1 - T_2$.
3. The molar flux $A_1 \dot{n}_1$.
4. The time interval t during which Part 1 moves to Part 2.

The effects are estimated in terms of the underlying temperature difference T_0 .

The net molar flux per unit area out of Part 1 is the difference between the outward flux due to evaporation and the inward flux due to the pressure P in the container.

$$\dot{n}_1 = \frac{P_V(T_1) - P}{(2\pi MRT_1)^{1/2}} = \frac{(P - P_0) + K_{PT}((\Delta T_0 + \Delta T_1)/T_1)}{(2\pi MRT_1)^{1/2}} \quad (29)$$

Here, K_{PT} is the dimensionless slope defined by Eq. (2), $P_0 \equiv P_V(T_0)$ is the reference pressure, T_0 is the reference temperature, and $T_1 = T_1 - (T_0 + T_0)$ is the temperature difference across the thickness of Part 1. Multiplying Eq. (29) by the surface area A_1 and keeping only first order in T/T_0 gives the molar flux (mol s^{-1}):

$$A_1 \dot{n}_1 = -A_2 \dot{n}_2 = \frac{K_{PT} P_0}{(2\pi MRT_0)^{1/2}} \left(\frac{A_1 A_2}{A_1 + A_2} \right) \left(\frac{T_1 - T_2}{T_0} \right) \quad (30)$$

To use Eq. (30), assume that conditions are near steady state, so that the pressure changes slowly:

$$A_1 \dot{n}_1 + A_2 \dot{n}_2 = \frac{\dot{P}V}{RT_0} \simeq 0. \quad (31)$$

Solving Eq. (31) yields the relative pressure difference

$$\frac{P - P_0}{P_0} = K_{PT} \left[\left(\frac{A_1}{A_1 + A_2} \right) \frac{(\Delta T_0 + \Delta T_1)}{T_0} + \left(\frac{A_2}{A_1 + A_2} \right) \frac{\Delta T_2}{T_0} \right]. \quad (32)$$

Quite reasonably, Eq. (32) says that the pressure is the vapor pressure at the area-weighted average temperature:

$$P = P_V \left(\frac{A_1 T_1 + A_2 T_2}{A_1 + A_2} \right). \quad (33)$$

Multiplying Eq. (29) by the area A_1 and the heat of vaporization H and using Eq. (32) gives the transpiration heat current through the vapor.

$$\begin{aligned} \dot{Q}_t &= A_1 \dot{n}_1 \Delta H \\ &= \left[\frac{K_{PT} P_0 \Delta H}{(2\pi M R T_0)^{1/2}} \left(\frac{A_1 A_2}{A_1 + A_2} \right) \left(\frac{\Delta T_0}{T_0} \right) \right] \left(1 + \frac{\Delta T_1}{\Delta T_0} - \frac{\Delta T_2}{\Delta T_0} \right) \\ &\equiv \dot{Q}_{t0} \left(1 + \frac{\Delta T_1}{\Delta T_0} - \frac{\Delta T_2}{\Delta T_0} \right) \end{aligned} \quad (34)$$

The conduction heat current through Part 1 of the solid is

$$\dot{Q}_{1c} = - \left[\frac{A_1 \lambda \Delta T_0}{L_1} \right] \left(\frac{\Delta T_1}{\Delta T_0} \right) \equiv -\dot{Q}_{1c0} \left(\frac{\Delta T_1}{\Delta T_0} \right). \quad (35)$$

Equating the transpiration and conduction heat currents gives

$$\dot{Q}_{t0} = - \left(1 + \frac{\Delta T_1}{\Delta T_0} - \frac{\Delta T_2}{\Delta T_0} \right) \equiv -\dot{Q}_{1c0} \left(\frac{\Delta T_1}{\Delta T_0} \right). \quad (36)$$

which leads to the following expressions for the temperature differences across Part 1 and Part 2.

$$\frac{\Delta T_1}{\Delta T_0} = \frac{-1}{(1 + g_{12} + g_{ct})} \quad \text{and} \quad \frac{\Delta T_2}{\Delta T_0} = \frac{g_{12}}{1 + g_{12} + g_{ct}} \quad (37)$$

(Evaporative cooling causes T_1 to be negative.) In Eqs. (37) the geometry ratio

$$g_{12} \equiv - \frac{\dot{Q}_{1c0}}{\dot{Q}_{2c0}} = \frac{A_1}{A_2} \frac{L_2}{L_1} \quad (38)$$

was obtained by equating the two conduction heat currents, and the parameter g_{ct} was defined by

$$g_{ct} = \frac{\dot{Q}_{1c0}}{\dot{Q}_{t0}} \equiv g_0 \left(\frac{L}{L_1} \right) \left(1 + \frac{A_1}{A_2} \right). \quad (39)$$

Here L is a reference length, say the depth L_2 of Part 2, and

$$g_0 \equiv \frac{(2\pi MRT_0)^{1/2} \lambda}{K_{PT}^2 R P_0 L}. \quad (40)$$

is a dimensionless parameter that is small except when $P_0 < 1$ Pa.

Equations (37) for the temperature differences allow the following quantities to be written in terms of T_0 :

- The difference between the surface temperatures of Part 1 and Part 2:

$$\frac{T_1 - T_2}{\Delta T_0} = \frac{g_{ct}}{(1 + g_{12} + g_{ct})}. \quad (41)$$

- The molar flux (mol s^{-1}) from Part 1 to Part 2:

$$A_1 \dot{n}_1 = -A_2 \dot{n}_2 = \frac{\lambda A_1 \Delta T_0}{\Delta H (1 + g_{12} + g_{ct}) L_1}. \quad (42)$$

- The difference between the pressure and the reference pressure:

$$\frac{P - P_0}{P_0} = K_{PT} \frac{\Delta T_0}{T_0} \left[\frac{g_{12} + g_{ct} A_1 / (A_1 + A_2)}{1 + g_{12} + g_{ct}} \right]. \quad (43)$$

7.2 Details: Diffusion time constant

This section gives details about Figure 6 and Figure 7, which illustrate the outgassing from a sample of depth L and volume V_{sample} into a vapor volume ($V_1 + V_2$). The figures are based on the following equation, which is an adaptation of Crank's Eq. (4.45) [17]:

$$\frac{c(z, t)}{c_0} = \left(\frac{1}{1 + \gamma} \right) - \left(\frac{\gamma}{1 + \gamma} \right) \sum_{n=1}^{\infty} \frac{2(1 + \gamma)}{1 + \gamma + \gamma^2 q_n^2} \frac{\cos(q_n z / L)}{\cos(q_n)} \exp\left(\frac{-t}{\tau_n}\right). \quad (44)$$

Here, q_n is the nonzero positive root of $\tan(q_n) = -\gamma q_n$ and the time constants are $\tau_n \equiv \pi^2 \tau_D / q_n^2$, where $\tau_D \equiv L^2 / (\pi^2 D)$ is the characteristic diffusion time constant. The dimensionless partition parameter γ is the equilibrium amount of impurity in the vapor space divided by the amount in the sample:

$$\gamma \equiv \frac{(\text{moles B in vapor})}{(\text{moles B in solid})} = \frac{k_H \left(\frac{c_0}{c_s} \right) x_0 \frac{(V_1 + V_2)}{RT}}{c_0 V_{\text{sample}}} \simeq \frac{M_A P_{\text{VB}}}{\rho RT} \left(\frac{V_1 + V_2}{V_{\text{sample}}} \right). \quad (45)$$

Here, m , M_A , and ρ are respectively the mass, molar mass, and density of the sample, and $c_S = \rho/M_A \approx 10^4 \text{ mol m}^{-3}$ is the molar density of the sample. The partition parameter is related to c_0 and c_∞ , the equilibrium impurity concentrations at $t < 0$ and $t = \infty$, by

$$\frac{c_\infty}{c_0} = \frac{1}{1+\gamma}. \quad (46)$$

The moderate-volatility impurities considered here have $P_{VB} < 10^4 \text{ Pa}$, and the dimensions of the present apparatus give $(V_1 + V_2)/V_{\text{sample}} \approx 29$. Thus, $\gamma = 1$ which causes the sum in Eq. (44) to converge slowly at $t = 0$. However, the expression becomes useful at relatively small times because, for small γ , the time constants can be approximated as

$$\tau_n \equiv \frac{\pi^2 \tau_D}{q_n^2} \simeq \frac{\tau_D}{n^2}. \quad (47)$$

For example, at $t/\tau_D = 1$, the second term is only 5 % as large as the first term.

7.3 Details: Outgassing from a decomposing sample

Make the following assumptions about the sample.

1. The only components are compound A and impurity B. Denote the mole fraction of B by

$$x \equiv \frac{\text{moles B in liquid}}{\text{moles A in liquid}} \quad \text{and} \quad y \equiv \frac{\text{moles B in vapor}}{\text{moles A in vapor}} \simeq \frac{P_B}{P_{VA}}, \quad (48)$$

where P_{VA} is the vapor pressure of A and P_B is the partial pressure of B.

2. The vapor pressure P_{VA} equilibrates instantaneously. This ignores evaporative cooling.
3. In equilibrium, the total pressure is given by Raoult's law:

$$P = x_A P_{VA} + x_B P_{VB}. \quad (49)$$

The decomposition may actually produce multiple impurity species with mole fractions x_{B1} , x_{B2} , etc. In that case, Raoult's law can still be written as Eq. (49)

by defining $x_B \equiv \sum_i x_{Bi}$ as the sum of the impurity mole fractions and $P_{VB} \equiv \sum_i (x_{Bi}/x_B) P_{VBi}$ as an effective impurity vapor pressure.

4. Compound A decomposes in the liquid into volatile impurity B with reaction rate k_A , and impurity B is removed from the vapor, perhaps by wall adsorption, with reaction rate k_B . Observations of $P(t)$ for TEMAH gave support for the

removal of B: the pressure in the hot manifold was observed to decrease when the impurity partial pressure was large and the manifold was isolated from the liquid sample.

5. Impurity B is transported between the liquid and vapor by a rate that is proportional to the difference $P_{VBx} - P_B$, which implies that details of diffusion within the sample can be ignored.

These assumptions lead to the following coupled equations that describe the rates of change in the liquid and vapor.

$$\begin{aligned} \dot{x} &= -k_D (x - y/\alpha) + k_A \\ \beta \dot{y} &= +k_D (x - y/\alpha) - \beta k_B y \end{aligned} \quad (50)$$

The parameters α and β are given by

$$\begin{aligned} \alpha &\equiv \frac{(\text{vapor pressure of compound B})}{(\text{vapor pressure of impurity A})} = \frac{P_{VB}}{P_{VA}} \gg 1 \\ \beta &\equiv \frac{(\text{moles A in vapor})}{(\text{moles A in liquid})} = \frac{(V_1 + V_2)P_{VA}}{RT} \frac{M_A}{\rho V_{\text{sample}}} \ll 1. \end{aligned} \quad (51)$$

Note that $\gamma \equiv \alpha\beta$ is the partition parameter defined by Eq. (45). Setting the left-hand sides of Eqs. (50) to zero gives the final, equilibrium mole fractions,

$$x(\infty) = \frac{1}{\alpha\beta} \frac{k_A}{k_B} \quad \text{and} \quad y(\infty) = \frac{1}{\beta} \frac{k_A}{k_B}, \quad (52)$$

and the final, equilibrium impurity pressure,

$$P_B(\infty) = \frac{k_A}{\beta k_B} P_{VA}. \quad (53)$$

The coupled Equations (50) can be solved by Laplace transform techniques, yielding

$$y(t) = y(\infty) + \exp\left[\frac{-Bt}{2\beta}\right] \left\{ \begin{aligned} &\left[y(0) - y(\infty) \right] \cosh\left[\frac{(B^2 - 4\beta^2 k_B k_D)^{1/2} t}{2\beta}\right] \\ &- \left[y(0) + y(\infty) - \frac{2A}{B} \right] \frac{B}{(B^2 - 4\beta^2 k_B k_D)^{1/2}} \sinh\left[\frac{(B^2 - 4\beta^2 k_B k_D)^{1/2} t}{2\beta}\right] \end{aligned} \right\}, \quad (54)$$

where

$$\begin{aligned} A &\equiv k_D [x(0) + \beta y(0)] \\ B &\equiv \alpha^{-1} k_D + \beta (k_B + k_D) \simeq k_D (\alpha^{-1} + \beta). \end{aligned} \quad (55)$$

Make the approximation

$$(B^2 - 4\beta^2 k_B k_D)^{1/2} \simeq B \left[1 - 2 \left(\frac{\alpha\beta}{1+\alpha\beta} \right)^2 \frac{k_B}{k_D} \right], \quad (56)$$

and define the time constants for diffusion and for removal of B by

$$\frac{1}{\tau_D} \equiv \frac{B}{\beta} \simeq \left(\frac{1+\gamma}{\gamma} \right) k_D \quad \text{and} \quad \frac{1}{\tau_B} \equiv \frac{\beta k_B k_D}{B} \simeq \left(\frac{\gamma}{1+\gamma} \right) k_B, \quad (57)$$

where $\gamma \equiv \alpha\beta$. Equation (54) can then be written as

$$y(t) = y(\infty) + [y(0) - y(\infty)] e^{-t/\tau_B} + [x(0) - \alpha y(0)] \left(\frac{1}{1+\gamma} \right) e^{-t/\tau_B} (1 - e^{-t/\tau_D}). \quad (58)$$

Adding unity, multiplying by P_{VA} , and re-arranging yields the total time-dependent pressure:

$$P(t) = P_{VA} + P_B(0) + [P_B(\infty) - P_B(0)] (1 - e^{-t/\tau_B}) + [P_{VB} x(0) - P_B(0)] \left(\frac{1}{1+\gamma} \right) e^{-t/\tau_B} (1 - e^{-t/\tau_D}). \quad (59)$$

In Eq. (59), note that

- The fit cannot separately obtain P_{VA} and $P_B(0)$.
- $P_B(\infty) \gg P_B(0)$.

Thus, a practical form of Eq. (59) for fitting to $P(t)$ data is

$$P_{\text{fit}}(t) = P_{\text{fit}}(0) + P_B(\infty) (1 - e^{-t/\tau_B}) + P_1 \left(\frac{1}{1+\gamma} \right) e^{-t/\tau_B} (1 - e^{-t/\tau_D}). \quad (60)$$

Assumption (5) above requires that the rates k_A and k_B be small, namely

$$k_A \ll k_D \quad \text{and} \quad k_B \ll k_D. \quad (61)$$

Fits to $P(t)$ for TEMAH found that the values of k_A satisfied Eq. (61), but that some values of k_B were comparable to k_D . (See Figure 21 of the companion article [1].) Removing the requirement of Eq. (61) causes the factor $(1 + \gamma)$ that appears in Eqs. (57) and (60) to be modified as follows:

$$(1 + \gamma) \rightarrow (1 + \gamma + k_B/k_D). \quad (62)$$

Fits with this modification shifted the rate constants by as much as a factor of 2, but had no effect on the values of $P_{\text{fit}}(0)$,

7.4 Details: Obtaining P_{VA} from $P_{\text{fit}}(t)$

Figure 10 shows two cycles of cyclic pumping followed by the beginning of a long measurement of $P(t)$. During each cycle the sample tube (volume V_1) was opened at $t = t_0$ to the total manifold volume ($V_1 + V_2$). At $t = t_1$ the sample tube was closed while the rest of the manifold was evacuated, and at $t = t_2$ the sample tube was re-opened. At $t = 0$ the sample tube was left open and $P(t)$ was measured for 6 h.

In periodic steady state the rate of impurity removal is matched by the rate of decomposition, and $P(t_0) = P(t_2)$ for each cycle. Also, the partial pressure of the impurity P_B at the beginning of the cycle, $t = t_0$, is related to its value at the end of the cycle, $t = t_2$, just before the volume expansion, by

$$P_B(t_0) = P_B(t_2) V_{12}, \quad (63)$$

because opening the sample container to the rest of the manifold decreases the impurity partial pressure by the volume ratio $V_{12} \equiv V_1/(V_1 + V_2)$. Equation (63) applies to the 0.5 h pumping cycle. Now, note that $P_B(t_0) = P_B(0)$, and rewrite Eq. (63) in terms of the function $P_{\text{fit}}(t)$ that was fit to the 6 h measurement interval that followed.

$$\begin{aligned} P_B(0) &= \{P_B(0) + [P_B(t_1) - P_B(0)] + [P_B(t_2) - P_B(t_1)]\} V_{12} \\ &\simeq \left\{ P_B(0) + [P_{\text{fit}}(t_1) - P_{\text{fit}}(0)] + \left[\frac{P_{\text{fit}}(t_2) - P_{\text{fit}}(t_1)}{V_{12}} \right] \right\} V_{12} \end{aligned} \quad (64)$$

The last term was obtained by assuming that closing the sample container did not change the molar flow rate of B into the vapor. Solving for $P_B(0)$ and using $P_B(0) = P_{\text{fit}}(0) - P_{VA}$ yields

$$P_{VA} = \frac{P_{\text{fit}}(0)}{(1 - V_{12})} + P_{\text{fit}}(t_1) - \frac{P_{\text{fit}}(t_2)}{(1 - V_{12})}. \quad (65)$$

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Figure 1.
Time dependent pressure measured for TEMAH.

Figure 2.
Simplified diagram of the vapor pressure apparatus.

Figure 3. Time-dependent pressures that were measured after opening the sample tube containing diethyl phthalate to the evacuated hot manifold. The inset shows that the boil depth calculated from Eq. (12) was less than 1 mm for temperatures below 70 °C.

Figure 4.

Transpiration drives a mass flux from a warm spot to a cold spot. The difference between the surface temperatures T_1 and T_2 is small compared to the container's underlying temperature difference T_0 . The slow decrease of the measured pressure P will depend on T_0 , the thicknesses L_1 and L_2 , and the surface areas A_1 and A_2 .

Figure 5.

Transpiration with a liquid sample. UPPER: Transpiration from the surface close to the container wall causes the temperature difference $T_1 - T_2$ to be small.

LOWER: Simple model of the surface temperature.

Figure 6.

Evolution of the impurity concentration $x(z,t)$ after pumping briefly on a sample that was previously in concentration equilibrium. Distance z from the bottom of the condensed sample is scaled by the sample height L , and time is scaled by the characteristic diffusion time $\tau_D \equiv L^2/D$. The relative concentration decrease equals the partition parameter, $\gamma = 0.001$.

Figure 7. Evolution of the surface concentration of the impurity $c(L,t)$, which is proportional to impurity's partial pressure. The inset uses a linear time scale.

Figure 8.

Pressures measured at 39 °C for three samples of TEMAH. The samples were partially purified by cyclic pumping, after which $P(t)$ was measured for 6 h. UPPER: The $P(t)$ curves for the two off-nominal samples differed because those samples had larger impurity concentrations; one sample also had a longer pumping cycle. LOWER: The curves are fits of Eq. (25) to $P(t)$. The data influenced by evaporative cooling were avoided by using only data at times $t > t_{\text{first}}$. INSET: The three large points at $t = 0$ are values of the vapor pressure P_{VA} that Eq. (28) obtained from fits to the three sets of $P(t)$.

Figure 9.

Pressures measured at 119 °C for two samples of TEMAH. The samples were partially purified by cyclic pumping, after which $P(t)$ was measured for 6 h. UPPER: The $P(t)$ curve for the off-nominal sample differed because a longer pumping cycle was used and because that sample had a larger impurity concentration. LOWER: The curves are fits of Equation (25) to $P(t)$. The data influenced by evaporative cooling were avoided by using only data at times $t > t_{\text{first}}$. The two large points at $t = 0$ are values of the vapor pressure P_{VA} that Eq. (28) obtained from fits to the two sets of $P(t)$.

Figure 10. Cyclic pumping, followed by a long measurement of $P(t)$. In steady state, $P(t_0) = P(t_2)$ for each cycle.

Table 1

Apparatus dimensions.

quantity		value	unit
sample container volume	V_1	14	cm ³
evacuated volume	V_2	15	cm ³
sample volume	V_{sample}	1	cm ³
sample surface area	A	1	cm ²
sample depth	L	1	cm
sample diameter	$2a$	1.2	cm

Table 2

Properties of naphthalene near its melting temperature of 353.4 K. Unless noted otherwise, the values are for the liquid and were obtained from Reference [2].

quantity		value	unit
molar mass	M	0.128	kg mol ⁻¹
density	ρ	978	kg m ⁻³
vapor pressure	P_V	994	Pa
vapor pressure slope	$K_{PT} = (T/P_V)(dP_V/dT)$	17.6	
enthalpy of vaporization	$H = K_{PT}RT$	5.1×10^4	J mol ⁻¹
volumetric heat capacity	c_P	2.2×10^6	J m ⁻³ K ⁻¹
thermal conductivity	λ	0.12	W m ⁻¹ K ⁻¹
thermal diffusivity	$D_T = \lambda/c_P$	5.5×10^{-8}	m ² s ⁻¹
vapor viscosity	η_V	7×10^{-6}	Pa s
vapor mean free path	$l = (2RT/M)^{1/2}(\eta_V/P)$	1.5×10^{-6}	m
vapor thermal conductivity	λ_V	0.012 [3]	W m ⁻¹ K ⁻¹
solid thermal conductivity	λ_S	0.37 [4]	W m ⁻¹ K ⁻¹

Table 3

The thermal penetration depth, $\delta_z \equiv (4D_T t)^{1/2}$, and the transient pressure drop P associated with the cooling caused by one pumping cycle, during which the sample tube is opened to an evacuated manifold of volume V_2 . The calculation used Eq. (9), Eq. (10), and the values for liquid naphthalene at 80 °C (Table 2).

$t(\text{s})$	$\delta_z(\text{mm})$	P/P_V
1	0.05	0.14
10	1.5	0.04
100	4.7	0.014

Table 4

Example calculations, made with Eqs. (14) and (15), of the pressure error $P = P - P_0$ and the characteristic time t for the transpiration of naphthalene at 80 °C. The thickness of Part 2 is $L_2 = 10$ mm.

T_0 (K)	A_1/A_2	L_1 (mm)	P/P_0	t (h)
0.1	1	0.1	0.005	9
0.1	1	0.01	0.005	0.9
0.03	1	0.1	0.0015	30
0.03	1	0.01	0.0015	3
0.03	0.1	0.01	0.0015	0.3

Estimates of the mass diffusion constant D and concentration relaxation time $\tau_D = L^2/(\pi^2 D)$ in a liquid sample of thickness $L = 10$ mm at 80 °C. The diffusion constant for TEMAH was calculated by making the visual estimate of the viscosity $\eta \approx 10$ cP.

Table 5

liquid A	impurity B	P_{VB}/P_{VA}	η_A (cP)	D ($10^{-9} \text{ m}^2 \text{ s}^{-1}$)	τ_D (h)
naphthalene	nitrogen	3.6×10^5	0.97 [15]	3.6	0.8
diethyl phthalate	nitrogen	2.5×10^7	20 [16]	0.23	12
diethyl phthalate	maleic anhydride	8.9×10^1	20 [16]	0.16	18
TEMAH	methylethylamine	2.4×10^3	10	0.37	8