

# Gas Saturation Vapor Pressure Measurements of Mononitrotoluene Isomers from (283.15 to 313.15) K<sup>†</sup>

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A gas saturation apparatus capable of simultaneous measurements on 18 samples was used for this work. The vapor pressures of 2-nitrotoluene (2-NT), 3-nitrotoluene (3-NT), 4-nitrotoluene (4-NT), and tetradecane (a control compound) were measured with this apparatus over the temperature range (283.15 to 313.15) K. Over this temperature range, the vapor pressure of 2-NT ranged from (5.53 to 61.1) Pa; the vapor pressure of 3-NT ranged from (3.39 to 37.8) Pa; and the vapor pressure of 4-NT ranged from (1.25 to 26.4) Pa. The enthalpies of vaporization or sublimation were determined using the Clausius–Clapeyron equation.

## Introduction

There are substantial needs for low-density saturated vapor pressure measurements on pure compounds for scientific, commercial, and environmental applications.<sup>1–3</sup> For most low-volatility compounds, there are few (if any) reported vapor pressures at temperatures near ambient, even though this is often the temperature range of greatest interest. The mononitrotoluenes are a typical case. Vapor pressure data are available for 2-nitrotoluene (2-NT), 3-nitrotoluene (3-NT), and 4-nitrotoluene (4-NT), but almost all of the data are for temperatures above 323 K.<sup>4–9</sup> At lower temperatures, there is only one set of data for 2-NT<sup>10</sup> and one set of data for 4-NT.<sup>11</sup> No vapor pressures for 3-NT have been reported in this temperature range.

Additional vapor pressure measurements for the mononitrotoluenes at ambient temperatures would be useful for multiple reasons. For example, 2-NT and 4-NT are detection taggants added to plastic explosives.<sup>12</sup> These taggants have higher vapor pressures than the explosive itself and facilitate detection of the explosive material by instruments such as ion mobility spectrometers.<sup>12,13</sup> The vapor pressures of such taggants at ambient temperatures are also related to their useful lifetime (i.e., to how quickly they dissipate from the plastic explosive). Additionally, nitroaromatic compounds are an important class of environmental pollutants because of their stability and their tendency to leach into groundwater.<sup>14</sup> Ambient temperature vapor pressures are needed to understand the fate of these pollutants in the environment; for example, calculation of the air–water partition coefficient requires the vapor pressure of the pure compound.<sup>14</sup>

Descriptions of vapor pressure measurement methods exist elsewhere.<sup>2,15–20</sup> Methods that directly measure the pressure exerted by the vapor phase (e.g., static gauged bombs and ebulliometry) are often not suited to measurements on low-volatility samples for multiple reasons. One reason is that the contributions of volatile impurities to measured pressures can be substantial even at extremely low impurity mole fractions.<sup>15,18</sup> This is due to the fact that impurities can have vapor pressures that are orders of magnitude greater than that of the sample

compound. Second, these methods typically require sample masses of at least a few grams. For many compounds, a large amount of highly pure material can be difficult to obtain.

A variety of “indirect” methods are capable of measuring the vapor pressures of low-volatility compounds; however, the gas saturation method and the effusion method (when very high purity samples are available) are generally considered to be the most accurate of these methods for low vapor pressures.<sup>2</sup> The gas saturation method<sup>2,21–23</sup> is a simple technique that involves the saturation of a carrier gas stream with the vapor of a condensed phase of the compound of interest. The most common approach is to strip the vapor from a measured volume of the saturated carrier gas using an adsorber or cold trap and then measure the recovered mass with an appropriate analytical method. Then the vapor pressure is calculated from the ideal gas equation, eq 1

$$p_{\text{sat}} = (m \cdot R \cdot T)/(V \cdot M) \quad (1)$$

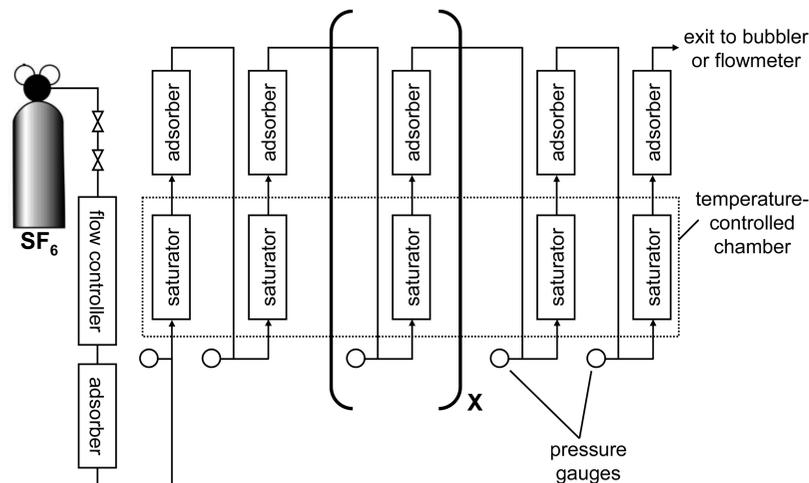
where  $p_{\text{sat}}$  is the vapor pressure;  $m$  is the recovered mass of the vapor;  $R$  is the gas constant;  $T$  is the temperature of the saturator;  $V$  is the volume of carrier gas at the temperature and pressure of the saturator; and  $M$  is the molar mass of the compound.

The gas saturation method has several advantages.<sup>2,21–23</sup> Calibration is not required. Impurities have a relatively small effect on the measured vapor pressures, assuming that a technique like gas chromatography is used to determine the amount of solute vapor, so samples of limited purity can be used. Little sample is needed for a measurement (typically tens of milligrams or less), again assuming that a sensitive analytical technique is used to determine the amount of vapor. Finally, the apparatus is simple and inexpensive to build and operate. On the other hand, traditional gas saturation methods have had two significant drawbacks. First, measurement times can be quite long if a large volume of carrier gas is needed to collect a sufficient amount of vapor for analysis. Second, the method is susceptible to certain types of systematic errors (e.g., leaks) that can be difficult to detect.

The “concatenated” gas saturation method<sup>21</sup> was developed to compensate for the drawbacks mentioned above. In this type of apparatus, several saturator–adsorber pairs are linked in series so that multiple measurements can be made simultaneously with the same carrier gas stream. This approach greatly speeds data

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**Figure 1.** Concatenated gas saturation apparatus featuring several saturator–adsorber pairs linked in series. The apparatus used for this work has 18 saturator–adsorber pairs ( $X = 14$ ).

collection. It also allows for strategies that ensure data quality. For example, a control compound with a well-known vapor pressure curve can be measured simultaneously with the sample compounds. If a measurement yields the expected vapor pressure for the control compound, one has a high level of confidence in the other vapor pressures that were measured simultaneously.

Herein, a new concatenated gas saturation apparatus is described. It has 18 saturator–adsorber pairs linked in series and is therefore capable of 18 simultaneous measurements of  $p_{\text{sat}}$ . This apparatus was used to measure the vapor pressures of 2-NT, 3-NT, 4-NT, and tetradecane (a control sample) over the temperature range (283.15 to 313.15) K.

## Experimental Section

**Chemicals.** Reagent-grade acetone, used as a solvent in this work, was obtained from a commercial source and used as received. It has a stated purity of 99.5 %, which is consistent with our own routine analyses of such solvents by gas chromatography. The 2-NT, 3-NT, 4-NT, and tetradecane were also obtained from a commercial source and used as received. All had stated purities of 99 %, which is again consistent with our own GC analyses. Sulfur hexafluoride ( $\text{SF}_6$ ) with a purity of 99.9 % was obtained from a commercial source and transferred into an aluminum cylinder to facilitate mass determinations.

**Concatenated Gas Saturation Apparatus.** The concatenated gas saturation apparatus was designed and constructed at NIST. Its design is similar to an earlier apparatus for which a detailed description has been published (the main differences being the thermostat and the number of saturator–adsorber pairs).<sup>21</sup> The principal components of the apparatus are illustrated schematically in Figure 1. The carrier gas supply includes an aluminum gas cylinder, pressure regulator, and flow controller. The cylinder–regulator assembly must be removed between measurements to determine the mass of carrier gas that was used. To facilitate this procedure, the cylinder–regulator assembly is connected to the flow controller by a short stainless steel capillary with a valve at each end. Closing these two valves allows the cylinder–regulator assembly to be removed with the loss of only the capillary’s volume of carrier gas (<1 mg of  $\text{SF}_6$ ). Carrier gas from the flow controller first passes through an adsorbent column packed with the same material used in the adsorbers (see below). The gas then flows through the 18 saturator–adsorber pairs. The saturators are located inside a

temperature-controlled forced-air chamber, while the adsorbers are located on a manifold above the chamber (at room temperature, approximately 21 °C). The temperature-controlled chamber, which is capable of operating between (238 and 450) K, is surrounded by a thick layer of insulation with a metal casing on both sides (the drywell plate). Between each saturator–adsorber pair, a Bourdon tube pressure gauge displays the pressure drop. At the end of the saturator–adsorber series, the carrier gas flows through a flowmeter or an indicating bubbler before it is expelled into the laboratory at ambient pressure. The flowmeter and bubbler are used for diagnostic purposes only—to set the flow rate to an approximate value or to verify the flow of carrier gas at a glance (the volume of carrier gas is determined indirectly as described below).

Each saturator consists of a PTFE tube (1 m in length with an inside diameter of 0.48 cm) filled with 3 mm glass beads. The relatively large glass beads do not impede the flow of gas through the saturators, which helps limit pressure drop across the apparatus. Each saturator forms a loop inside the temperature-controlled chamber and terminates at the drywell bottom plate. The saturator end fittings are standard compression fittings, allowing for easy installation and removal. The surface area of each saturator, including the tube wall and glass beads, is approximately 0.024 m<sup>2</sup>.

The main body of each adsorber consists of a stainless-steel tube (7.5 cm in length with an inside diameter of 0.86 cm) packed with the porous polymer adsorbent poly(2,6-diphenyl-1,4-phenylene oxide),<sup>24–26</sup> as shown in Figure 2. PTFE inserts at either end of the adsorber act as flow conditioners and reduce dead volume. Plugs of silanized glass wool hold the adsorbent in place. Reducing unions at each end of the main body of the adsorber allow the connection of stainless steel capillary tubes. The capillary at the outlet end of the adsorber directs the carrier gas into the next saturator. The capillary tube on the inlet side is an integral part of the adsorber—it is a “stinger” that goes through the drywell plate and penetrates into the outlet end of the saturator. The stinger prevents the loss of solute as the carrier gas flows from the temperature-controlled saturator to the room-temperature adsorber. The connection between the stinger and saturator is shown schematically in Figure 3. This connection includes two PTFE plugs that reduce dead volume and prevent physical contact between the stinger and the coated glass beads.

**Vapor Pressure Measurements.** First, each saturator was coated with one of the nitrotoluenes or with tetradecane. This

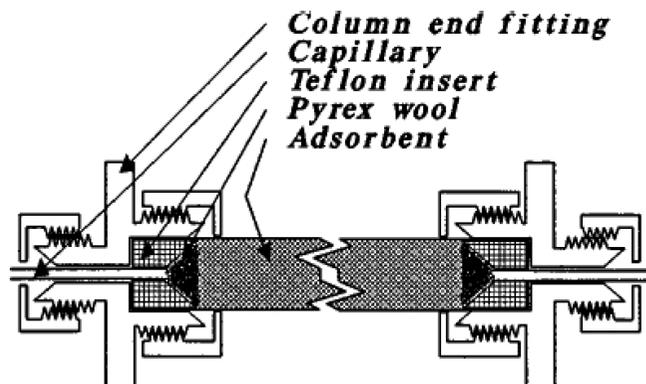


Figure 2. Schematic view of the main body of an adsorber.

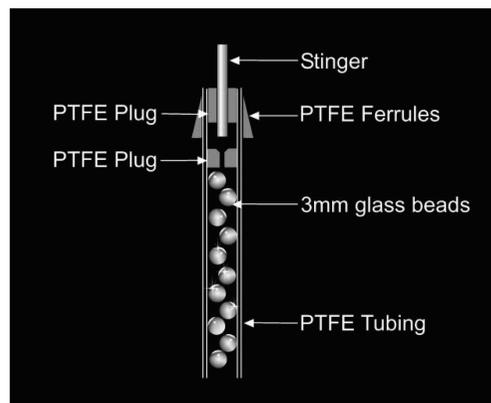


Figure 3. Schematic view of the connection between the saturator and the "stinger" part of the adsorber. This connection is designed to prevent the loss of solute as the carrier gas flows out of the saturator and into the adsorber.

was done by wetting the saturator with a 10 % solution of one of the compounds in acetone and then removing the acetone by gently flowing helium through the adsorber at room temperature for 0.5 h. Approximately 1 mL of solution was used to wet each saturator, which means that approximately 0.1 g of the compound was deposited. Given the surface area of the saturator (approximately  $0.024 \text{ m}^2$ ), we estimate that the average thickness of the resulting coating was  $4 \mu\text{m}$ . The saturators were then installed in the temperature-controlled chamber of the apparatus. The saturators only had to be coated once for all of the vapor pressure measurements because  $\leq 6 \text{ mg}$  of any compound evaporated from a saturator during a measurement.

Before starting a measurement, the  $\text{SF}_6$  supply cylinder was weighed on a two-pan balance with a sensitivity of 2.5 mg. To eliminate a buoyancy correction, an evacuated ballast cylinder was placed on the other balance pan (along with class S standard weights). After weighing, the cylinder was placed in a separate enclosure on the gas saturation apparatus. This enclosure served to protect the cylinder from handling and dust. Each adsorber was installed with its stinger inserted directly into the end of the paired saturator. The temperature was set, and after thermal equilibration, the flow of  $\text{SF}_6$  was initiated. The flow rate of carrier gas was between (0.4 and 0.5) L per day, which means that the residence time of the carrier gas in a saturator was approximately 0.5 h. Total flow times ranged from 5 days (at 313.15 K) to 40 days (at 283.15 K). The atmospheric pressure was logged at regular intervals to obtain an average atmospheric pressure for the measurement.

Upon passage of what was deemed a sufficient quantity of carrier gas, the flow of  $\text{SF}_6$  was stopped and the cylinder weighed again. For this series of measurements, the change in

cylinder mass ranged from (9 to 65) g, depending on the measurement temperature (the actual cylinder mass is about 15 kg). Each adsorber (including the stinger) was removed from the apparatus and eluted with acetone. The elution was done with a syringe pump set to deliver acetone at a rate of  $0.25 \text{ mL} \cdot \text{min}^{-1}$ . The eluent from each adsorber was collected into two vials. The first 5 mL of eluent was collected in a glass vial, and it typically contained all of the detectable solute. The next 5 mL of eluent was collected in a second vial, and it never contained more than 2 % of the recovered solute. This method ensures that all detectable solute has been stripped from the adsorber. After elution, the adsorbers were dried with a flow of warm helium before using them for the next vapor pressure measurement. The unmanipulated eluent fractions were analyzed by gas chromatography with flame ionization detection (GC-FID). Research-grade nitrogen was used as the carrier and makeup gas. The split/splitless injection inlet was used in the splitless mode and maintained at 523.15 K. The samples were separated on a 30 m capillary column coated with a  $0.1 \mu\text{m}$  film of (5 %-phenyl)-methylpolysiloxane. The moderate polarity of nitrotoluenes gives a somewhat poor peak shape on this stationary phase, but the nitrotoluene peaks were well separated from the solvent peaks. The temperature program consisted of 1 min at 323.15 K, followed by a  $100 \text{ K} \cdot \text{min}^{-1}$  gradient to 338.15 K, followed by a  $10 \text{ K} \cdot \text{min}^{-1}$  gradient to 423.15 K.

The mass change of the  $\text{SF}_6$  cylinder was used to calculate the moles of  $\text{SF}_6$  carrier gas. The volume of carrier gas,  $V$  in eq 1, at the experimental temperature and average atmospheric pressure, was then calculated using an equation of state for  $\text{SF}_6$  that is explicit in Helmholtz energy,<sup>27</sup> as implemented in REFPROP.<sup>28</sup> The mass of vapor collected in the adsorber,  $m$  in eq 1, was determined by calibrated gas chromatography, as described above.

**Avoiding Systematic Errors in the Measurement of  $p_{\text{sat}}$ .** With the gas saturation technique, there are several potential pitfalls that can cause systematic errors in  $p_{\text{sat}}$ . For the concatenated apparatus used herein, which has a large number of connections along the carrier gas stream, a likely source of systematic error is a leak of the carrier gas. Downstream from a leak, less carrier gas is flowing through the apparatus than one assumes (at least, that is the case with our method of determining carrier gas flow by mass). This means that less-than-expected amounts of solute are carried into the adsorbers, resulting in values of  $p_{\text{sat}}$  that are systematically low. We employed three strategies for guarding against leaks. First, the apparatus was thoroughly leak-checked with helium (with a thermal conductivity sensor) before any measurements were made. Second, simultaneous measurements on each compound were done in triplicate, and these measurements were spaced along the apparatus in a particular way. Specifically, 2-NT was measured with the 4th, 10th, and 16th saturator–adsorber pairs; 3-NT was measured with the 5th, 11th, and 17th saturator–adsorber pairs; and 4-NT was measured with the 2nd, 8th, and 14th saturator–adsorber pairs. This way, comparisons of  $p_{\text{sat}}$  measured in different parts of the apparatus can be used to detect (and even pinpoint) leaks that occur within the saturator–adsorber chain. Third, the  $p_{\text{sat}}$  of a control compound, tetradecane, was measured at the same time as the nitrotoluenes using the 6th, 12th, and 18th saturator–adsorber pairs. Thus, if the 6th saturator–adsorber pair yielded the expected value of  $p_{\text{sat}}$  for tetradecane, we could assume that the measurements made with the first through fifth saturator–adsorber pairs were unaffected by a leak. This arrangement makes it possible to retain any valid data, even if there is a leak somewhere downstream. It should be noted that we saw

no evidence of a leak anywhere in the system during these measurements. Spacing the samples in this way also allows one to detect inefficient trapping by carry-over to the next adsorber (something that was not observed during these measurements).

Some other possible sources of systematic error are inefficient trapping of the sample vapor in the adsorbers, incomplete elution of a sample from the adsorbers, insufficient analytical sensitivity when determining the amount of sample in the eluent, reaction or decomposition of a sample during the measurement, and a carrier gas flow rate that is too fast. The successful measurements on tetradecane provide direct evidence against several of these. Efficient sample trapping was demonstrated by the lack of solute carry-over (see above). This was anticipated because this type of adsorber has been found to be at least 99.99 % efficient for other polar organic compounds.<sup>21</sup> The elution procedure is specifically designed to ensure that all detectable solute has been stripped from the adsorber. Calibration curves show that GC-FID is sufficiently sensitive in the range of these experiments. We have no reason to suspect that the nitrotoluenes would react or decompose under the mild conditions of these measurements. The flow rate of carrier gas was between (0.4 and 0.5) L per day, which means that the residence time of the carrier gas in a saturator was approximately 0.5 h. This is important because it allows ample time for the vapor phase to become saturated with solute, and it decreases the driving force for physically carrying the condensed phase into the adsorbers.

**Uncertainties in the Measurement of Vapor Pressure.** A detailed analysis of the uncertainties in the measurement of vapor pressure with a concatenated gas saturation apparatus of similar design has been published.<sup>21</sup> The main differences from the previous apparatus are that the present apparatus has a different type of thermostat and a greater number of saturator–adsorber pairs. Temperature control and measurement in the thermostat has a standard uncertainty of 0.5 K, which was determined by measuring the temperature fluctuation in the thermostat at each set-point with an ITS-90 calibrated platinum resistance thermometer with an uncertainty of 0.01 K. An uncertainty of 0.5 K in the temperature control results in a relative standard uncertainty of  $\leq 6\%$  in the measured vapor pressures of the nitrotoluenes. The pressure in the saturators is not directly controlled. There is a pressure drop across the apparatus of approximately 1 kPa at the flow rates used for this work. Additionally, since the carrier gas exits the apparatus at ambient pressure, barometric variability contributed an uncertainty of approximately 2 kPa to the experimental pressure. The combined uncertainty in the experimental pressure leads to a relative standard uncertainty of 3 % in the measured vapor pressures. The determination of carrier gas volume, by weighing the SF<sub>6</sub> cylinder and using an equation of state, results in a relative standard uncertainty of  $< 0.1\%$  in the measured vapor pressures. Analysis of the mass of recovered vapor by gas chromatography has a relative standard uncertainty of 2 %. The relative standard uncertainty for saturator efficiency is estimated to be 1 %.<sup>21</sup> The adsorber efficiency is not detectably less than 1 and is, therefore, not assigned an uncertainty. The relative standard uncertainty estimated for the elution efficiency is  $\leq 1\%$ . The sum of these uncertainties in quadrature gives a combined relative standard uncertainty of 7 % for the method and apparatus.

There are also uncertainties caused by impurities in the nitrotoluenes and with the use of the ideal gas law (eq 1).<sup>21</sup> In an ideal-mixture approximation, the partial pressure of the major component of a sample is equal to the product of its mole fraction and its vapor pressure. The mass fraction purity of the

nitrotoluenes and tetradecane is estimated to be 0.99 (see above). It is likely that the average molar mass of the impurities is similar to the molar mass of the sample compound; in that case, the mole fraction purity of the sample compound is also 0.99, which would result in a 1 % shift in the measured vapor pressures. The worst case scenario is if the impurity has a low molar mass (e.g., water); in that case, the mole fraction purity of the nitrotoluene could be as low as 0.93, which would result in a 7 % shift in the measured vapor pressures.<sup>21</sup> In a similar way, solubility of the carrier gas in the condensed phase can cause a shift in the measured vapor pressures. The mole fraction solubility of SF<sub>6</sub> in tetradecane is 0.008 at 298.15 K and 0.1 MPa,<sup>29</sup> hence, the expected shift in the measured vapor pressure of the control sample is 0.8 %. The solubility of SF<sub>6</sub> in the nitrotoluenes is not known; for the purposes of our uncertainty analysis, we assume that the magnitude of the effect is the same as for tetradecane. The Poynting correction to the pure-liquid fugacity is also small—on the order of 1 %. Any nonideality of saturated solute vapor is expected to be negligible because the pressures are low and there is no reason to suspect an effect like dimerization. Interaction of the solute vapor with the carrier gas could cause a significant change in the measured vapor pressure, but the interaction virial coefficients are not known for these systems. It has been estimated that this effect could change the measured vapor pressures by as much as 10 %.<sup>21</sup> Instead of trying to correct for these effects, we treat them all as uncertainties in the measured data.

We can take an optimistic or a conservative view of combined uncertainty in these measurements. Optimistically, assuming an “impurity effect” of 1 % and an “interaction virial coefficient effect” of zero, the quadrature sum of uncertainties associated with the measurements is 7 %, and the expanded ( $k = 2$ ) uncertainty is 14 %. Conservatively, assuming an “impurity effect” of 7 % and an “interaction virial coefficient effect” of 10 %, the quadrature sum of uncertainties associated with the measurements is 14 %, and the expanded ( $k = 2$ ) uncertainty is 28 %.

## Results and Discussion

The vapor pressures ( $p_{\text{sat}}$ ) of 2-NT, 3-NT, 4-NT, and tetradecane were measured at temperatures of (283.15, 293.15, 303.15, and 313.15) K. Three simultaneous measurements of  $p_{\text{sat}}$  were made for each compound at each temperature, and the mean values are given in the tables and figures. The relative standard deviations of the replicate measurements ranged from 4 % to 11 % and did not seem to depend on the temperature or the compound.

The gas saturation method does not require calibration. However, as discussed in the Experimental Section, there are some potential problems (e.g., leaks) that must be guarded against. Our primary strategy for ensuring the quality of the data for the nitrotoluenes was to make simultaneous measurements on a control compound, tetradecane. We chose tetradecane for a variety of reasons: its vapor pressure curve is well-known;<sup>30</sup> in the temperature range studied, its vapor pressure curve is similar to those of the nitrotoluenes; it is stable and unreactive; it is available commercially at low cost and with an acceptable purity. If the measured values of  $p_{\text{sat}}$  for tetradecane are the same as reference values, within the experimental uncertainty, that gives us confidence in the values of  $p_{\text{sat}}$  for other compounds that were measured simultaneously.

Reference values of  $p_{\text{sat}}$  for tetradecane were taken from the NIST ThermoData Engine (TDE).<sup>31</sup> The reference values are shown in Table 1 along with the combined standard uncertainty

**Table 1. Comparison of  $p_{\text{sat}}$  Reference Data for Tetradecane with  $p_{\text{sat}}$  Determined by the Concatenated Gas Saturation Method**

$T$ K	TDE		gas saturation	
	$p_{\text{sat}}/\text{Pa}$	uncertainty Pa	$p_{\text{sat}}/\text{Pa}$	uncertainty Pa
283.15	0.401	0.016	0.427	0.060
293.15	1.15	0.04	1.21	0.17
303.15	3.01	0.09	3.22	0.45
313.15	7.32	0.19	8.10	1.13

**Table 2. Vapor Pressures of Nitrotoluenes Determined by the Concatenated Gas Saturation Method**

$T$ K	2-NT <sup>a</sup> $p_{\text{sat}}/\text{Pa}$	3-NT <sup>a</sup> $p_{\text{sat}}/\text{Pa}$	4-NT <sup>a</sup> $p_{\text{sat}}/\text{Pa}$
283.15	5.53 <sup>b</sup>	3.39 <sup>c</sup>	1.25 <sup>c</sup>
293.15	12.7 <sup>b</sup>	8.55 <sup>b</sup>	3.79 <sup>c</sup>
303.15	29.7 <sup>b</sup>	19.5 <sup>b</sup>	10.2 <sup>c</sup>
313.15	61.1 <sup>b</sup>	37.8 <sup>b</sup>	26.4 <sup>c</sup>

<sup>a</sup> The expanded ( $k = 2$ ) uncertainty of these data is 14 %. <sup>b</sup> This is the vapor pressure of the liquid phase. <sup>c</sup> This is the vapor pressure of the solid phase.

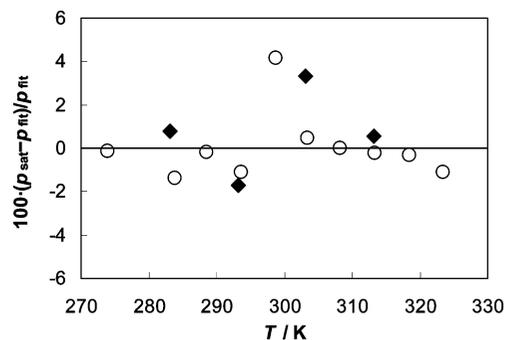
that was estimated by TDE for these values. For comparison, the values of  $p_{\text{sat}}$  for tetradecane that were measured in the concatenated gas saturation apparatus also are given in Table 1. The difference between the TDE reference values and our measured values is between 5 % and 11 %. This is excellent evidence that the gas saturation apparatus is functioning properly. It also gives credence to the more optimistic uncertainty estimate given in the Experimental Section—that is, an expanded uncertainty of 14 % (as shown in Table 1).

The standard molar enthalpy of vaporization,  $\Delta H_{\text{vap}}$ , at the mean temperature of the experimental range can be derived from the integrated form of the Clausius–Clapeyron equation. The reference data from Table 1 yields  $\Delta H_{\text{vap}}(298.15 \text{ K}) = 71.4 \text{ kJ}\cdot\text{mol}^{-1}$ . The gas saturation data from Table 1 yield  $\Delta H_{\text{vap}}(298.15 \text{ K}) = 71.6 \text{ kJ}\cdot\text{mol}^{-1}$  (with a standard uncertainty of  $1.3 \text{ kJ}\cdot\text{mol}^{-1}$ ), which is in excellent agreement with the value derived from the reference data. Our gas-saturation value for  $\Delta H_{\text{vap}}$  is also in excellent agreement with recommended values based on calorimetric measurements.<sup>32</sup>

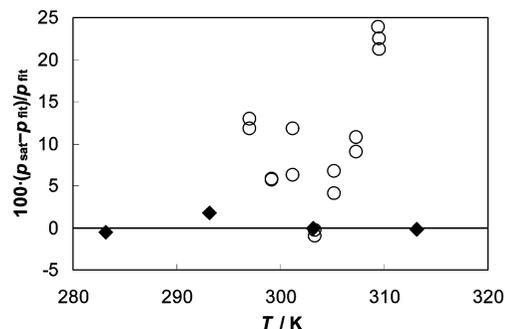
Table 2 shows the mean values of  $p_{\text{sat}}$  for the three nitrotoluenes that were measured in the gas saturation apparatus. Given the results for tetradecane (see above), we estimate an expanded uncertainty of 14 % for these measurements. Over the entire temperature range, 2-NT had the highest vapor pressure, and 4-NT had the lowest. In this temperature range, the condensed phase of 2-NT is a liquid, and the condensed phase of 4-NT is a solid. The condensed phase of 3-NT is a solid at 283.15 K and a liquid for the other three temperatures.

Verevkin and Heintz have reported<sup>10</sup>  $p_{\text{sat}}$  data for 2-NT in the same temperature range that we measured. Their data, which cover the temperature range (274 to 323) K, also were measured with a gas saturation method, although many of the experimental details differ from the current study.<sup>10</sup> Our values of  $p_{\text{sat}}$  are in excellent agreement with the vapor pressure curve reported by Verevkin and Heintz, as shown by the deviation plot in Figure 4. A Clausius–Clapeyron plot for our data yields  $\Delta H_{\text{vap}}(298.15 \text{ K}) = 59.6 \text{ kJ}\cdot\text{mol}^{-1}$  (with a standard uncertainty of  $1.6 \text{ kJ}\cdot\text{mol}^{-1}$ ). A Clausius–Clapeyron plot for the data of Verevkin and Heintz yields an enthalpy of vaporization of  $\Delta H_{\text{vap}}(298.15 \text{ K}) = 59.05 \text{ kJ}\cdot\text{mol}^{-1}$  (with a reported uncertainty of  $0.25 \text{ kJ}\cdot\text{mol}^{-1}$ ),<sup>10</sup> which is also in excellent agreement with our value.

No previously reported  $p_{\text{sat}}$  data exist for 3-NT in the temperature range that we studied, so it is not possible to make



**Figure 4.** Deviation plot of  $\blacklozenge$ , our gas saturation data, and  $\circ$ , the data of Verevkin and Heintz for 2-NT. Values of  $p_{\text{fit}}$  were obtained from a linear fit to the Clausius–Clapeyron plot for the data of Verevkin and Heintz.



**Figure 5.** Deviation plot of  $\blacklozenge$ , our gas saturation data and  $\circ$ , the data of Lenchitz and Velicky for 4-NT. Values of  $p_{\text{fit}}$  were obtained from a linear fit to the Clausius–Clapeyron plot for our data.

comparisons. We can derive a value of  $\Delta H_{\text{vap}}$  for 3-NT by use of the data points that correspond to the liquid phase of 3-NT (i.e., the data points at 293.15 K, 303.15 K, and 313.15 K). In this way, we find that  $\Delta H_{\text{vap}}(303.15 \text{ K}) = 56.6 \text{ kJ}\cdot\text{mol}^{-1}$  (with a standard uncertainty of  $2.5 \text{ kJ}\cdot\text{mol}^{-1}$ ), which is not significantly different from the value for 2-NT.

Lenchitz and Velicky have reported<sup>11</sup> vapor pressure data for 4-NT in the same temperature range that we measured. Their data, which cover the temperature range (297 to 310) K, were measured by Knudsen effusion.<sup>11</sup> It is important to note that the values reported in the original publication<sup>11</sup> contain a unit conversion error and are an order of magnitude lower than they should be. This mistake was discovered when these data were being compiled for use in TDE. Herein, we use the corrected values, as given in TDE.<sup>31</sup> Figure 5 shows a deviation plot for our data and the (corrected) data of Lenchitz and Velicky. The values of  $p_{\text{sat}}$  reported by Lenchitz and Velicky are as much as 24 % higher than our vapor pressure curve, which is outside of the expanded uncertainty of our data. Since 4-NT is a solid over the temperature range we studied, it is the standard molar enthalpy of sublimation,  $\Delta H_{\text{sub}}$ , that is derived from a Clausius–Clapeyron plot. Such a plot of our data for 4-NT yields  $\Delta H_{\text{sub}}(298.15 \text{ K}) = 74.8 \text{ kJ}\cdot\text{mol}^{-1}$  (with a standard uncertainty of  $1.0 \text{ kJ}\cdot\text{mol}^{-1}$ ). As expected, the value of  $\Delta H_{\text{sub}}$  for 4-NT is larger than the values of  $\Delta H_{\text{vap}}$  for 2-NT and 3-NT. A Clausius–Clapeyron plot of Lenchitz and Velicky's data shows some curvature, covers a limited temperature range, and has a different mean temperature than our data. Nevertheless, an enthalpy of sublimation of  $\Delta H_{\text{sub}}(303.28 \text{ K}) = 79.1 \text{ kJ}\cdot\text{mol}^{-1}$  was derived (without a reported uncertainty),<sup>11</sup> which is outside of the expanded uncertainty in our value.

## Conclusions

We have confidence in the vapor pressure data measured with the new concatenated gas saturation apparatus because vapor

pressures for the control compound, tetradecane, were within experimental uncertainty of reference values. Our vapor pressure data for 2-NT are in excellent agreement with previously reported data that were also measured by a gas saturation method. Additionally, we have reported the first set of vapor pressure data for 3-NT near room temperature and what we believe is an improved set of data for 4-NT in the same temperature range.

## Literature Cited

- (1) Ambrose, D.; Davies, R. H. The correlation and estimation of vapour pressures. III. Reference values for low-pressure estimations. *J. Chem. Thermodyn.* **1980**, *12*, 871–879.
- (2) Delle Site, A. The vapor pressure of environmentally significant organic chemicals: A review of methods and data at ambient temperature. *J. Phys. Chem. Ref. Data* **1997**, *26*, 157–193.
- (3) Ambrose, D.; Young, C. L. Vapor-Liquid Critical Properties of Elements and Compounds. 1. An Introductory Survey. *J. Chem. Eng. Data* **1995**, *40*, 345–357.
- (4) Aim, K. Saturated Vapor Pressure Measurements on Isomeric Mononitrotoluenes at Temperatures between 380 and 460 K. *J. Chem. Eng. Data* **1994**, *39*, 591–594.
- (5) Ambrose, D.; Gundry, H. A. The vapour pressure of *p*-nitrotoluene. *J. Chem. Thermodyn.* **1980**, *12*, 559–561.
- (6) Berliner, J. F. T.; May, O. E. Studies in vapor pressure. II. The mononitrotoluenes. *J. Am. Chem. Soc.* **1926**, *48*, 2630–2634.
- (7) Dreisbach, R. R.; Shrader, S. A. Vapor Pressure-Temperature Data on Some Organic Compounds. *Ind. Eng. Chem.* **1949**, *41*, 2879–2880.
- (8) Mann, C. A.; Montonna, R. E.; Larian, M. G. Sulfite Turpentine. *Ind. Eng. Chem.* **1936**, *28*, 598–601.
- (9) Stull, D. R. Vapor Pressure of Pure Substances - Organic Compounds. *Ind. Eng. Chem.* **1947**, *39*, 517–540.
- (10) Verevkin, S. P.; Heintz, A. Thermochemistry of substituted benzenes: quantification of ortho-, para-, meta-, and buttress interactions in alkyl-substituted nitrobenzenes. *J. Chem. Thermodyn.* **2000**, *32*, 1169–1182.
- (11) Lenchitz, C.; Velicky, R. W. Vapor Pressure and Heat of Sublimation of Three Nitrotoluenes. *J. Chem. Eng. Data* **1970**, *15*, 401–403.
- (12) Perr, J. M.; Furton, K. G.; Almirall, J. R. Solid phase microextraction ion mobility spectrometer interface for explosive and taggant detection. *J. Sep. Sci.* **2005**, *28*, 177–183.
- (13) Cotte-Rodríguez, I.; Handberg, E.; Noll, R. J.; Kilgour, D. P. A.; Cooks, R. G. Improved detection of low vapor pressure compounds in air by serial combination of single-sided membrane introduction with fiber introduction mass spectrometry (SS-MIMS-FIMS). *Analyst* **2005**, *130*, 679–686.
- (14) Beneš, M.; Dohnal, V. Limiting activity coefficients of some aromatic and aliphatic nitro compounds in water. *J. Chem. Eng. Data* **1999**, *44*, 1097–1102.
- (15) Ambrose, D. *Experimental Thermodynamics*; Neindre, L. B., Vodar, B., Eds.; Butterworths: London, 1975; Vol. II.
- (16) Merten, U.; Bell, W. E. *The Characterization of High-Temperature Vapors*; Margrave, J. L., Ed.; Wiley: New York, NY, 1967.
- (17) Norman, J. H.; Winchell, P. *Techniques of Metals Research*; Rapp, R. A., Ed.; Interscience: New York, NY, 1970.
- (18) Ditchburn, R. W.; Gilmour, J. C. The Vapor Pressures of Monatomic Vapors. *Rev. Mod. Phys.* **1941**, *13*, 310–327.
- (19) Partington, J. R. *An Advanced Treatise on Physical Chemistry*; Longmans, Green: New York, NY, 1951.
- (20) Thomson, G. W. *Physical Methods of Organic Chemistry*, 2nd ed.; Weissberger, A., Ed.; Interscience: New York, NY, 1949.
- (21) Bruno, T. J.; Mayrath, J. E. Concatenated gas saturation vapor pressure apparatus. *Rev. Sci. Instrum.* **1997**, *68*, 2864–2870.
- (22) Carruth, G. F.; Kobayashi, R. Vapor Pressure of Normal Paraffins Ethane through *n*-Decane from Their Triple Points to about 10 mm Hg. *J. Chem. Eng. Data* **1973**, *18*, 115–126.
- (23) Mokbel, I.; Razzouk, A.; Hajjaji, A.; Msakni, N.; Jose, J. A gas saturation apparatus for very low vapor or sublimation pressure measurements ( $10^{-3}$  Pa): Vapor-liquid equilibria of *n*-alkanes (*n*-C<sub>10</sub>, *n*-C<sub>24</sub>, *n*-C<sub>28</sub>). *J. Chem. Eng. Data* **2007**, *52*, 1720–1725.
- (24) Bruno, T. J.; Svoronos, P. D. N. *CRC Handbook of Basic Tables for Chemical Analysis*, 2nd ed.; CRC Press: Boca Raton, 2003.
- (25) Dettmer, K.; Engewald, W. Adsorbent materials commonly used in air analysis for adsorptive enrichment and thermal desorption of volatile organic compounds. *Anal. Bioanal. Chem.* **2002**, *373*, 490–500.
- (26) Kumar, A.; Viden, I. Volatile organic compounds: Sampling methods and their worldwide profile in ambient air. *Environ. Monit. Assess.* **2007**, *131*, 301–321.
- (27) Wagner, W.; Guder, C. A Reference Equation of State for the Thermodynamic Properties of Sulfur Hexafluoride (SF<sub>6</sub>) for Temperatures from the Melting Line to 625 K and Pressures up to 150 MPa. *J. Phys. Chem. Ref. Data* **2009**, *38*, 33–94.
- (28) Lemmon, E. W.; McLinden, M. O.; Huber, M. L. *REFPROP, Reference Fluid Thermodynamic and Transport Properties*, Version 8; NIST Standard Reference Database #23; National Institute of Standards and Technology: Gaithersburg, MD, 2007.
- (29) Hesse, P. J.; Battino, R.; Scharlin, P.; Wilhelm, E. Solubility of gases in liquids. 20. Solubility of He, Ne, Ar, Kr, N<sub>2</sub>, O<sub>2</sub>, CH<sub>4</sub>, CF<sub>4</sub>, and SF<sub>6</sub> in *n*-alkanes *n*-C<sub>l</sub>H<sub>2l+2</sub> ( $6 \leq l \leq 16$ ) at 298.15 K. *J. Chem. Eng. Data* **1996**, *41*, 195–201.
- (30) Lemmon, E. W.; Goodwin, A. R. H. Critical properties and vapor pressure equation for alkanes C<sub>n</sub>H<sub>2n+2</sub>: Normal alkanes with  $n \leq 36$  and isomers for  $n = 4$  through  $n = 9$ . *J. Phys. Chem. Ref. Data* **2000**, *29*, 1–39.
- (31) Frenkel, M.; Chirico, R. D.; Diky, V.; Muzny, C.; Lemmon, E. W.; Yan, X.; Dong, Q. *ThermoData Engine (TDE)*, Version 2.0; NIST Standard Reference Database #103; National Institute of Standards and Technology: Gaithersburg, MD, 2004.
- (32) Růžička, K.; Majer, V. Simultaneous Treatment of Vapor-Pressures and Related Thermal Data between the Triple and Normal Boiling Temperatures for *n*-Alkanes C<sub>5</sub>-C<sub>20</sub>. *J. Phys. Chem. Ref. Data* **1994**, *23*, 1–39.

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