

Solid Vapor Pressure and Enthalpy of Sublimation for Ammonium Perfluorooctanoate

Catherine A. Barton,^{*,†} Miguel A. Botelho,[‡] and Mary A. Kaiser[‡]

DuPont Engineering Research and Technology, 1007 Market Street, DuPont Building 12036, Wilmington, Delaware 19898, and DuPont Corporate Center for Analytical Sciences, Experimental Station 402, Wilmington, Delaware 19880

A modified gas saturation method was used to directly determine the solid vapor pressure of ammonium perfluorooctanoate (APFO). Measurements were made over the temperature range from (45 to 60) °C. Pressures ranged from (0.04 ± 0.007) Pa to (0.17 ± 0.028) Pa. A relationship was developed for determining vapor pressure as a function of temperature for conditions near the test range, and an environmentally relevant vapor pressure of (0.003 ± 0.0005) Pa was calculated at 25 °C. This ambient vapor pressure for the ammonium salt of perfluorooctanoate (PFO) is 3 orders of magnitude lower than the ambient vapor pressure of the acid form, perfluorooctanoic acid (PFOA), which is approximately 4.1 Pa at 25 °C. This finding underscores the importance of knowing what compound is present in the environment and using the appropriate properties to be able to predict environmental fate and transport behavior. The enthalpy of sublimation was calculated as 90.9 kJ·mol⁻¹. It is hypothesized that APFO may undergo a multistage sublimation process.

Introduction

The solid vapor pressure of perfluorooctanoic acid (PFOA), an environmentally relevant material, is 4.1 at 25 °C, based on a recent publication.¹ Because the ammonium salt of this material, ammonium perfluorooctanoate (APFO), has been used for over 50 years in manufacturing, the potential also exists for APFO to exist in manufacturing settings and in the environment. For that reason, similar vapor pressure measurements were conducted for APFO and are reported here. The enthalpy of sublimation was also calculated.

Experimental Section

Materials. APFO (CAS Registry No. 3825-26-1) is a white solid at room temperature. APFO used in this experiment was supplied by DuPont as a 20 % aqueous solution. The aqueous solution was evaporated and the remaining solid assayed against a PFOA standard of known purity. Perfluorocarboxylic acids (C5 to C14) were determined via the LC/MS/MS method (below). The APFO purity is 102 % with perfluoropentanoic acid at 0.6 % and perfluorohexanoic acid at 0.8 %. The other perfluorocarboxylic acids were not detected (at a detection limit of 0.5 ppb). Standards were obtained from a vendor, and the purity was verified by full-scan liquid chromatography tandem mass spectrometry (LC/MS/MS). The standards used for measurement of perfluorocarboxylic acids are shown in Table 1.

Apparatus and Procedures. Vapor pressure was measured using the EPA gas saturation method.² A schematic of the apparatus is given in Figure 1. The entire experimental apparatus was set up in a ventilated enclosure. Approximately 5 g (weighed to ± 0.00001 g) of the finely ground ammonium salt was placed in a preweighed glass column (gas chromatographic inlet liner 19251-60540, Agilent, Little Falls, DE). Preweighed

Table 1. Standards Used for Measurement of Carboxylic Acids

acid	supplier	purity	CAS No.
C5	Aldrich (Milwaukee, WI)	97 %	2706-90-3
C6	Fluka (Milwaukee, WI)	97 %	307-24-4
C7	Aldrich (Milwaukee, WI)	99 %	375-85-9
C8	Oakwood (West Columbia, SC)	98.7 %	335-67-1
C9	Aldrich (Milwaukee, WI)	97 %	375-95-1
C10	Aldrich (Milwaukee, WI)	98 %	335-76-2
C11	Aldrich (Milwaukee, WI)	95 %	2058-94-8
C12	Aldrich (Milwaukee, WI)	95 %	307-55-1
C13	Aldrich (Milwaukee, WI)	97 %	72629-94-8
C14	Aldrich (Milwaukee, WI)	97 %	376-06-7

deactivated borosilicate glass wool (Restek Corporation, Bellefonte, PA) was used to contain the powder within the column. The glass column was placed in a gas chromatographic oven (HP series 6890, Agilent, Little Falls, DE). The temperature was set with the oven controls and verified by a National

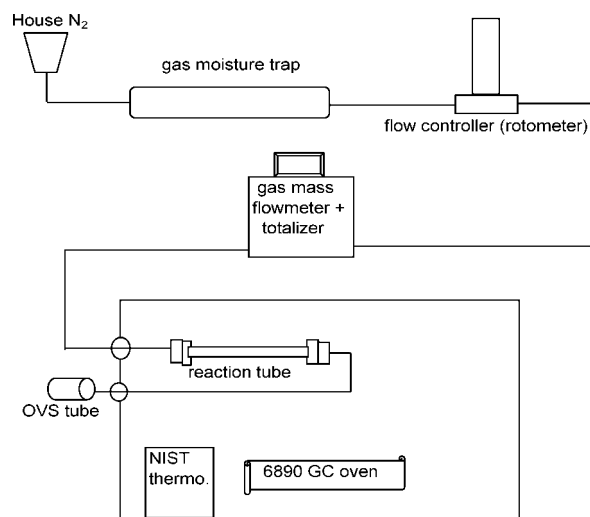


Figure 1. Schematic of gas saturation method test apparatus.

* Corresponding author. E-mail: catherine.a.barton@usa.dupont.com.

† DuPont Engineering Research and Technology.

‡ DuPont Corporate Center for Analytical Sciences.

Institute of Standards and Technology (NIST, Gaithersburg, MD)-traceable thermometer (catalog number 62344-7364, VWR International, Inc., West Chester, PA). The oven temperature was held constant within 0.4 °C. The column was connected to the nitrogen supply and the flow set at the desired flow rate. The nitrogen passed through a gas moisture trap (catalog number MT120-4-D, Agilent, Little Falls, DE), a NIST-traceable 65 mm aluminum flow controller (catalog number 32044-00, Cole-Palmer, Vernon Hills, IL), and a gas mass-flow meter with flow totalizer (catalog numbers K-32648-04 and K-32650-70, Cole-Palmer, Vernon Hills, IL). Latex tubing (6.35 mm, VWR International, Inc., West Chester, PA) connected the nitrogen source to the gas moisture trap and the gas moisture trap to the flow controller. All other connections were made with low-density polyethylene tubing (6.35 mm, Cole-Palmer, Vernon Hills, IL). Approximately 30 min was required for the flow to stabilize at the set point. The measured pressure drop across the apparatus was 14.7 Pa.

The unmodified gas saturation method calls for the transported substance to be trapped for analysis, or in-line analysis can be used. Due to difficulties in finding a sufficiently adsorbent trapping medium, this study used a modified method to quantify the mass of transported material in lieu of direct analysis. In some cases, up to 7 days was required to collect a single data point. These long time periods made it difficult to find an adsorption medium to efficiently trap the low levels of APFO.

The quantity of transported material was measured as the difference in mass of APFO in the packed column before and after the inert carrier gas flowed through the column. To determine the mass lost after the desired time interval, the nitrogen flow was stopped and the packed column disconnected. At ambient temperatures, the column was then weighed to the nearest 0.01 mg, and the loss of mass was calculated. The accuracy of the balance was verified before taking each measurement. A 5 g Class S-1 (NIST Classification) calibration mass was weighed at the same time and recorded to ensure consistency in the mass measurement. In this experiment, the temperature measurement uncertainty was ± 1 °C, and the pressure measurement uncertainty was ± 4.9 Pa.

Perfluorocarboxylic Acid Determinations. A Waters 1525EF binary pump and a Waters 2777 sample manager with a Micromass Quatro Ultima tandem mass spectrometry system was used for the perfluorocarboxylic acid determinations. A 2.1 mm \times 15 cm Zorbax SB-C₁₈ liquid chromatography column (Agilent Technologies, Little Falls, DE), 3.5 μ m particle size, was thermostatted at 60 °C. Elution was performed by making 25 μ L injections of samples and running according to the following gradient conditions:

mobile phase A: 0.15% acetic acid in water

B: 0.15% acetic acid in methanol

gradient:	time (min)	%A	%B	flow, mL/min
	0	85	15	0.5
	50	30	70	0.3
	50.01	0	100	0.3
	55	0	100	0.3
	55.01	85	15	0.3
	60	85	15	0.3

Data Reduction. The vapor pressure of APFO (P_{org}) can be computed using the following equations³

$$m_{\text{gas}} = \frac{Q_{\text{D}}}{0.0224 \left[\frac{273.15 + t_{\text{exh}}}{273.15} \right] \left[\frac{101325}{P_{\text{T}}} \right]} \quad (1)$$

$$m_{\text{org}} = W_{\text{org}}/M \quad (2)$$

$$y = m_{\text{org}}/(m_{\text{org}} + m_{\text{gas}}) \quad (3)$$

$$P_{\text{org}} = y(P_{\text{amb}} + \Delta P) = y(P_{\text{T}}) \quad (4)$$

where m_{gas} = moles of carrier gas; Q_{D} = volume of dry gas in m³; t_{exh} = exhaust temperature in degree C; P_{amb} = ambient air pressure, 101 325 Pa; m_{org} = moles of sublimed APFO; W_{org} = mass of sublimed APFO in grams; M = molar mass of APFO, 431.1 in g \cdot mol⁻¹; P_{org} = vapor pressure in Pa; y = mole fraction of test chemical in carrier gas, dimensionless; ΔP = pressure drop through the system, 14.7 Pa; and P_{T} = total pressure = ($P_{\text{amb}} + \Delta P$) in Pa.

For the modified method used in this work, the mass of APFO sublimed, W_{org} , was determined based on measured mass loss in the apparatus before and after testing at a given temperature and flow rate. Measurements were made at 1 mL \cdot min⁻¹ and 3 mL \cdot min⁻¹ and at temperatures ranging from approximately (45 to 60) °C.

The enthalpy of sublimation is the heat required to change one mole of solid into one mole of gas. The enthalpy of sublimation of APFO can be derived from the Clausius–Clapeyron equation that shows the temperature dependence of the vapor pressure¹

$$\ln(p) = \frac{-\Delta_{\text{vap}}H}{RT} + C \quad (5)$$

where p = vapor pressure; $\Delta_{\text{vap}}H$ = the enthalpy of sublimation; R = the universal gas constant, 8.314 J \cdot mol⁻¹ \cdot K⁻¹; T = absolute temperature; and C is a constant which includes the entropy of sublimation.

Using the vapor pressure measurements determined at various temperatures, the Clausius–Clapeyron equation can be solved to obtain a mean value for $\Delta_{\text{vap}}H$ within the temperature range tested.

Results and Discussion

Measured Vapor Pressure of APFO. APFO vapor pressure measurements and uncertainties are shown in Table 2. The standard errors (standard deviations normalized to the square root of n) were calculated from the scatter of the individual determinations. Reported relative standard deviations (S_r) are a measure of the repeatability or precision of the measurement equipment. The precision reported in this work (0.49 to 0.60) is within the range of precision values for the gas saturation

Table 2. Solid Vapor Pressures for APFO Measured at Three Temperatures by the Modified Gas Saturation Method

mean $t/^\circ\text{C}^a$	mean p/Pa^a	SE/ Pa^b	precision ^c
45.4	0.04	0.007	0.60
55.5	0.09	0.013	0.49
60.4	0.17	0.028	0.56

^a Mean temperatures and vapor pressures were calculated from 11 individual measurements ($n = 11$) at (45.4 and 55.5) °C and $n = 12$ for 60.4 °C. ^b SE, the standard error, is the standard deviation normalized to the square root of n . ^c Precision defines the repeatability of the test measurement within the same laboratory and with the same operator and is calculated as the relative standard deviation of each batch of samples.

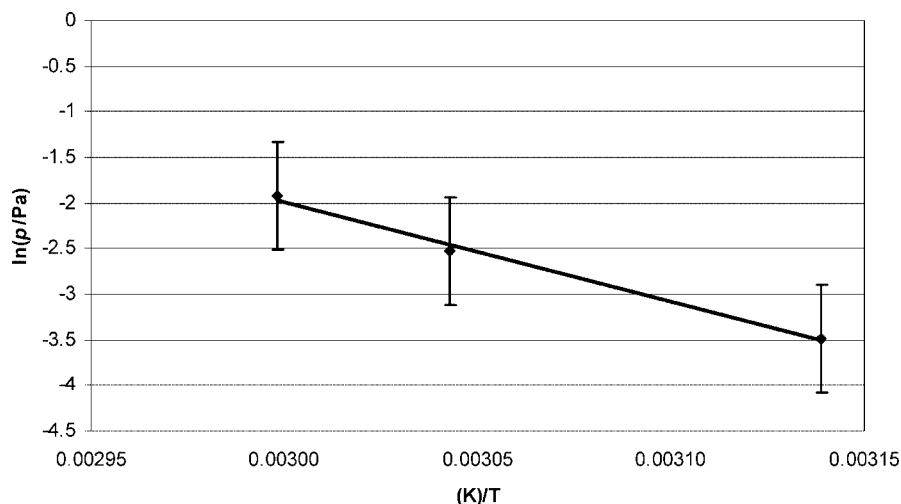


Figure 2. Clausius–Clapeyron relationship for APFO, used to derive the enthalpy of sublimation ($\Delta_{\text{vap}}H$) using eq 1. Uncertainty is represented by error bars showing the 95 % confidence intervals ($n = 11$ to 12).

method published by the American Society of Testing and Materials (ASTM), reported as 0.23 to 3.7 for materials with similar vapor pressure.³

Enthalpy of Sublimation of APFO. The enthalpy of sublimation for APFO was calculated using the Clausius–Clapeyron equation. A plot of $\ln(p)$ vs $1/T$ is shown in Figure 2, which is represented by the following equation (with $R^2 = 0.994$)

$$\ln(p/\text{Pa}) = \frac{-10936}{T} + 30.814 \quad (6)$$

The enthalpy of sublimation is calculated from the slope of eq 6, where

$$\text{slope} = -10936 = (\Delta H)(R)$$

$$\Delta H = (-10936 \cdot 8.314) = 90922 \text{ J}\cdot\text{mol}^{-1}$$

The enthalpy of sublimation is calculated from the slope of eq 6 resulting in a value of 90.9 kJ·mol⁻¹. Error bars shown in Figure 2 represent the 95 % confidence intervals of the data.

Ambient Vapor Pressure of APFO. Equation 6 was used to calculate the ambient vapor pressure of APFO at 25 °C. Ambient vapor pressure is an important property for modeling behavior of substances in the environment.⁴ The calculated vapor pressure of APFO at 25 °C is (0.003 ± 0.0005) Pa. It is notable that the ambient vapor pressure of the PFOA, the acid form of perfluorooctanoate (PFO), was reported as 5.2 Pa at 27.1 °C.¹ On the basis of the difference of approximately 3 orders of magnitude in the ambient vapor pressure of the salt and the acid forms of PFO, it is important to understand which species is present when using property information to predict and model environmental fate and transport.

Sublimation Mechanism for APFO. The sublimation mechanism for ammonium salts was recently explored by Zhu et al.⁵ using NH₄Cl as an example. The authors speculate a multistage process is involved. This multistage sublimation model can be applied to hypothesize the mechanism of sublimation for APFO. In the first step, PFO⁻NH₄⁺ molecules “relax” from the crystal structure on the solid surface. Others have referred to this phenomenon as a “drastic reorientation of the surface atoms”.⁶ The second step involves proton transfer between the NH₄⁺ and PFO⁻ species, resulting in the formation of a PFOH ←H···NH₃ complex (where PFOH is perfluorooctanoic acid, or PFOA). The same proton transfer reaction in ammonium salts has been noted by other authors.^{7,8} Through first-principles calculations, Zhu et al.

determine that the rate-limiting step in this multistage sublimation process is the second step, which in this case is the formation of the PFOH ←H···NH₃ complex. In the final step, the complex dissociates to NH₃(g) and PFOH(g). This dissociation likely takes place 10 000 times faster than the formation of the complex that occurred in the second step.

This multistage model implies that the molecular complex PFOH ←H···NH₃ desorbs from the solid surface as one compound but very quickly dissociates into the gas phase as the separate species, NH₃(g) and PFOH(g). It also implies that when perfluorooctanoate is found in the gas phase, it may well be in the neutral acid form (PFOH or PFOA).

Conclusions

The present work provides vapor pressure measurements for APFO at temperatures near ambient using a modified gas saturation method. The vapor pressure/temperature relationship is extrapolated to calculate an ambient vapor pressure, which is useful for environmental modeling. This ambient vapor pressure is approximately 3 orders of magnitude lower than the acid form, PFOA, underscoring the difference in volatility between the salt and acid forms of PFO. This work also presents a calculated enthalpy of sublimation and hypothesizes that a multistage sublimation process is occurring for APFO.

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Supporting Information Available:

Flow, temperature and calculated vapor pressure and uncertainty for individual measurements are included. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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