VAPOR PRESSURE DATA AND ANALYSIS FOR SELECTED HD DECOMPOSITION PRODUCTS: 1,4-THIOXANE, DIVINYL SULFOXIDE, CHLOROETHYL ACETYLSULFIDE, AND 1,4-DITHIANE

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14. ABSTRACT:

Recent work from our laboratory focused on the physical properties of chemical warfare agents and their surrogates, precursors, and degradation products. This report documents vapor pressure data for four sulfur-containing decomposition products from bis-(2-chloroethyl) sulfide (HD). These data were measured using an ASTM International method that is based on differential scanning calorimetry (DSC). The data presented herein were used to determine temperature–vapor pressure correlations. The fit constants were used to determine temperature-dependent thermodynamic properties and to enable interpolation and limited extrapolation of the data. The new data are compared to previous literature. In most cases, the agreement is good. In all cases, the DSC data expand the range of previously reported measurements.

15. SUBJECT TERMS

Vapor pressure	Antoine equation
Enthalpy of vaporization	Volatility
Clausius–Clapeyron equation	Entropy of vaporization
Chemical Abstracts Service (CAS)	Divinyl sulfoxide (DVSO), CAS no. 1115-15-7
1,4-Dithiane (DTH), CAS no. 505-29-3	1,4-Thioxane (THX), CAS no. 15980-15-1
Chloroethyl acetylsulfide (CEAS), CAS no. 55847-36-4	Bis-(2-chloroethyl) sulfide (HD), CAS no. 505-60-2

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PREFACE

The work described in this report was authorized under the Chemical and Biological Technology Base Program. The work was started in December 2017 and completed in May 2018. The data reported here are contained in U.S. Army Edgewood Chemical Biological Center (ECBC; Aberdeen Proving Ground, MD) notebooks 99-0095 and 06-0114.

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**VAPOR PRESSURE DATA AND ANALYSIS FOR SELECTED
HD DECOMPOSITION PRODUCTS: 1,4-THIOXANE, DIVINYL SULFOXIDE,
CHLOROETHYL ACETYLSULFIDE, AND 1,4-DITHIANE**

1.   INTRODUCTION

The U.S. Army Edgewood Chemical Biological Center (ECBC; Aberdeen Proving Ground, MD) has a long history of interest in the thermophysical properties of chemical warfare agents (CWAs) and related compounds.[1–8] Knowledge of the physical properties of materials is critical for understanding their behavior in the environment as well as in the laboratory. Vapor pressure is an important physical property for a wide variety of chemical defense related applications, including evaluation of toxicological properties, estimation of persistence, assessment of air filtration system efficiency, prediction of downwind time–concentration profiles after dissemination, and generation of controlled challenge concentrations for detector testing.

Recently, our laboratory investigated and documented the experimental vapor pressures and thermodynamic properties that were derived from these data, which included temperature correlations and temperature-dependent volatility and enthalpy of volatilization (vaporization for liquids and sublimation for solids) for selected CWA and related precursors, degradation products, and simulants.[9–20] Our most recent report focused on exploring correlations to allow extrapolation of high-temperature data to ambient temperature to facilitate the accurate prediction of vapor pressure and related properties at practical untested conditions.[21]

This report documents vapor pressure measurements, correlations, and thermodynamic properties that were derived from vapor pressure data for four organosulfur CWA degradation products that are of interest to the chemical defense community because of their structural similarity to bis-(2-chloroethyl) sulfide, which is commonly known as mustard gas or HD. The measurements were performed using differential scanning calorimetry (DSC). These four organosulfur compounds may serve as candidate testing surrogates or signature compounds for HD. The structures, full names, and Chemical Abstracts Service (CAS) registry numbers for the subject compounds are provided in Figure 1.

1,4-Dithiane (DTH)	1,4-Thioxane (THX)	Divinyl Sulfoxide (DVSO)	Chloroethyl Acetylsulfide (CEAS)
CAS No. 505-29-3	CAS No. 15980-15-1	CAS No. 1115-15-7	CAS No. 693-07-2
$C_4H_8S_2$, MW = 120.24	C_4H_8SO, MW = 104.17	C_4H_6SO, MW = 102.15	C_3H_7SCl, MW = 110.61
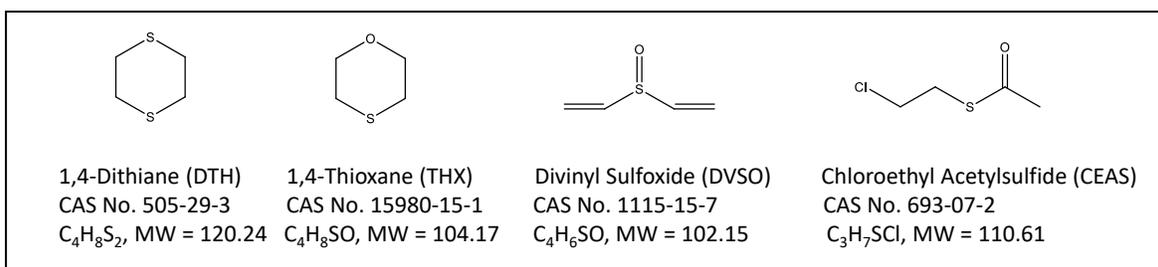
Figure 1. Structures and identification of title compounds.

2.		EXPERIMENTAL PROCEDURES

2.1		Materials and Method

The source and purity of the materials studied are listed in Table 1.

Table 1. Sample Information for Title Compounds

Compound	Purity (%)	Source
DTH	97	Aldrich
THX	98	Aldrich
DVSO	99	In-house
CEAS	99	In-house

A TA Instruments (New Castle, DE) model 910 DSC system with a 2200 controller was used for this work, and the measurements were carried out in accordance with ASTM International method E1782, *Standard Test Method for Determining Vapor Pressure by Thermal Analysis*.[22] The method and instrumentation have been described in detail in a previous publication.[12]

Other than a few distillation data points, literature vapor pressure data are not available for CEAS, DVSO, THX, and liquid DTH. Literature data measured using three complementary methods have been reported for (solid) DTH.

2.2		Data Analysis

Correlating vapor pressure data as a function of temperature to permit interpolation within the experimental range and accurate extrapolation beyond the range can be challenging due to the number of equations that are available for this purpose, inadequately documented experimental work, poor data quality, or limited experimental range. High-quality vapor pressure data that are measured over a wide range typically exhibit negative curvature on a standard vapor pressure (P) plot (ln P vs reciprocal temperature), which corresponds to a decreasing enthalpy of vaporization with increasing temperature. The commonly used Clausius–Clapeyron correlation, eq 1, has no curvature due to the assumption of a constant enthalpy of vaporization with temperature and is usually used to correlate data over narrow temperature ranges for subsequent limited extrapolations. An Antoine fit, eq 2, can accommodate curvature of the data but depending on range and quality, may exhibit thermodynamically prohibited positive curvature rather than the expected negative curvature that is characteristic of high-quality data. However, an Antoine fit may also produce excessive negative curvature depending on data quality and range. As a result, correlations can improperly estimate vapor pressure at untested conditions outside the experimental temperature range.

$$\ln(P) = a - b/T \tag{1}$$

$$\ln(P) = a - b/(c + T) \tag{2}$$

where P is vapor pressure in pascal; T is absolute temperature in kelvin; and a, b, and c are fit constants.

Equation 3 gives the Antoine equation in another common units system (Torr-°C), which is currently deemed obsolete by most journals.

$$\log(p) = A - B/(C + t) \tag{3}$$

where p is pressure in Torr; t is temperature in Celsius; and A, B, and C are fit constants.

Conversion of the constants from eq 2 to eq 3 may be accomplished using the substitutions provided in eqs 4–6.[13,21]

$$A = [a - \ln(101325/760)]/\ln(10) \tag{4}$$

$$B = b/\ln(10) \tag{5}$$

$$C = c + 273.15 \tag{6}$$

The a and b constants are divided by $\ln(10)$ to convert from natural log to log base 10, and the a constant requires the $\ln(101325/760)$ term to account for the different pressure units.

A 2016 publication by Brozena et al. describes methodology to correlate vapor pressure data using the Antoine equation, which is optimized using a least-squares method.[23] This method also applies to the Clausius–Clapeyron equation, where the c constant is assigned a value of 0.

The ability to accurately predict vapor pressure at ambient temperatures is of particular concern when only high-temperature data are available. While correlating vapor pressure data with the Antoine equation, Thomson found that, "In many cases which have been studied C lies between 220 and 240 [$c = -53$ to -33 for pascal units]" and suggested using $C = 230$ ($c = -43$) as a "good average value" for correlation of vapor pressure data "for organic compounds which are liquid at room temperature".[24] Our data for more than 25 compounds that were measured using complementary methods are consistent with Thomson's observation. We recently demonstrated that using the suggested c constant produces more accurate predictions of ambient temperature vapor pressure than does extrapolating high-temperature data using an unconstrained Antoine equation.[21] As a result, we have adopted Thomson's recommendation by constraining the Antoine equation c constant to -43 in this report for compounds lacking data in the ambient temperature range. The recommended equations are given in two common units systems (Torr-°C and Pa-K).

The literature data for the title compounds are primarily reduced-pressure boiling points, which we have typically found to be unreliable, especially at pressures below 500 Pa. These values are included in the figures but were not used to determine the temperature–pressure correlations.

Several thermodynamic properties can be calculated from the vapor pressure correlation. The enthalpy of vaporization, ΔH_{vap} (J/mol), is calculated as shown in eq 7.

$$\Delta H_{vap} = b \times R \times [T/(c + T)]^2 \tag{7}$$

where b and c are eq 2 coefficients, and R is the gas constant (8.3144 J/mol K).

The saturation concentration, C_{sat} (mg/m^3), which is often referred to as volatility, is calculated as a function of temperature according to eq 8.

$$C_{sat} = P \times MW/R \times T \tag{8}$$

where MW is molecular weight and R is 8.3144 Pa m^3/mol K.

The entropy of vaporization, ΔS_{vap} (J/mol K), is calculated according to eq 9 by dividing the enthalpy of vaporization at the normal boiling point (NBPt) by the NBPt. Trouton's rule states that ΔS_{vap} should be near 21 cal/mol K (88 J/mol K).

$$\Delta S_{vap} = \Delta H_{vap}/NBPt \tag{9}$$

3.   RESULTS

The experimental data, pressure–temperature correlations, comparisons to literature data, and calculated properties for each of the title compounds are provided in the sections that follow.

3.1   THX

The 16 data points measured for THX using DSC at 28.80 to 149.60 °C are listed in Table 2. The measurements covered a wide pressure range including atmospheric pressure. The boiling endotherms were sharp with no indication of specimen degradation. Initial analysis of the DSC data with an unconstrained Antoine equation resulted in a large negative c constant that is characteristic of excessive negative curvature.[21] As a result, the DSC data were correlated using an Antoine equation with the c constant constrained to –43 in accordance with Thomson's recommendation.[24] The resulting Antoine equation is given in Table 2, along with the experimental data, the calculated values, and the percent difference at each experimental temperature. The current experimental data, the Antoine correlation, and the literature data, which include NBPts[25–27] and reduced-pressure boiling points at 67 °C (44 Torr)[28] and 51 °C (25 Torr),[29] are shown in Figure 2. The unconstrained Antoine fit with greater curvature is also shown for comparison. Calculated values for THX vapor pressure, volatility, and enthalpy of

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vaporization at selected temperatures are provided in Table 3. The calculated NBPt for THX is 147.52 °C. The entropy of vaporization, 98.1 J/mol K, which was calculated on the basis of the DSC data, is higher than the value that was expected on the basis of Trouton's rule.

Table 2. Experimental Vapor Pressure Data and Comparison to Calculated Values for THX

Temperature (°C)	Experimental Vapor Pressure (Torr)	(Pa)*	Calculated Vapor Pressure (Torr)	(Pa)	Difference[†] (%)
28.78	5.10×10^0	6.799×10^2	5.911×10^0	7.881×10^2	−13.73
32.63	7.00×10^0	9.333×10^2	7.412×10^0	9.882×10^2	−5.56
36.25	9.00×10^0	1.200×10^3	9.115×10^0	1.215×10^3	−1.23
39.59	1.10×10^1	1.467×10^3	1.098×10^1	1.464×10^3	0.20
42.03	1.30×10^1	1.733×10^3	1.254×10^1	1.672×10^3	3.65
44.69	1.50×10^1	2.000×10^3	1.445×10^1	1.927×10^3	3.79
46.86	1.69×10^1	2.253×10^3	1.620×10^1	2.160×10^3	4.31
52.40	2.22×10^1	2.960×10^3	2.150×10^1	2.866×10^3	3.28
58.03	2.96×10^1	3.946×10^3	2.835×10^1	3.780×10^3	4.39
64.19	3.92×10^1	5.226×10^3	3.790×10^1	5.053×10^3	3.42
73.04	5.85×10^1	7.799×10^3	5.636×10^1	7.514×10^3	3.79
86.05	9.84×10^1	1.312×10^4	9.698×10^1	1.293×10^4	1.47
95.83	1.497×10^2	1.996×10^4	1.417×10^2	1.890×10^4	5.61
117.92	3.051×10^2	4.068×10^4	3.088×10^2	4.117×10^4	−1.19
149.09	7.575×10^2	1.010×10^5	7.940×10^2	1.059×10^5	−4.58
149.64	7.618×10^2	1.016×10^5	8.062×10^2	1.075×10^5	−5.47
$\log(p) = 7.479973 - 1736.984 /(t + 230.15)$ $\ln(P) = 22.11604 - 3999.554/(T - 43.000)$					

*Calculated from Torr values.

[†]$100 \times (P_{exptl} - P_{calc})/P_{calc}$, where P_{exptl} is experimental vapor pressure, and P_{calc} is calculated vapor pressure.
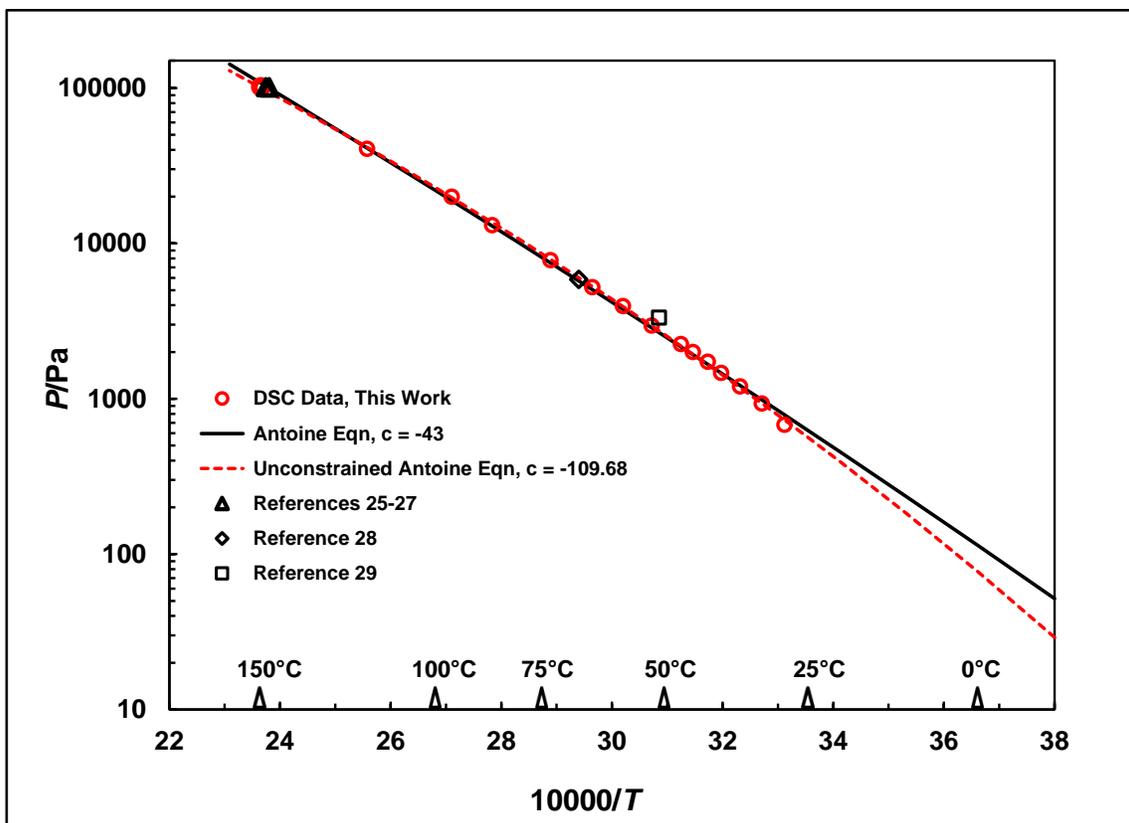
Figure 2. Vapor pressure data and Antoine equation correlations for THX.

Table 3. Calculated Vapor Pressure, Volatility, and Enthalpy of Vaporization for THX at Selected Temperatures

Temperature	Vapor Pressure		Volatility	ΔH_{vap}
(ºC)	(Torr)	(Pa)	(mg/m^3)	(kJ/mol)
–20*	1.639×10^{-1}	2.185×10^1	1.081×10^3	48.26
–10*	3.890×10^{-1}	5.186×10^1	2.469×10^3	47.51
0*	8.566×10^{-1}	1.142×10^2	5.238×10^3	46.84
10*	1.766×10^0	2.355×10^2	1.042×10^4	46.23
20*	3.437×10^0	4.583×10^2	1.959×10^4	45.67
25*	4.702×10^0	6.269×10^2	2.634×10^4	45.41
30	6.355×10^0	8.473×10^2	3.502×10^4	45.16
40	1.123×10^1	1.497×10^3	5.989×10^4	44.68
50	1.904×10^1	2.539×10^3	9.844×10^4	44.25
60	3.115×10^1	4.153×10^3	1.562×10^5	43.84
80	7.577×10^1	1.010×10^4	3.584×10^5	43.11
100	1.655×10^2	2.206×10^4	7.408×10^5	42.48
120	3.306×10^2	4.408×10^4	1.405×10^6	41.92
140	6.128×10^2	8.170×10^4	2.478×10^6	41.43
147.52	7.600×10^2	1.013×10^5	3.018×10^6	41.26

*Extrapolated.

3.2   DVSO

Twelve data points were measured for DVSO by DSC in this work at 65.25 to 192.65 °C. The boiling endotherms were sharp, and no evidence of degradation was detected up to atmospheric pressure. Initial analysis of the DSC data with an unconstrained Antoine equation resulted in a large negative c constant that is characteristic of excessive negative curvature. As a result, the DSC data were correlated using an Antoine equation with the c constant constrained to –43, as recommended by Thomson. These data are listed in Table 4 and illustrated in Figure 3 with nine literature data points: 18 Torr at 86–87 °C,[30] 16 Torr at 81 °C,[31] 8 Torr at 72–74 °C,[32] 1 Torr at 42 °C,[33] 1 Torr at 46 °C,[34] and 3.5 Torr at 58–59 °C, 5–6 Torr at 67–68 °C, 16 Torr at 81 °C, and 13 Torr at 70 °C.[35] The constrained and unconstrained Antoine equations are shown in Figure 3, along with the literature and DSC data. Calculated values for vapor pressure, volatility, and enthalpy of vaporization at selected temperatures are provided in Table 5. The calculated NBPt for DVSO is 191.09 °C. The entropy of vaporization, 99.8 J/mol K, which was calculated on the basis of the DSC data, is higher than the value that was expected on the basis of Trouton's rule.

Table 4. Experimental Vapor Pressure Data and Comparison to Calculated Values for DVSO

Temperature (°C)	Experimental Vapor Pressure		Calculated Vapor Pressure		Difference[†] (%)
	(Torr)	(Pa)*	(Torr)	(Pa)	
65.25	7.30×10^0	9.733×10^2	7.350×10^0	9.799×10^2	–0.67
69.22	8.40×10^0	1.120×10^3	9.031×10^0	1.204×10^3	–6.98
72.37	1.030×10^1	1.373×10^3	1.059×10^1	1.412×10^3	–2.76
80.03	1.620×10^1	2.160×10^3	1.540×10^1	2.054×10^3	5.16
88.83	2.340×10^1	3.120×10^3	2.316×10^1	3.088×10^3	1.04
97.17	3.420×10^1	4.560×10^3	3.341×10^1	4.455×10^3	2.36
106.43	5.020×10^1	6.693×10^3	4.913×10^1	6.550×10^3	2.18
117.68	8.030×10^1	1.071×10^4	7.634×10^1	1.018×10^4	5.21
132.10	1.285×10^2	1.713×10^4	1.290×10^2	1.720×10^4	–0.41
145.27	2.000×10^2	2.666×10^4	2.012×10^2	2.683×10^4	–0.63
157.78	3.002×10^2	4.002×10^4	2.984×10^2	3.978×10^4	0.60
192.65	7.566×10^2	1.009×10^5	7.912×10^2	1.055×10^5	–4.34
$\log(p) = 7.609767 - 1992.024/(t + 230.15)$ $\ln(P) = 22.41491 - 4586.804(T - 43.0000)$					

*Calculated from Torr value.
[†]$100 \times (P_{exptl} - P_{calc})/P_{calc}$, where P_{exptl} is experimental vapor pressure, and P_{calc} is calculated vapor pressure.
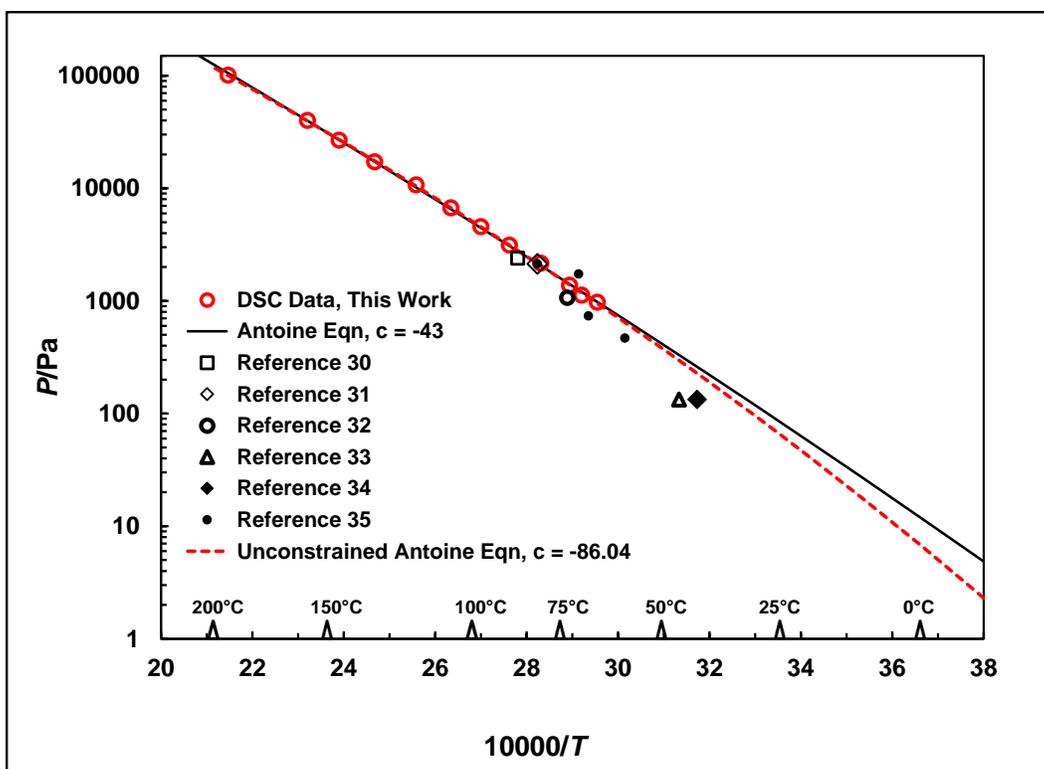
Figure 3. Vapor pressure data and Antoine equation correlations for DVSO.

Table 5. Calculated Vapor Pressure, Volatility, and Enthalpy of Vaporization for DVSO at Selected Temperatures

Temperature	Vapor Pressure		Volatility	ΔH_{vap}
(°C)	(Torr)	(Pa)	(mg/m³)	(kJ/mol)
–20*	1.351×10^{-2}	1.801×10^{0}	8.743×10^{1}	55.34
–10*	3.642×10^{-2}	4.855×10^{0}	2.267×10^{2}	54.49
0*	9.004×10^{-2}	1.200×10^{1}	5.400×10^{2}	53.72
10*	2.065×10^{-1}	2.753×10^{1}	1.194×10^{3}	53.02
20*	4.430×10^{-1}	5.907×10^{1}	2.476×10^{3}	52.37
25*	6.346×10^{-1}	8.461×10^{1}	3.487×10^{3}	52.07
30*	8.965×10^{-1}	1.195×10^{2}	4.844×10^{3}	51.79
40*	1.722×10^{0}	2.296×10^{2}	9.007×10^{3}	51.24
50*	3.157×10^{0}	4.208×10^{2}	1.600×10^{4}	50.74
60*	5.550×10^{0}	7.399×10^{2}	2.729×10^{4}	50.28
80	1.538×10^{1}	2.051×10^{3}	7.134×10^{4}	49.44
100	3.768×10^{1}	5.023×10^{3}	1.654×10^{5}	48.72
120	8.331×10^{1}	1.111×10^{4}	3.471×10^{5}	48.08
140	1.691×10^{2}	2.254×10^{4}	6.704×10^{5}	47.51
160	3.191×10^{2}	4.255×10^{4}	1.207×10^{6}	47.01
180	5.662×10^{2}	7.548×10^{4}	2.047×10^{6}	46.55
191.09	7.600×10^{2}	1.013×10^{5}	2.682×10^{6}	46.32

*Extrapolated.

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3.3 CEAS

The data in this report for CEAS consist of nine points measured by DSC at 42.86 to 181.00 ºC. The boiling endotherms were sharp over the range studied, and no indication of decomposition was observed. Preliminary analysis of the DSC data produced an Antoine equation with a large negative c constant that is characteristic of excessive negative curvature. Accordingly, the Antoine c constant was constrained to –43, as recommended by Thomson. These data are listed in Table 6, along with the recommended Antoine equation. The data are plotted in Figure 4, along with the following four literature data points: 17 Torr at 76–76.5 °C,[36] 7.5 Torr at 62 °C and 4 Torr at 54 °C,[37] and 4 Torr at 51 °C.[38] Both the constrained and unconstrained Antoine correlations are also shown in Figure 4. Calculated values for vapor pressure, volatility, and enthalpy of vaporization at selected temperatures are provided in Table 7. The calculated NBPt for CEAS is 179.12 °C. The entropy of vaporization of CEAS, 102.1 J/mol K, which was calculated on the basis of the DSC data, is higher than the value that was expected on the basis of Trouton's rule.

Table 6. Experimental Vapor Pressure Data and Comparison to Calculated Values for CEAS

Temperature (°C)	Experimental Vapor Pressure		Calculated Vapor Pressure		Difference[†] (%)
	(Torr)	(Pa)*	(Torr)	(Pa)	
42.86	2.70×10^0	3.600×10^2	2.966×10^0	3.955×10^2	–8.98
49.94	4.60×10^0	6.133×10^2	4.520×10^0	6.026×10^2	1.78
63.06	9.80×10^0	1.307×10^3	9.346×10^0	1.246×10^3	4.90
73.17	1.60×10^1	2.133×10^3	1.567×10^1	2.090×10^3	2.11
87.26	3.06×10^1	4.080×10^3	3.049×10^1	4.065×10^3	0.37
105.65	6.90×10^1	9.199×10^3	6.682×10^1	8.909×10^3	3.26
119.24	1.157×10^2	1.543×10^4	1.132×10^2	1.509×10^4	2.25
141.75	2.506×10^2	3.341×10^4	2.488×10^2	3.317×10^4	0.72
181.00	7.555×10^2	1.007×10^5	7.995×10^2	1.066×10^5	–5.53
$\log(p) = 7.706491 - 1975.025/(t + 230.15)$ $\ln(P) = 22.63762 - 4547.664/(T - 43.000)$					

*Calculated from Torr value.

[†]$100 \times (P_{exptl} - P_{calc})/P_{calc}$, where P_{exptl} is experimental vapor pressure, and P_{calc} is calculated vapor pressure.
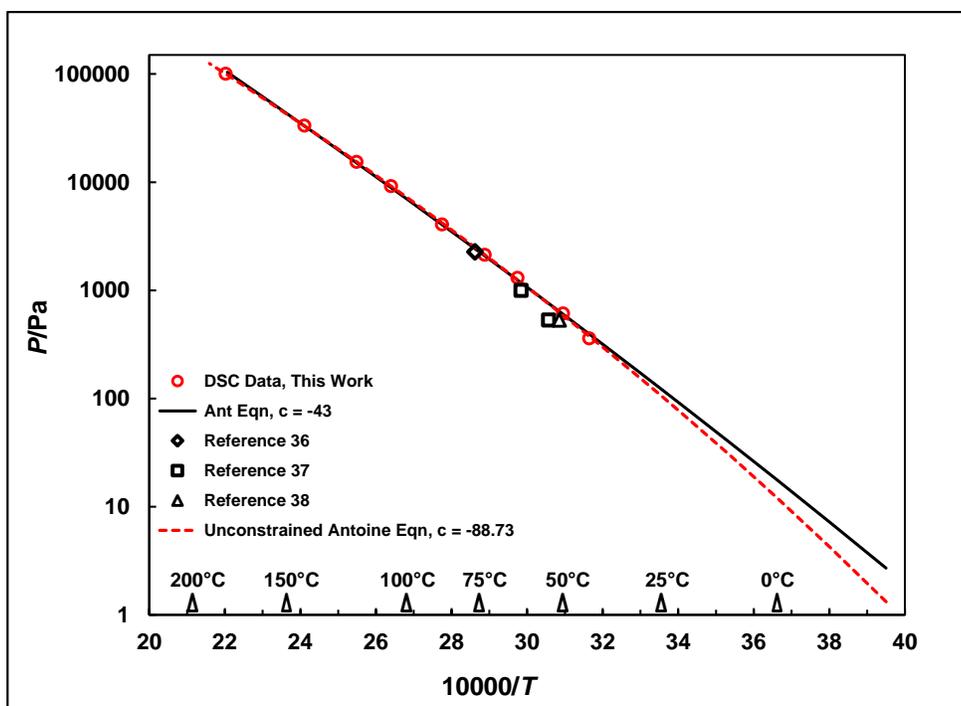
Figure 4. Vapor pressure data and Antoine equation correlations for CEAS.

Table 7. Calculated Vapor Pressure, Volatility, and Enthalpy of Vaporization
for CEAS at Selected Temperatures

Temperature	Vapor Pressure		Volatility	ΔH_{vap}
(°C)	(Torr)	(Pa)	(mg/m³)	(kJ/mol)
−20*	2.034×10^{-2}	2.712×10^{0}	1.786×10^{2}	54.87
−10*	5.435×10^{-2}	7.246×10^{0}	4.591×10^{2}	54.02
0*	1.334×10^{-1}	1.778×10^{1}	1.085×10^{3}	53.26
10*	3.036×10^{-1}	4.048×10^{1}	2.384×10^{3}	52.56
20*	6.473×10^{-1}	8.630×10^{1}	4.908×10^{3}	51.93
25*	9.244×10^{-1}	1.232×10^{2}	6.891×10^{3}	51.63
30*	1.302×10^{0}	1.736×10^{2}	9.546×10^{3}	51.34
40*	2.487×10^{0}	3.315×10^{2}	1.765×10^{4}	50.81
50	4.535×10^{0}	6.047×10^{2}	3.120×10^{4}	50.31
60	7.936×10^{0}	1.058×10^{3}	5.294×10^{4}	49.85
70	1.338×10^{1}	1.784×10^{3}	8.665×10^{4}	49.42
80	2.180×10^{1}	2.907×10^{3}	1.372×10^{5}	49.02
100	5.300×10^{1}	7.066×10^{3}	3.157×10^{5}	48.30
120	1.164×10^{2}	1.552×10^{4}	6.581×10^{5}	47.67
140	2.348×10^{2}	3.131×10^{4}	1.263×10^{6}	47.11
160	4.408×10^{2}	5.877×10^{4}	2.262×10^{6}	46.61
179.12	7.600×10^{2}	1.013×10^{5}	3.735×10^{6}	46.17

*Extrapolated

3.4   DTH

The vapor pressure of solid DTH (melting range of 111–112 °C)[39] was originally reported by DeWit et al.[40] as smoothed values over a range of subambient temperatures. More recently, an Antoine equation was published by Williams et al.[20] that was based on those values and on data measured at ECBC using DSC and vapor saturation. The c constant for the published unconstrained Antoine fit is a small positive number, which indicates the inappropriate positive curvature of the vapor pressure correlation that would correspond to a thermodynamically prohibited increase in enthalpy of sublimation (ΔH_{sub}) with increasing temperature. The correlation is better expressed as a Clausius–Clapeyron equation ($c = 0$) to eliminate the positive curvature and, as a result, we refitted the solid-phase vapor pressure values from the earlier publications. The earlier experimental and new calculated values are listed in Table 8, along with the percent differences. The differences between the values calculated on the basis of Williams' Antoine equation and our new Clausius–Clapeyron correlation are negligible in comparison with the experimental uncertainty of the measurements.

Table 8. Experimental Vapor Pressure Data and Comparison to Calculated Values
for Solid-Phase DTH

Temperature (°C)	Experimental Vapor Pressure		Calculated Vapor Pressure		Difference[*] (%)
	(Torr)	(Pa)	(Torr)	(Pa)	
De Wit et al., Reference 40			New Correlation		
−16.2	7.50×10^{-4}	1.0×10^{-1}	7.560×10^{-4}	1.008×10^{-1}	−0.79
−10.83	1.50×10^{-3}	2.0×10^{-1}	1.506×10^{-3}	2.008×10^{-1}	−0.40
−7.59	2.25×10^{-3}	3.0×10^{-1}	2.253×10^{-3}	3.003×10^{-1}	−0.10
−5.24	3.00×10^{-3}	4.0×10^{-1}	2.998×10^{-3}	3.997×10^{-1}	0.08
−3.39	3.75×10^{-3}	5.0×10^{-1}	3.741×10^{-3}	4.988×10^{-1}	0.24
−1.86	4.50×10^{-3}	6.0×10^{-1}	4.483×10^{-3}	5.977×10^{-1}	0.38
−0.55	5.25×10^{-3}	7.0×10^{-1}	5.226×10^{-3}	6.967×10^{-1}	0.47
0.60	6.00×10^{-3}	8.0×10^{-1}	5.971×10^{-3}	7.961×10^{-1}	0.49
1.62	6.75×10^{-3}	9.0×10^{-1}	6.715×10^{-3}	8.953×10^{-1}	0.52
2.53	7.50×10^{-3}	1.0×10^{0}	7.450×10^{-3}	9.933×10^{-1}	0.67
Williams et al., Reference 20			New Correlation		
23.5	6.89×10^{-2}	9.18×10^{0}	6.852×10^{-2}	9.135×10^{0}	0.49
82.55	8.00×10^{0}	1.067×10^{3}	8.688×10^{0}	1.158×10^{3}	−7.88
86.26	1.00×10^{1}	1.333×10^{3}	1.117×10^{1}	1.489×10^{3}	−10.47
89.23	1.42×10^{1}	1.893×10^{3}	1.360×10^{1}	1.814×10^{3}	4.38
94.19	1.99×10^{1}	2.653×10^{3}	1.878×10^{1}	2.504×10^{3}	5.97
97.50	2.435×10^{1}	3.246×10^{3}	2.318×10^{1}	3.090×10^{3}	5.06
100.87	2.870×10^{1}	3.826×10^{3}	2.860×10^{1}	3.813×10^{3}	0.34
101.13	2.930×10^{1}	3.906×10^{3}	2.907×10^{1}	3.875×10^{3}	0.80
103.84	3.470×10^{1}	4.626×10^{3}	3.432×10^{1}	4.576×10^{3}	1.10
$\log(p) = 11.50414 - 3758.056/(t + 273.15)$ $\ln(P) = 31.38203 - 8653.244/T$					

[*]$100 \times (P_{exptl} - P_{calc})/P_{calc}$, where P_{exptl} is experimental vapor pressure, and P_{calc} is calculated vapor pressure.

The new DTH vapor pressure data presented in this report are for the liquid phase. Nine sharp boiling endotherms have been measured at 124.3 to 199.8 °C by DSC at pressures up to atmospheric with no indication of degradation. Thomson's recommendation does not apply in this case because DTH is solid at ambient temperature. Thus, the Antoine equation correlation was not constrained. The resulting Antoine equation, new experimental data, calculated values, and percent differences between them are listed in Table 9.

The liquid- and solid-phase data are plotted in Figure 5, along with additional literature values from Chang[41] (140–150 °C at 28 Torr) and Yur'ev (95–115 °C at 50 Torr).[42] The change in the slope in Figure 5 corresponds to the melting temperature of DTH, which was determined to be 109.28 °C by locating the intersection point of the liquid- and solid-phase correlation equations. As expected, this value is close to the reported melting range and confirms the internal consistency of both data sets. Yur'ev's value is consistent with our data, but Chang's is significantly different from that predicted by our correlation. The reason for the difference is unknown.

Table 9. Experimental Vapor Pressure Data and Comparison to Calculated Values for Liquid-Phase DTH

Temperature (°C)	Experimental Vapor Pressure		Calculated Vapor Pressure		Difference[†] (%)
	(Torr)	(Pa)*	(Torr)	(Pa)	
124.25	8.360×10^1	1.115×10^4	8.337×10^1	1.112×10^4	0.36
129.57	1.000×10^2	1.333×10^4	1.006×10^2	1.341×10^4	–0.60
136.77	1.289×10^2	1.719×10^4	1.285×10^2	1.713×10^4	0.35
145.40	1.702×10^2	2.269×10^4	1.702×10^2	2.269×10^4	0.00
150.62	2.003×10^2	2.670×10^4	2.004×10^2	2.671×10^4	–0.04
158.01	2.501×10^2	3.334×10^4	2.506×10^2	3.340×10^4	–0.18
164.21	3.020×10^2	4.026×10^4	3.002×10^2	4.003×10^4	0.57
168.90	3.414×10^2	4.552×10^4	3.429×10^2	4.572×10^4	–0.44
199.84	7.647×10^2	1.020×10^5	7.645×10^2	1.019×10^5	0.10
$\log(p) = 7.215290 - 1801.325/(t + 215.9890)$ $\ln(P) = 21.50659 - 4147.704/(T - 57.16102)$					

*Converted from Torr value.
[†]$100 \times (P_{exptl} - P_{calc})/P_{calc}$, where P_{exptl} is experimental vapor pressure, and P_{calc} is calculated vapor pressure.
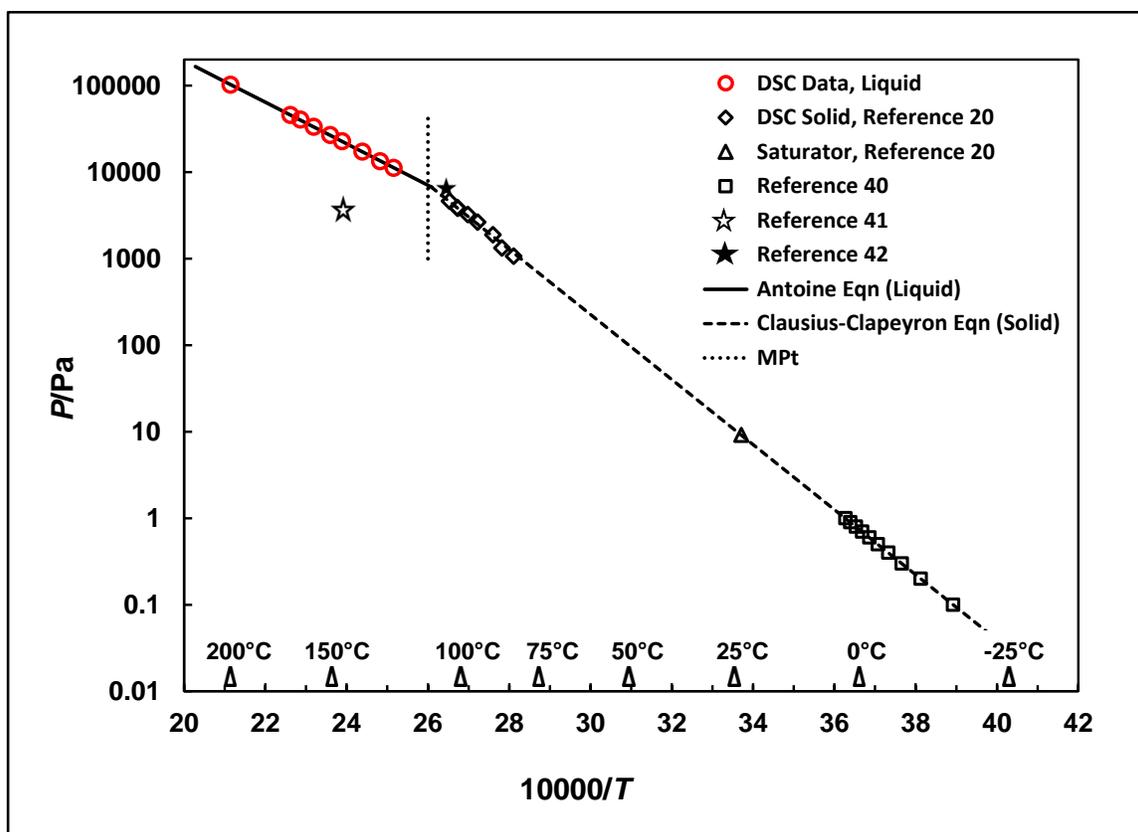
Figure 5. Vapor pressure data and correlations for DTH.

Table 10 provides a list of calculated vapor pressure, volatility, and enthalpy of volatilization (i.e., vaporization for liquid and sublimation for solid) values for both solid and liquid DTH at selected temperatures. Because the solid data are represented by a Clausius–Clapeyron fit, the enthalpy of sublimation is constant over the temperature range. The calculated NBPt for DTH is 199.59 °C. The enthalpy of fusion for DTH is 24.28 kJ/mol, which was determined by calculating the difference in enthalpies of vaporization for liquid DTH and sublimation for solid DTH at the melting temperature. The entropy of vaporization for DTH is 94.4 J/mol K, which was calculated on the basis of the liquid-phase DSC data and is slightly higher than the value expected on the basis of Trouton's rule.

Table 10. Calculated Vapor Pressure, Volatility, and Enthalpy of Volatilization for Liquid- and Solid-Phase DTH at Selected Temperatures

Temperature (°C)	Vapor Pressure		Volatility (mg/m³)	Enthalpy of Volatilization (kJ/mol)
	(Torr)	(Pa)		
Solid-Phase DTH				ΔH_{sub}
–20*	4.560×10^{-4}	6.079×10^{-2}	3.473×10^{0}	
–10	1.672×10^{-3}	2.228×10^{-1}	1.225×10^{1}	
0	5.571×10^{-3}	7.427×10^{-1}	3.932×10^{1}	
10	1.705×10^{-2}	2.274×10^{0}	1.161×10^{2}	
20	4.837×10^{-2}	6.449×10^{0}	3.181×10^{2}	
25	7.935×10^{-2}	1.058×10^{1}	5.131×10^{2}	
30	1.281×10^{-1}	1.707×10^{1}	8.144×10^{2}	71.95
40	3.187×10^{-1}	4.248×10^{1}	1.962×10^{3}	
50	7.494×10^{-1}	9.991×10^{1}	4.470×10^{3}	
60	1.674×10^{0}	2.232×10^{2}	9.686×10^{3}	
80	7.288×10^{0}	9.717×10^{2}	3.979×10^{4}	
100	2.710×10^{1}	3.613×10^{3}	1.400×10^{5}	
109.28	4.756×10^{1}	6.341×10^{3}	2.398×10^{5}	
Liquid-Phase DTH				ΔH_{vap}
109.28	4.757×10^{1}	6.341×10^{3}	2.398×10^{5}	47.67
120	7.145×10^{1}	9.526×10^{3}	3.504×10^{5}	47.22
140	1.430×10^{2}	1.906×10^{4}	6.672×10^{5}	46.45
160	2.657×10^{2}	3.542×10^{4}	1.183×10^{6}	45.77
180	4.642×10^{2}	6.184×10^{4}	1.973×10^{6}	45.16
199.59	7.600×10^{2}	1.013×10^{5}	3.100×10^{6}	44.63

*Extrapolated

4. DISCUSSION

It is desirable to have vapor pressure data generated using complementary methods over a wide range; however, that is not always possible for a number of reasons, including sample instability, thermal degradation, and phase change within the experimental range. The literature data for solid-phase DTH provide a good example of the benefit resulting from the availability of complementary methods over a wide experimental range. Although the new data in this report for THX, DVSO, and CEAS are limited to those obtained using DSC only, the measurements for each compound covered a wide range of pressures (up to atmospheric), and each data set is internally consistent. DSC data for liquid-phase DTH covers a limited range due to its high melting point.

Because of the absence of reliable data in the ambient temperature range, correlations of the new DSC data for THX, DVSO, and CEAS were calculated using a constrained 3-parameter Antoine equation with Thomson's suggested *c* constant of –43. Even though the extrapolation to ambient temperature is relatively short for THX, the vapor pressure calculated at 0 °C, based on the constrained Antoine equation (114.2 Pa), is about 50% higher

than the value calculated using the unconstrained equation (77.30 Pa). The constrained Antoine equation for DVSO results in an extrapolated value (12.00 Pa) that is nearly twice that of the unconstrained Antoine equation (6.84 Pa) at 0 °C. The constrained Antoine equation for CEAS produces a value (17.78 Pa) that is about 40% higher than that of the unconstrained Antoine equation (12.15 Pa) at 0 °C. These differences demonstrate the challenge that is attendant to the extrapolation of vapor pressure data. Extrapolation beyond the experimental range should always be done with caution, but we feel Thomson's approach is preferred, when appropriate, over either a Clausius–Clapeyron or unconstrained Antoine fit for predicting vapor pressure at untested conditions.

Trouton's rule states that the ΔS_{vap} for many compounds is near 21 cal/mol K (88 J/mol K). Notable exceptions include hydrogen-bonded species such as water and organic alcohols and acids, which have ΔS_{vap} values greater than 90 J/mol K. Entropy of vaporization values calculated from our data (Table 11) tend to be higher than those anticipated on the basis of Trouton's rule. We calculated ΔS_{vap} values for 700 compounds by calculating NBPts and heats of vaporization at the boiling points from the Antoine constants given in Yaws and Yang's compilation[43] using eqs 2, 7, and 9 herein. The entropies of vaporization, as a function of boiling point, which were calculated from our data and Yaws and Yang's compilation, are shown in Figure 6. Our analysis indicates that positive deviations from Trouton's rule are more common than are negative deviations. A clear trend to higher entropies of vaporization as NBPt and molecular weight increased was observed. It is possible that other properties, such as compound polarity and polarizability, may correlate with deviations from Trouton's rule. This appears to be a promising area for future investigation.

Table 11. Entropies of Vaporization Calculated from Antoine Equation Constants for Selected Compounds Studied at ECBC

Compound	ΔS_{vap}	Literature Reference
THX	98.10	This work
DVSO	99.80	
CEAS	102.10	
DTH	99.80	
Dicyclohexyl methylphosphonate (DCMP)	113.63	19
Diisobutyl methylphosphonate (DIBMP)	106.73	
Isopropyl methyl methylphosphonate (IMMP)	108.14	
Cyclohexyl methyl methylphosphonate (CMMP)	103.66	21
Dipinacolyl methylphosphonate (DPMP)	101.71	
Dimethyl ethylphosphonate (DMEP)	107.47	
Diethyl ethylphosphonate (DEEP)	94.51	
Cyclohexyl methylphosphonofluoridate (GF)	102.35	13
O-Ethyl-*S*-[2(diisopropylamino) ethyl] methylphosphonothiolate (VX)	113.51	15
O-Isobutyl-*S*-[2(diethylamino) ethyl] methylphosphonothiolate (RVX)	116.15	
Tri-*n*-propyl phosphate (TPPO)	108.79	16
Triethyl phosphate (TEPO)	110.82	
Diethyl malonate (DEM)	109.14	
Thiodiglycol (TDG)*	121.53	18
2-Dimethyl aminoethanethiol (DMA)	89.10	10
2-Diethyl aminoethanethiol (DEA)	89.12	
2-Diisopropyl aminoethanethiol (DIA)	96.30	
Dimethyl phosphonate (DMHP)	100.53	12
Dimethyl methylphosphonate (DMMP)	101.37	
Diethyl methylphosphonate (DEMP)	102.93	
Diisopropyl methylphosphonate (DIMP)	108.25	
2,2-Dimethylcyclopentanol (DMCP)*	113.14	44
2,2-Dimethylcyclopentyl methylphosphonofluoridate (GP)	104.29	
N,*N*′-Diisopropylcarbodiimide (DICDI)	93.82	9
2-Chloroethyl-3-chloropropyl sulfide (CECPRS)	109.76	14
Bis-(2-chloroethyl) sulfide (HD)	102.21	45

*Hydrogen-bonded compounds generally have entropies of vaporization higher than those predicted by Trouton's rule.
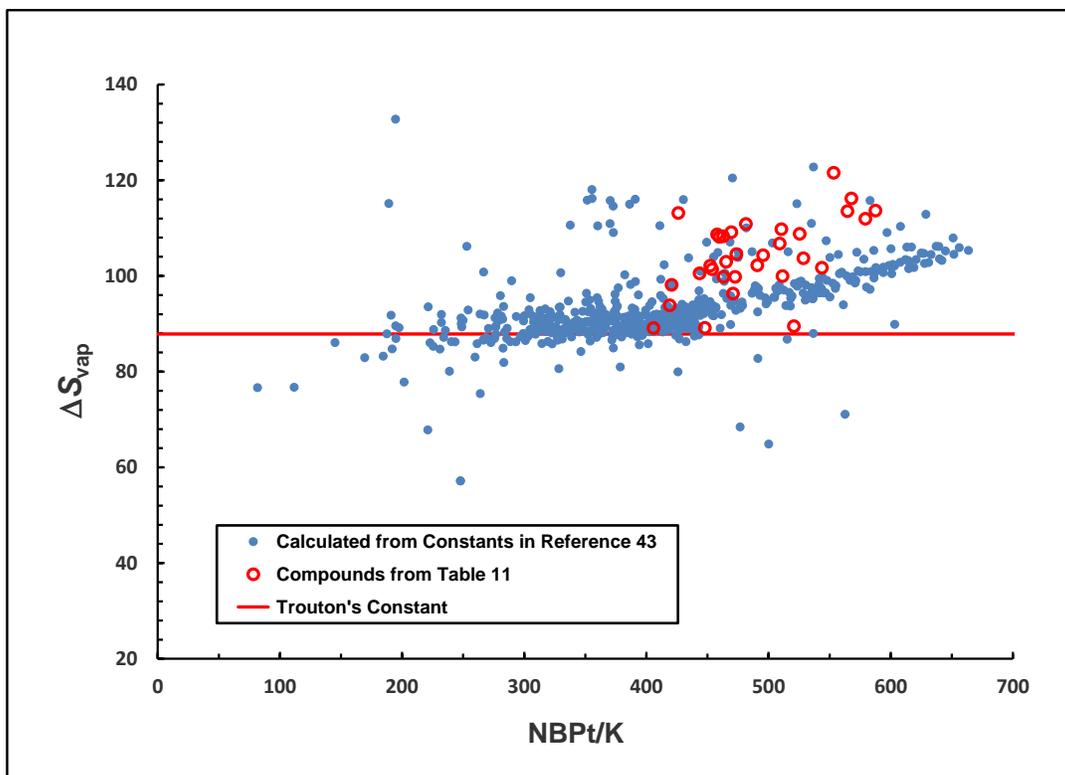
Figure 6. Calculated entropy of vaporization versus NBPt for selected compounds.

Figure 7 provides a comparison of the vapor pressures of the title compounds to those of HD and GB (isopropyl methylphosphonofluoridate; sarin, CAS no. 107-44-8). The latter is the most volatile of the standard nerve agents. Interestingly, the HD and DTH vapor pressure curves cross twice between –20 and 50 °C, which is primarily due to the change in the slopes of the curves at their melting points. DTH may be considered a candidate vapor pressure simulant for HD in the ambient temperature range, especially below 15 °C, where both compounds are in the solid phase.
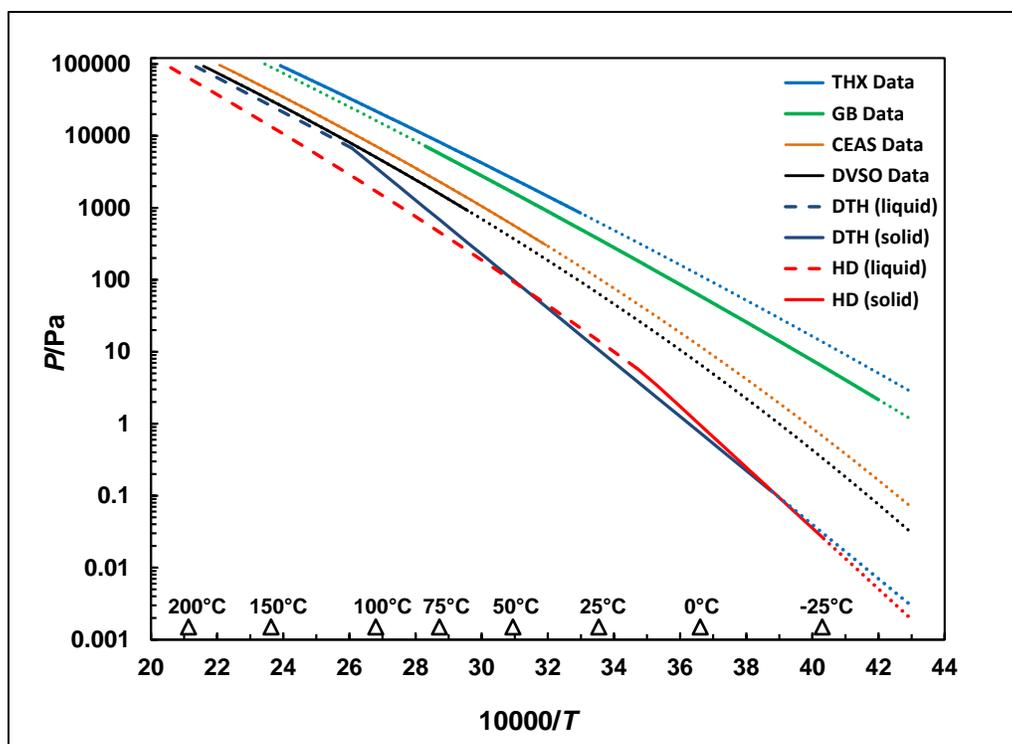
Figure 7. Vapor pressure comparison for title compounds and selected CWAs.
Dotted lines indicate extrapolation.

5.   CONCLUSIONS

        This report documents liquid-phase vapor pressure data that were measured using
DSC for four sulfur-containing decomposition products of the CWA, HD. These data display a
high degree of precision, as seen by the small differences between observed and calculated
values. Although the available literature distillation data for the title compounds are generally
consistent with our data, they are considered to be unreliable; therefore, the literature data were
not used to generate the correlations.

        Literature vapor pressure data for solid DTH that were measured using
complementary methods were reanalyzed. The intersection of the liquid- and solid-phase DTH
correlations was found to be close to the published melting range, indicating internal consistency
of the data sets and providing confidence in both.

        The absence of complementary vapor pressure data for THX, DVSO, and CEAS
makes extrapolation of the DSC data to the ambient temperature range problematic. The
approach suggested by Thomson was adopted to improve the reliability of such extrapolations.

        Entropies of vaporization, calculated on the basis of the current data, result in
values ~10% higher than those predicted by Trouton's rule. Similar results have been reported
for a variety of compounds.

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ACRONYMS AND ABBREVIATIONS

ΔH_{sub}	enthalpy of sublimation
ΔH_{vap}	enthalpy of vaporization
ΔS_{vap}	entropy of vaporization
CAS	Chemical Abstracts Service
CEAS	chloroethyl acetylsulfide
CECPRS	2-chloroethyl-3-chloropropyl sulfide
CMMP	cyclohexyl methyl methylphosphonate
C_{sat}	saturation concentration or volatility
CWA	chemical warfare agent
DCMP	dicyclohexyl methylphosphonate
DEA	2-diethyl aminoethanethiol
DEEP	diethyl ethylphosphonate
DEM	diethyl malonate
DEMP	diethyl methylphosphonate
DIA	2-diisopropyl aminoethanethiol
DIBMP	diisobutyl methylphosphonate
DICDI	N,N'-diisopropylcarbodiimide
DIMP	diisopropyl methylphosphonate
DMA	2-dimethyl aminoethanethiol
DMCP	2,2-dimethylcyclopentanol
DMEP	dimethyl ethylphosphonate
DMHP	dimethyl phosphonate
DMMP	dimethyl methylphosphonate
DPMP	dipinacolyl methylphosphonate
DSC	differential scanning calorimetry
DTH	1,4-dithiane
DVSO	divinyl sulfoxide
GB	isopropyl methylphosphonofluoridate; sarin
GF	cyclohexyl methylphosphonofluoridate
GP	2,2-dimethylcyclopentyl methylphosphonofluoridate
HD	bis-(2-chloroethyl) sulfide, mustard gas
IMMP	isopropyl methyl methylphosphonate
MW	molecular weight
NBPt	normal boiling point
P	pressure (pascal)
p	pressure (Torr)
P_{calc}	calculated vapor pressure
P_{exptl}	experimental vapor pressure
R	gas constant
RVX	O-isobutyl-S-[2(diethylamino) ethyl] methylphosphonothiolate
T	temperature (kelvin)
t	temperature (Celsius)
TDG	thiodiglycol
TEPO	triethyl phosphate

THX	1,4-thioxane
TPPO	tri-*n*-propyl phosphate
VX	*O*-ethyl-*S*-[2(diisopropylamino) ethyl] methylphosphonothiolate

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