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VAPOR PRESSURE DATA AND ANALYSIS FOR SELECTED ORGANOPHOSPHORUS COMPOUNDS, CMMP, DPMP, DMEP, AND DEEP: EXTRAPOLATION OF HIGH-TEMPERATURE DATA

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14. ABSTRACT: Experimental investigations from our laboratory continue to focus on the measurement of selected physical properties of chemical warfare agents (CWAs) and their surrogates, precursors, and degradation products. This report documents vapor pressure data and correlations for four phosphonate ester compounds that have molecular structures similar to those of CWAs. As a result, these materials may be considered to be CWA surrogates and can be used to evaluate the performance of defensive equipment, which requires accurate knowledge of the thermophysical properties of agents and their surrogates. These data were measured using an ASTM International (West Conshohocken, PA) method that is based on differential scanning calorimetry. The data presented herein were used to determine temperature–pressure correlations, and the fit constants were used to calculate temperature-dependent thermodynamic properties to enable the interpolation and limited extrapolation of the data. No ambient-temperature vapor pressure data are available for any of the title compounds, and a method is recommended herein to obtain the best estimates of vapor pressure in the ambient temperature range when data are not available.														
15. SUBJECT TERMS <table border="0" style="width: 100%;"> <tr> <td>Vapor pressure</td> <td>Antoine equation</td> <td>Clausius–Clapeyron equation</td> </tr> <tr> <td>Enthalpy of vaporization</td> <td>Volatility</td> <td>Differential scanning calorimetry (DSC)</td> </tr> <tr> <td>Vapor saturation</td> <td>Normal boiling point</td> <td></td> </tr> </table> <p>Cyclohexyl methyl methylphosphonate (CMMP), Chemical Abstracts Service (CAS) no. 7040-52-0 Dipinacolyl methylphosphonate (DPMP), CAS no. 7040-58-6 Dimethyl ethylphosphonate (DMEP), CAS no. 6163-75-3 Diethyl ethylphosphonate (DEEP), CAS no. 78-38-6</p>						Vapor pressure	Antoine equation	Clausius–Clapeyron equation	Enthalpy of vaporization	Volatility	Differential scanning calorimetry (DSC)	Vapor saturation	Normal boiling point	
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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 March 2015 and completed in May 2017. The data reported here are contained in ECBC notebooks 99-0095 and 02-0091.

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This report has been approved for public release.

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VAPOR PRESSURE DATA AND ANALYSIS FOR SELECTED ORGANOPHOSPHORUS COMPOUNDS, CMMP, DPMP, DMEP, AND DEEP: EXTRAPOLATION OF HIGH-TEMPERATURE DATA

1. INTRODUCTION

This report documents the vapor pressures of compounds of interest to the chemical warfare agent (CWA) defense community. Vapor pressure is an important physical property for a wide variety of chemical defense related applications, including prediction of downwind time–concentration profiles after dissemination, generation of controlled challenge concentrations for detector testing, toxicological evaluations, and assessment of the efficiency of air filtration systems.

The U.S. Army Edgewood Chemical Biological Center (Aberdeen Proving Ground, MD) has a long history of interest in the quantification of the physical properties of CWAs and related materials,^{1–8} including the development of correlations to enable accurate prediction of selected properties at untested temperatures. Knowledge of the physical properties of materials is critical for understanding their behavior in the environment as well as in the laboratory. One of the most important physical properties is vapor pressure. Recently, our laboratory investigated and documented the experimental vapor pressure data and properties derived from such data, including temperature correlations and temperature-dependent enthalpy of volatilization (vaporization for liquids and sublimation for solids) of selected CWAs and related compounds such as CWA precursors, degradation products, and simulants.^{9–20}

This report details vapor pressure measurements performed in accordance with ASTM International (West Conshohocken, PA) methods that are based on thermal analysis techniques, including differential scanning calorimetry (DSC).^{21,22} New data and correlations are presented herein for four organophosphorus compounds whose structures, full names, Chemical Abstracts Service (CAS) numbers, chemical formulas, and molecular weights (MWs) are shown in Figure 1. These compounds may serve as CWA testing surrogates due to their similarities in structural and physical properties to actual CWAs. Vapor pressure correlations with temperature, based on experimental data, are useful for interpolation and limited extrapolation.

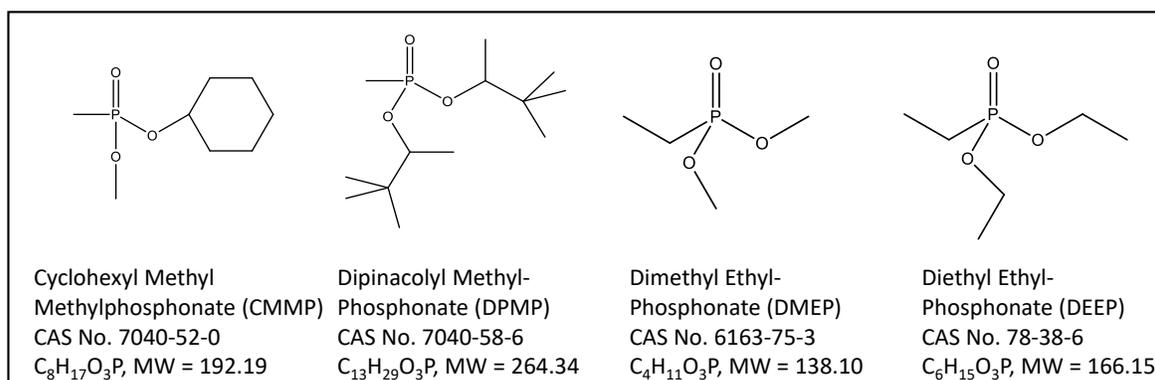


Figure 1. Structures and chemical names of title compounds.

2. EXPERIMENTAL PROCEDURES

2.1 Materials and Methods

The source and mole fraction purity of the materials studied are listed in Table 1. The methods used in this work closely follow ASTM International standards and have been described in detail in previous publications.^{15,23,24}

Table 1. Sample Information for Title Compounds

Compound	Source	Purity (%)
CMMP	In-house	98.6
DPMP	In-house	95.0
DMEP	In-house	98.2
DEEP	Fluka Analytical (Buchs, Switzerland)	98.0

2.2 Data Analysis

Vapor pressure data may be correlated using the Clausius–Clapeyron equation, eq 1, or the Antoine equation, eq 2, by minimizing the sum of the squares of the differences between the logarithms of each measured and calculated vapor pressure value.

$$\ln(P) = a - b/(T) \quad (1)$$

$$\ln(P) = a - b/(c + T) \quad (2)$$

where P is pressure (Pascal); T is absolute temperature (Kelvin); and a , b , and c are fit constants.

For a Clausius–Clapeyron fit, the correlation c constant is 0 and the standard vapor pressure plot ($\ln[P]$ versus reciprocal temperature) has no curvature due to the assumption of a constant enthalpy of vaporization. With a standard Antoine fit, the c constant varies based on the data. A negative Antoine c constant results in negative curvature that is typically observed with high-quality vapor pressure data measured over a wide range. This also results in decreasing enthalpy of vaporization with increasing temperature, as expected, based on thermodynamics. An Antoine fit that yields a positive c constant indicates inappropriate positive curvature and increasing enthalpy of vaporization with increasing temperature, which suggests significant error in the measured data.

One of the primary uses of the correlation equation is to predict vapor pressure values at untested conditions, with the goal of closely matching the predicted values to the measured values. In this report, we investigate an option for extrapolating high-temperature data to ambient temperature. Thomson²⁵ found that for many compounds, the Antoine equation c constant ranged between -53 and -33 and suggested -43 as “a good average value for organic compounds which [sic] are liquid at room temperature”. We tested Thomson’s recommendation by applying the $c = -43$ criterion to three literature data sets¹² that cover wide experimental

ranges and include data measured using complementary methods, in this case DSC at high temperatures and vapor saturation at ambient temperatures. For the three examples provided herein, we fitted only the high-temperature subset of each data set and constrained the c constant to -43 to assess how well the extrapolation of that modified fit to ambient temperature agrees with the correlated value at ambient temperature based on the unconstrained fit of the entire data set. The ability to accurately predict vapor pressure beyond the experimental range is of particular concern for the title compounds because the experimental data were measured using only a single method over limited high-temperature ranges.

Dimethyl methylphosphonate (DMMP, CAS no. 756-79-6) is our first example. Its vapor pressure data and analysis were reported in previous work from our laboratory.¹² Figure 2 shows the experimental data superimposed onto three least-squares fits that were derived using the DSC data only. These fits were composed of the standard Antoine and Clausius–Clapeyron correlations and the modified Antoine equation with the c constant constrained to -43 . Also shown is the literature Antoine equation that was based on both the DSC and saturator data for comparison. In this case, the standard (unconstrained) Antoine equation that was based on DSC data only yields a c constant of -86.53 and underestimates ambient temperature values. However, the Clausius–Clapeyron equation that was based only on DSC data overestimates ambient temperature values. The literature Antoine equation that was based on all data with a c constant of -51.7 , and the modified Antoine equation that was based on DSC data only with a c constant of -43 are virtually indistinguishable in Figure 2. Figure 3 shows the same plot for DMMP in the ambient temperature range on an expanded scale. The calculated differences between these two correlations, 1.0% at $25\text{ }^\circ\text{C}$ and 2.5% at $-10\text{ }^\circ\text{C}$, are more easily discerned in Figure 3.

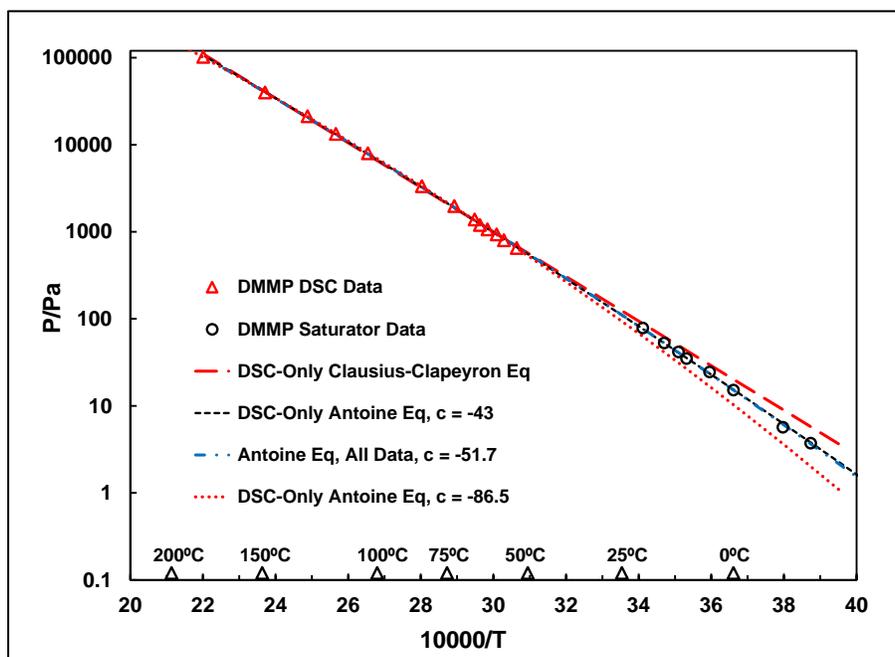


Figure 2. DMMP experimental data superimposed onto a standard Antoine fit based on all data. Also shown are three fits based on DSC data only: Clausius–Clapeyron, standard Antoine, and modified Antoine ($c = -43$).

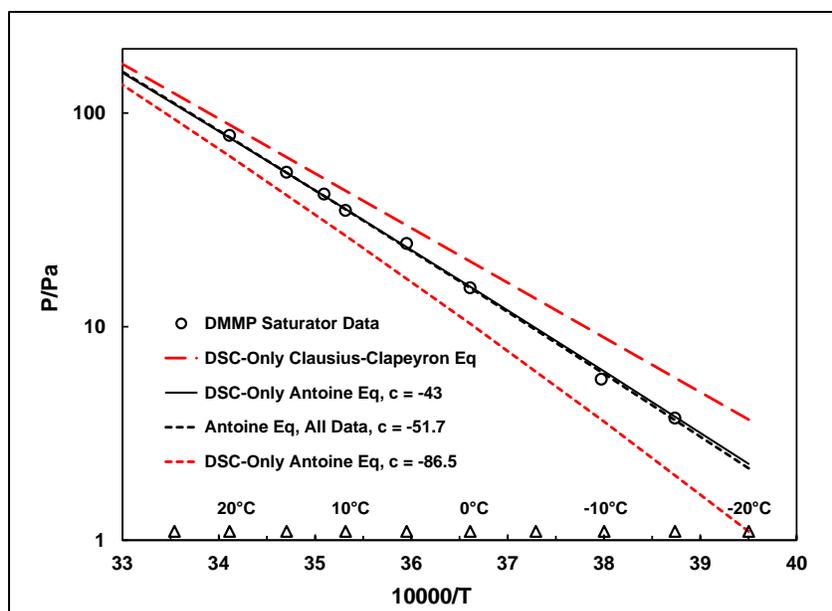


Figure 3. Expanded-scale DMMP saturator data superimposed onto a standard Antoine fit based on all data. Also shown are three fits based on DSC data only: Clausius–Clapeyron, standard Antoine, and modified Antoine ($c = -43$).

Although the agreement was not quite as good as that found for DMMP, similar results were found for diethyl methylphosphonate (DEMP; CAS no. 683-08-9) and diisopropyl methylphosphonate (DIMP; CAS no. 1445-75-6), which are shown using the expanded scale in Figures 4 and 5, respectively.

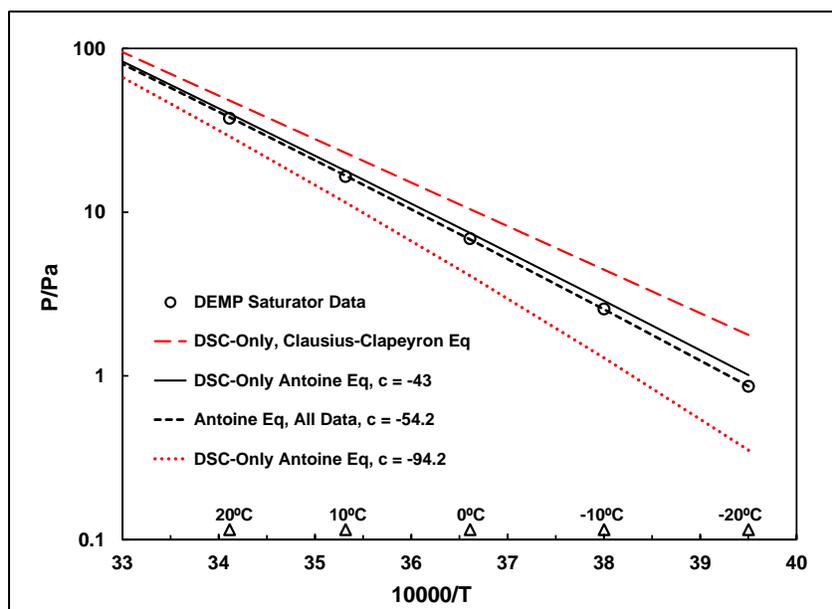


Figure 4. Expanded-scale DEMP saturator data superimposed onto a standard Antoine fit based on all data. Also shown are three fits based on DSC data only: Clausius–Clapeyron, standard Antoine, and modified Antoine ($c = -43$).

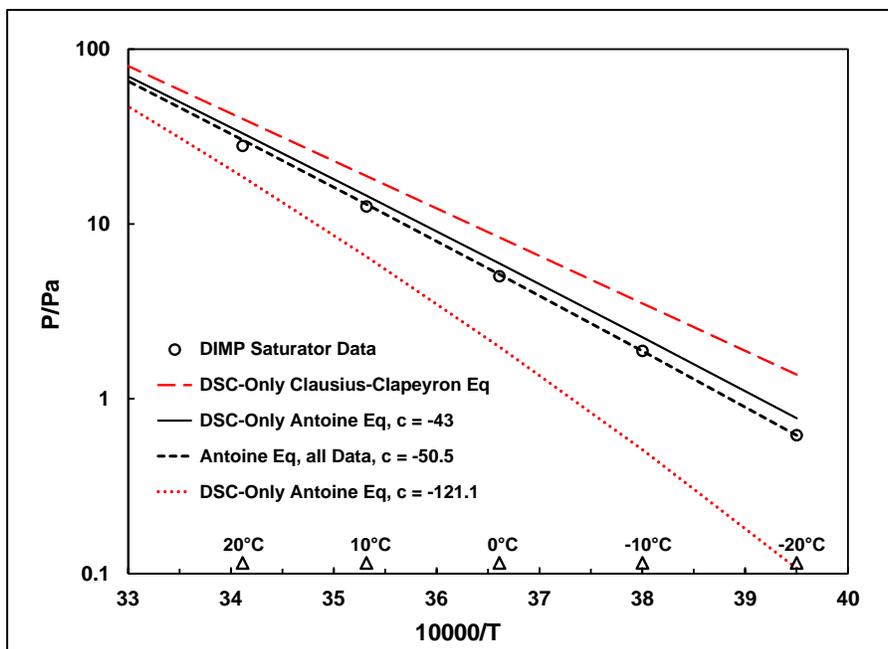


Figure 5. Expanded-scale DIMP saturator data superimposed onto a standard Antoine fit based on all data. Also shown are three fits based on DSC data only: Clausius-Clapeyron, standard Antoine, and modified Antoine ($c = -43$).

The standard Antoine correlations shown in Figures 2–5 are characteristic of similar fits that were based on data we measured over wide temperature ranges using complementary methods for more than 30 compounds. The resulting c values from those compounds average -56 , and the standard deviation is 18, which substantially overlaps the range suggested by Thomson.²⁵ Based on the agreement between the extrapolated values and measured data, the example compounds demonstrate that a correlation using Thomson’s c value will more accurately predict ambient vapor pressure from high-temperature data than will either a Clausius–Clapeyron fit or an unconstrained Antoine fit of the same data. As a result, the modified (or constrained) Antoine fit is of particular interest under the assumption that the title compounds behave in a similar manner.

The new vapor pressure data presented herein were correlated with three different equations: Clausius–Clapeyron, standard Antoine, and modified Antoine with the c constant constrained to -43 for comparison. The correlation equations are presented using two common units systems, one with temperature given in kelvin (T) and pressure in pascal (Pa) and the other with temperature in Celsius (t) and pressure in Torr (p).

Several thermodynamic properties can be calculated from the vapor pressure correlation. The enthalpy of vaporization, ΔH_{vap} , in joules per mole, is calculated by multiplying the derivative of the standard vapor pressure equation by RT^2 using

$$\Delta H_{\text{vap}} = b \times R \times [T/(c + T)]^2 \quad (3)$$

where b and c are eq 1 coefficients, and R is the gas constant (8.3144 J/mol K).

The saturation concentration, C_{sat} , often referred to as volatility, in milligrams per cubic meter, is calculated as a function of temperature from the vapor pressure, molecular weight, gas constant, and temperature using

$$C_{\text{sat}} = P \times \text{MW}/(R \times T) \quad (4)$$

where MW is molecular weight and R is 8.3144 Pa m³/mol K.

The entropy of vaporization, ΔS_{vap} , in joule per mole-kelvin is calculated by dividing the enthalpy of vaporization at the normal boiling point (NBPt), by the NBPt using

$$\Delta S_{\text{vap}} = \Delta H_{\text{vap}}/\text{NBPt} \quad (5)$$

3. RESULTS

The vapor pressures, pressure–temperature correlations, comparisons to literature data where available, and calculated properties for each of the title compounds are detailed in the following sections. Ambient temperature data are not available for the title compounds.

3.1 CMMP

Measurements for CMMP using DSC were attempted from 1267 Pa up to atmospheric pressure; however, problems were encountered at higher pressures due to thermal instability. Above 14,100 Pa, the thermal curves consisted of multiple, erratic endotherms rather than the expected single, sharp, boiling endotherm. Fourteen data points were measured in this work at 120.02 to 183.53 °C and are listed in Table 2. These data are shown in Figure 6, which also shows the three correlations to the experimental data. The correlation resulting from the standard Antoine fit has inappropriate positive curvature, as indicated by the positive c constant of 84.31. This result was likely due to the decomposition of CMMP at higher temperatures, which caused the reduced-pressure boiling points to appear to be at lower temperatures than they would have been in the absence of decomposition. Correlations with positive c constants are not expected based on thermodynamic considerations. This result was remedied in our earlier work by using a Clausius–Clapeyron fit ($c = 0$) when positive c values were indicated by the data. The Clausius–Clapeyron fit, shown in Figure 6, projects lower values at ambient temperatures than the unorthodox Antoine equation with positive curvature. Based on the results from the example compounds shown previously, we propose that the third correlation, the modified Antoine fit with the c constant set to -43 , represents the best prediction of the ambient vapor pressure for this compound, and we recommend its use.

In addition to the experimental data, Table 2 lists the values calculated at the experimental temperatures using the modified Antoine equation (shown at the bottom of Table 2) and the percent differences between experimental and calculated values. The agreement between experimental and correlated values for CMMP is typical of DSC data over a limited temperature range. Table 3 lists values for vapor pressure, volatility, and enthalpy of vaporization at selected temperatures. The calculated normal boiling point for CMMP is 255.43 °C, and the entropy of vaporization for CMMP, based on the fit to the DSC data, is 103.7 J/mol-K.

Table 2. Experimental Data and Calculated Vapor Pressure Values for CMMP

Temperature (°C)	Experimental Vapor Pressure		Calculated Vapor Pressure		Difference (%) ^b
	(Pa) ^a	(Torr)	(Pa)	(Torr)	
120.02	1267	9.5	1208	9.058	4.85
122.90	1360	10.2	1375	10.31	-1.10
123.28	1373	10.3	1398	10.49	-1.77
124.76	1453	10.9	1493	11.20	-2.66
127.67	1667	12.5	1696	12.72	-1.74
132.32	2053	15.4	2070	15.53	-0.81
136.80	2666	20.0	2497	18.73	6.79
141.06	3106	23.3	2971	22.29	4.56
146.55	3626	27.2	3696	27.73	-1.88
151.13	4293	32.2	4414	33.11	-2.74
158.40	5373	40.3	5799	43.50	-7.35
168.21	8026	60.2	8250	61.88	-2.72
173.90	10666	80.0	10040	75.33	6.23
183.53	14039	105.3	13840	103.8	1.44
$\ln(P) = 22.98149 - 5562.485/(T - 43)$ $\log(p) = 7.855829 - 2415.757/(t + 230.15)$					

^aExperimental Pa values were calculated from Torr values.

^b $100 \times (P_{\text{exptl}} - P_{\text{calc}})/P_{\text{calc}}$, where P_{exptl} is the experimental vapor pressure, and P_{calc} is the calculated vapor pressure.

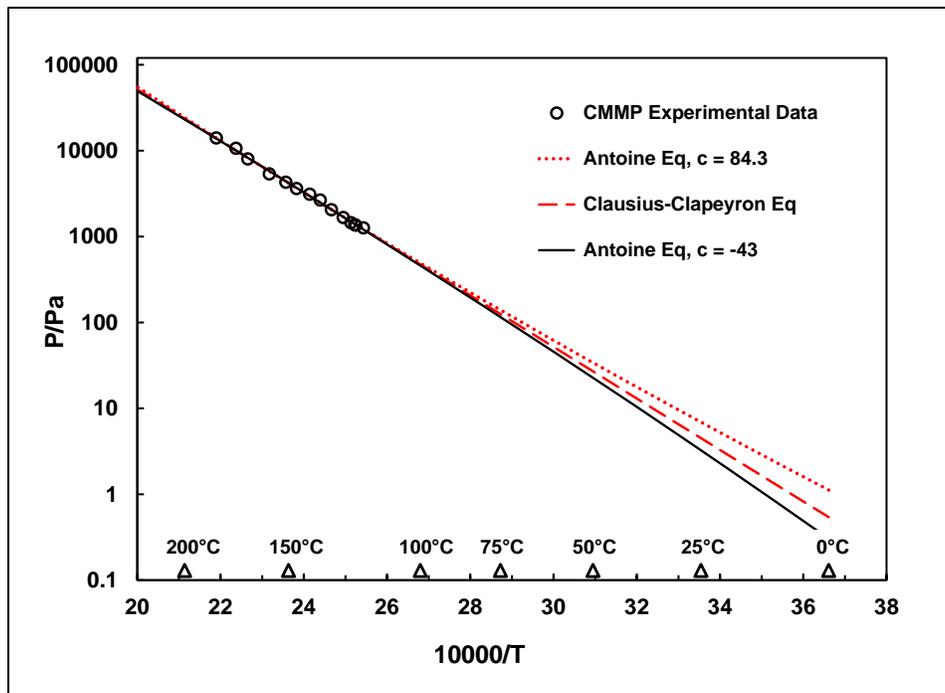


Figure 6. CMMP DSC experimental vapor pressure data and curves resulting from the Clausius–Clapeyron, standard Antoine, and modified Antoine correlations.

Table 3. Calculated Vapor Pressure, Volatility, and Enthalpy of Vaporization for CMMP at Selected Temperatures Based on Modified Antoine Equation

Temperature (°C)	Vapor Pressure (Pa)	Vapor Pressure (Torr)	Volatility (mg/m ³)	ΔH_{vap} (kJ/mol)
-20 ^a	3.057×10^{-2}	2.293×10^{-4}	2.792×10^0	67.11
-10 ^a	1.017×10^{-1}	7.631×10^{-4}	8.937×10^0	66.08
0 ^a	3.050×10^{-1}	2.288×10^{-3}	2.581×10^1	65.15
10 ^a	8.344×10^{-1}	6.258×10^{-3}	6.812×10^1	64.29
20 ^a	2.106×10^0	1.580×10^{-2}	1.661×10^2	63.52
25 ^a	3.256×10^0	2.443×10^{-2}	2.525×10^2	63.15
30 ^a	4.951×10^0	3.714×10^{-2}	3.775×10^2	62.80
40 ^a	1.093×10^1	8.195×10^{-2}	8.065×10^2	62.14
60 ^a	4.517×10^1	3.388×10^{-1}	3.134×10^3	60.97
80 ^a	1.555×10^2	1.166×10^0	1.018×10^4	59.96
100 ^a	4.609×10^2	3.457×10^0	2.855×10^4	59.08
120	1.207×10^3	9.050×10^0	7.094×10^4	58.31
140	2.846×10^3	2.135×10^1	1.593×10^5	57.62
160	6.150×10^3	4.613×10^1	3.282×10^5	57.01
180	1.233×10^4	9.245×10^1	6.287×10^5	56.45
200 ^a	2.316×10^4	1.737×10^2	1.131×10^6	55.96
220 ^a	4.113×10^4	3.085×10^2	1.928×10^6	55.51
240 ^a	6.958×10^4	5.219×10^2	3.134×10^6	55.10
255.43 ^a	1.013×10^5	7.600×10^2	4.431×10^6	54.80

^aExtrapolated.

3.2 DPMP

Measurements for DPMP using DSC were attempted from 1573 Pa to atmospheric pressure. Evidence of DPMP degradation was detected upon boiling at the two highest pressures tested; these points were not used. Ten data points resulting from broad boiling endotherms were measured in this work from 134.72 to 203.36 °C and are listed in Table 4. These data are shown in Figure 7, which also shows standard Antoine and Clausius–Clapeyron correlations and a modified Antoine correlation with Thomson’s recommended *c* value. As for CMMP, the standard Antoine correlation shows inappropriate positive curvature, as evidenced by the large positive *c* constant, which was presumably due to decomposition at high temperatures and the limited range of the data. The Clausius–Clapeyron fit eliminates the positive curvature; however, we propose that the modified Antoine fit be used to best approximate the ambient vapor pressure for DPMP.

In addition to the experimental data, Table 4 also lists the vapor pressure values that were calculated at the experimental temperatures using the modified Antoine equation and the percent differences between experimental and calculated values. These differences are greater than those usually seen for DSC data, particularly at the highest temperature reported here, which was likely due to thermal degradation. Table 5 lists values for DPMP vapor pressure,

volatility, and enthalpy of vaporization that were calculated at selected temperatures using the modified Antoine correlation coefficients. The calculated normal boiling point for DPMP is 270.57 °C, and the entropy of vaporization for DPMP is 101.7 J/mol-K.

The literature data for DPMP consist of two reduced-pressure boiling points, 1 Torr (133 Pa) at 103 °C²⁶ and 3 Torr (400 Pa) at 107 to 108 °C.²⁷ As shown in Figure 7, the higher point is in good agreement with our correlation, but the lower value is not. It has been our experience that vapor pressure values based on distillation data can be problematic, particularly at lower pressures, and we suspect that is the reason for the observed deviation.

Table 4. Experimental Data and Calculated Vapor Pressure Values for DPMP

Temperature (°C)	Experimental Vapor Pressure		Calculated Vapor Pressure		Difference (%) ^b
	(Pa) ^a	(Torr)	(Pa)	(Torr)	
134.72	1573.2	11.8	1528	11.46	2.97
135.13	1586.5	11.9	1555	11.66	2.06
139.16	2066.5	15.5	1840	13.80	12.32
146.92	2293.1	17.2	2519	18.90	-8.98
150.77	2813.1	21.1	2931	21.98	-4.01
159.07	3973.0	29.8	4019	30.15	-1.14
171.90	6026.2	45.2	6382	47.87	-5.58
180.72	8026.0	60.2	8625	64.70	-6.95
190.83	11999	90.0	11990	89.96	0.04
203.36	19718	147.9	17670	132.5	11.61
$\ln(P) = 22.79166 - 5640.914/(T - 43.000)$ $\log(p) = 7.773388 - 2449.818/(t + 230.15)$					

^aExperimental Pa values were calculated from Torr values.

^b $100 \times (P_{\text{exptl}} - P_{\text{calc}})/P_{\text{calc}}$.

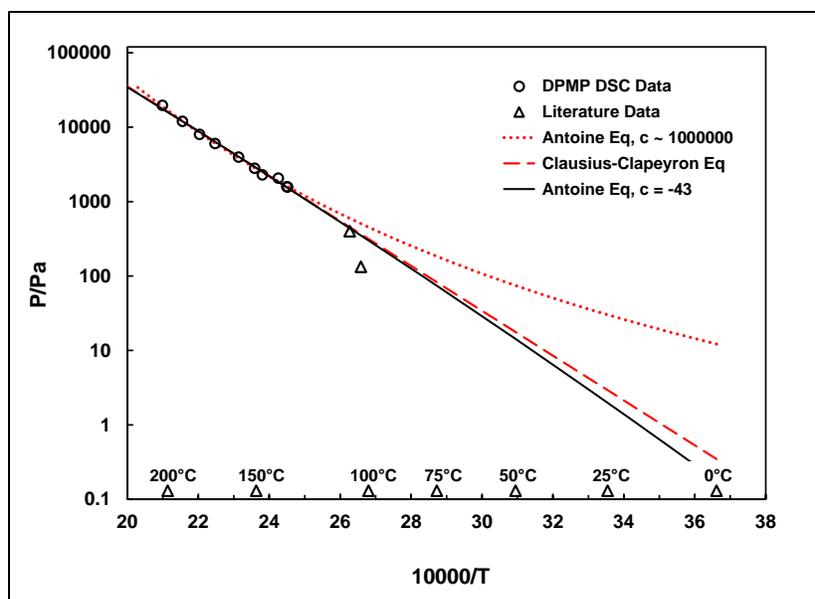


Figure 7. DPMP DSC and literature vapor pressure data and curves resulting from the Clausius–Clapeyron, standard Antoine, and modified Antoine correlations.

Table 5. Calculated Vapor Pressure, Volatility, and Enthalpy of Vaporization for DPMP at Selected Temperatures Based on Modified Antoine Equation

Temperature (°C)	Vapor Pressure (Pa)	Vapor Pressure (Torr)	Volatility (mg/m ³)	ΔH_{vap} (kJ/mol)
-20 ^a	1.741×10^{-2}	1.306×10^{-4}	2.187×10^0	68.06
-10 ^a	5.893×10^{-2}	4.420×10^{-4}	7.120×10^0	67.01
0 ^a	1.794×10^{-1}	1.346×10^{-3}	2.088×10^1	66.06
10 ^a	4.978×10^{-1}	3.734×10^{-3}	5.590×10^1	65.20
20 ^a	1.273×10^0	9.550×10^{-3}	1.381×10^2	64.41
25 ^a	1.981×10^0	1.486×10^{-2}	2.112×10^2	64.04
30 ^a	3.029×10^0	2.272×10^{-2}	3.177×10^2	63.69
40 ^a	6.760×10^0	5.070×10^{-2}	6.863×10^2	63.02
50 ^a	1.424×10^1	1.068×10^{-1}	1.401×10^3	62.40
60 ^a	2.851×10^1	2.138×10^{-1}	2.721×10^3	61.83
80 ^a	9.988×10^1	7.492×10^{-1}	8.992×10^3	60.81
100 ^a	3.006×10^2	2.255×10^0	2.561×10^4	59.91
120 ^a	7.976×10^2	5.983×10^0	6.450×10^4	59.13
140	1.905×10^3	1.429×10^1	1.466×10^5	58.43
160	4.160×10^3	3.120×10^1	3.054×10^5	57.81
180	8.420×10^3	6.316×10^1	5.907×10^5	57.25
200	1.596×10^4	1.197×10^2	1.072×10^6	56.75
220 ^a	2.858×10^4	2.144×10^2	1.843×10^6	56.29
240 ^a	4.871×10^4	3.653×10^2	3.018×10^6	55.87
260 ^a	7.947×10^4	5.961×10^2	4.739×10^6	55.49
270.57 ^a	1.013×10^5	7.600×10^2	5.925×10^6	55.30

^aExtrapolated.

3.3 DMEP

Using DSC, eight sharp boiling endotherms were measured for DMEP from 800 Pa to atmospheric pressure. The data points from 67.64 to 188.43 °C are listed in Table 6. These data are shown in Figure 8, which also shows the standard Antoine and Clausius–Clapeyron correlations and a modified Antoine correlation with $c = -43$. Notably, the standard Antoine equation has negative curvature that is reflected in the large negative c constant of -165.7 . We judged the curvature of the standard Antoine fit to be excessive, based on the large difference between the c value of -165.7 and that recommended by Thomson. The Clausius–Clapeyron fit eliminates the curvature; however, we again propose that the modified Antoine fit should be used to best approximate the ambient vapor pressure for DMEP.

Figure 8 also shows the literature isotenoscope data that were reported by Kosolapoff²⁸ for DMEP. Our DSC data cover a wider temperature range and are in good agreement with the isotenoscope data, with the exception of the lowest points that were discounted by the author of that work.

Table 6 lists the experimental vapor pressure data, the values calculated at experimental temperatures using the modified Antoine equation, and the percent differences. The differences between experimental and correlated values are larger than those usually seen for DSC data. Table 7 lists the values for vapor pressure, volatility, and enthalpy of vaporization, which were calculated at selected temperatures using the modified Antoine correlation coefficients. The calculated normal boiling point for DMEP is 184.83 °C, and the entropy of vaporization for DMEP is 108.7 J/mol-K.

Table 6. Experimental Data and Calculated Vapor Pressure Values for DMEP

Temperature (°C)	Experimental Vapor Pressure		Calculated Vapor Pressure		Difference (%) ^b
	(Pa) ^a	(Torr)	(Pa)	(Torr)	
67.64	799.9	6.0	958.2	7.187	-16.51
75.76	1466.5	11.0	1485	11.14	-1.24
86.31	2786.4	20.9	2537	19.03	9.83
100.66	5519.5	41.4	4977	37.33	10.91
113.45	9319.2	69.9	8652	64.90	7.71
129.11	16532.0	124.0	16140	121.1	2.42
148.81	32850.6	246.4	32870	246.5	-0.06
188.43	101325	760.0	112200	841.5	-9.69
$\ln(P) = 23.37031 - 4915.107/(T - 43.000)$ $\log(p) = 8.024694 - 2134.604/(t + 230.15)$					

^aExperimental values were calculated from Torr values.

^b $100 \times (P_{\text{exptl}} - P_{\text{calc}})/P_{\text{calc}}$.

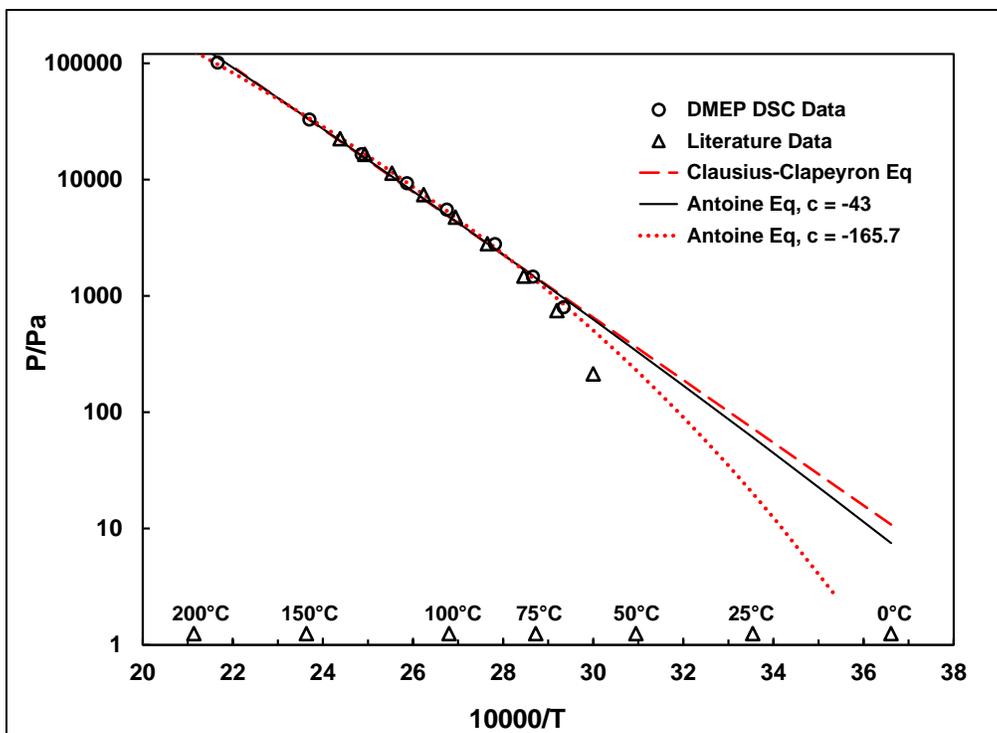


Figure 8. DMEP DSC and literature vapor pressure data and curves resulting from the Clausius–Clapeyron, standard Antoine, and modified Antoine correlations.

Table 7. Calculated Vapor Pressure, Volatility, and Enthalpy of Vaporization for DMEP at Selected Temperatures Based on Modified Antoine Equation

Temperature (°C)	Vapor Pressure (Pa)	Vapor Pressure (Torr)	Volatility (mg/m ³)	ΔH_{vap} (kJ/mol)
-20 ^a	9.819×10^{-1}	7.365×10^{-3}	6.443×10^1	59.30
-10 ^a	2.841×10^0	2.131×10^{-2}	1.793×10^2	58.39
0 ^a	7.495×10^0	5.622×10^{-2}	4.557×10^2	57.56
10 ^a	1.824×10^1	1.368×10^{-1}	1.070×10^3	56.81
20 ^a	4.133×10^1	3.100×10^{-1}	2.342×10^3	56.12
25 ^a	6.075×10^1	4.556×10^{-1}	3.384×10^3	55.80
30 ^a	8.797×10^1	6.598×10^{-1}	4.820×10^3	55.49
40 ^a	1.770×10^2	1.328×10^0	9.390×10^3	54.91
50 ^a	3.389×10^2	2.542×10^0	1.742×10^4	54.37
60 ^a	6.204×10^2	4.654×10^0	3.093×10^4	53.88
80	1.850×10^3	1.387×10^1	8.700×10^4	52.98
100	4.831×10^3	3.624×10^1	2.150×10^5	52.20
120	1.131×10^4	8.481×10^1	4.777×10^5	51.52
140	2.414×10^4	1.811×10^2	9.705×10^5	50.91
160	4.768×10^4	3.576×10^2	1.828×10^6	50.37
180	8.814×10^4	6.611×10^2	3.231×10^6	49.88
184.83	1.013×10^5	7.600×10^2	3.675×10^6	49.77

^aExtrapolated.

3.4 DEEP

Using DSC, 16 sharp boiling endotherms were measured for DEEP from 693 Pa to atmospheric pressure. The data points from 71.47 to 203.24 °C are listed in Table 8. These data are shown in Figure 9, which also shows the standard Antoine and Clausius–Clapeyron correlations and the modified Antoine equation with $c = -43$. As observed for DMEP, the standard Antoine equation for DEEP has negative curvature that is reflected by the large negative c constant of -109.4 . We judged the curvature of the standard Antoine fit to be excessive, based on the large difference between this c value and Thomson’s recommended -43 . The Clausius–Clapeyron fit eliminates the positive curvature; however, we again propose that the modified Antoine fit should be used to best approximate the ambient vapor pressure for DEEP.

Figure 9 also shows the seven literature isoteniscope data points that were reported by Kosolapoff²⁸ for DEEP. The DSC data agree well with Kosolapoff’s five highest points and cover a wider temperature range. Kosolapoff’s two lowest points were acknowledged by the author to be unreliable and do not agree well with the DSC data.

Table 8 lists the experimental vapor pressure data, the values calculated at the experimental temperatures using the modified Antoine equation, and the percent differences. The agreement between experimental and correlated values is typical of high-quality DSC data.

Table 8. Experimental and Calculated Vapor Pressure Values for DEEP

Temperature (°C)	Experimental Vapor Pressure		Calculated Vapor Pressure		Difference (%) ^b
	(Pa) ^a	(Torr)	(Pa)	(Torr)	
71.47	693.3	5.20	762.3	5.717	-9.05
74.99	893.3	6.70	920.2	6.902	-2.92
78.88	1093	8.20	1127	8.456	-3.02
81.96	1333	10.00	1319	9.895	1.06
86.34	1707	12.80	1641	12.31	3.99
94.15	2413	18.10	2387	17.90	1.11
98.86	3000	22.50	2966	22.25	1.14
103.77	3786	28.40	3696	27.72	2.46
111.40	5346	40.10	5137	38.53	4.07
117.33	6693	50.20	6569	49.27	1.88
121.06	7959	59.70	7636	57.27	4.24
129.09	10710	80.30	10450	78.35	2.50
133.95	12870	96.50	12540	94.07	2.58
147.09	20020	150.20	20080	150.6	-0.30
162.74	33320	249.90	33770	253.3	-1.35
203.24	101100	758.00	108910	816.9	-7.21
$\ln(P) = 22.95613 - 4922.389/(T - 43.000)$ $\log(p) = 7.844816 - 2137.766/(t + 230.15)$					

^aExperimental Pa values were calculated from Torr values.

^b $100 \times (P_{\text{exptl}} - P_{\text{calc}})/P_{\text{calc}}$.

Table 9 lists the values for vapor pressure, volatility, and enthalpy of vaporization, which were calculated at selected temperatures using the modified Antoine correlation coefficients. The calculated normal boiling point for DEEP is 200.50 °C, and the entropy of vaporization for DEEP is 104.5 J/mol-K.

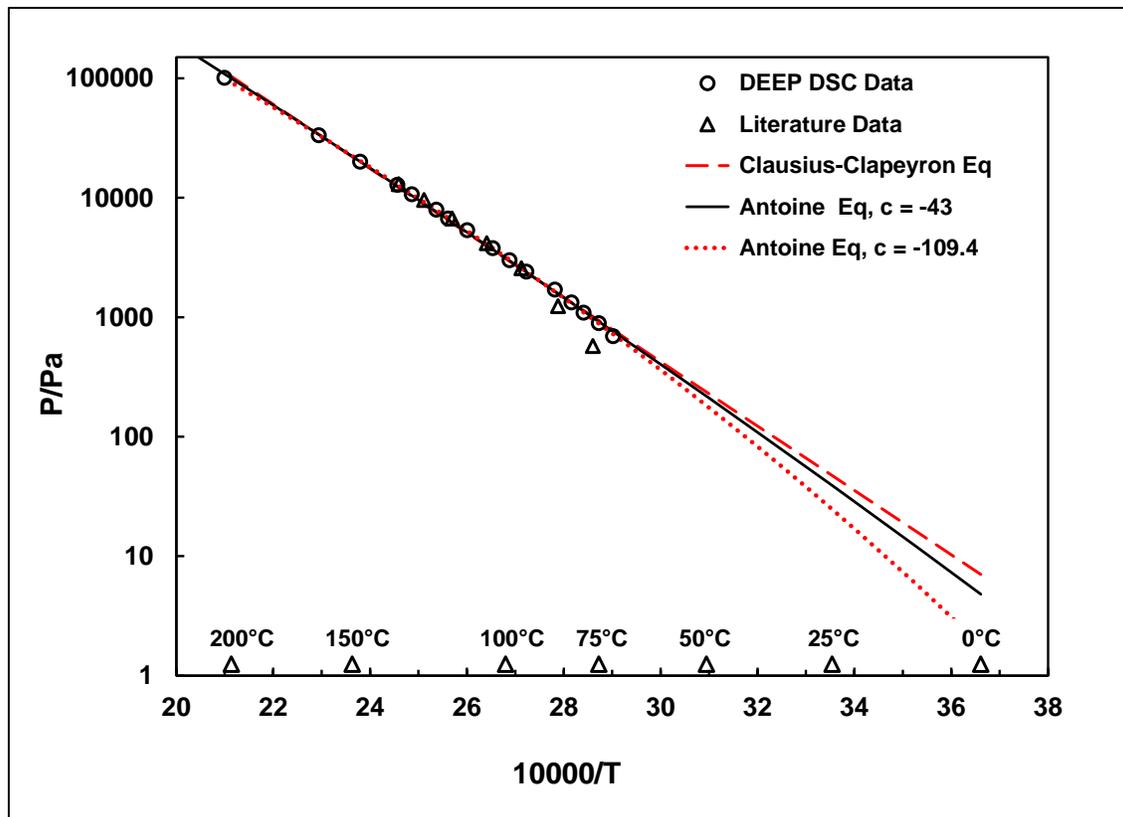


Figure 9. DEEP DSC and literature vapor pressure data and curves resulting from the Clausius–Clapeyron, standard Antoine, and modified Antoine correlations.

Table 9. Calculated Vapor Pressure, Volatility, and Enthalpy of Vaporization for DEEP at Selected Temperatures, Based on Modified Antoine Equation

Temperature (°C)	Vapor Pressure (Torr)	Vapor Pressure (Pa)	Volatility (mg/m ³)	ΔH_{vap} (kJ/mol)
-20 ^a	4.702×10^{-3}	6.268×10^{-1}	4.948×10^1	59.39
-10 ^a	1.362×10^{-2}	1.816×10^0	1.379×10^2	58.48
0 ^a	3.599×10^{-2}	4.799×10^0	3.511×10^2	57.65
10 ^a	8.770×10^{-2}	1.169×10^1	8.252×10^2	56.90
20 ^a	1.990×10^{-1}	2.653×10^1	1.809×10^3	56.21
25 ^a	2.926×10^{-1}	3.902×10^1	2.615×10^3	55.88
30 ^a	4.240×10^{-1}	5.653×10^1	3.727×10^3	55.57
40 ^a	8.542×10^{-1}	1.139×10^2	7.268×10^3	54.99
50 ^a	1.637×10^0	2.182×10^2	1.350×10^4	54.45
60 ^a	2.999×10^0	3.999×10^2	2.399×10^4	53.96
80	8.956×10^0	1.194×10^3	6.757×10^4	53.06
100	2.343×10^1	3.123×10^3	1.673×10^5	52.28
120	5.489×10^1	7.319×10^3	3.720×10^5	51.60
140	1.173×10^2	1.564×10^4	7.566×10^5	50.99
160	2.320×10^2	3.093×10^4	1.427×10^6	50.45
180	4.292×10^2	5.722×10^4	2.523×10^6	49.96
200	7.499×10^2	9.998×10^4	4.223×10^6	49.52
200.50	7.600×10^2	1.013×10^5	4.275×10^6	49.51

^aExtrapolated.

4. DISCUSSION

This report documents new DSC vapor pressure data that were measured above the ambient temperature range for four organophosphorus esters and provides correlations that may be used to estimate values within and beyond the experimental ranges. Literature data for the title compounds are limited. Two distillation data points, well above ambient temperature, have been reported for DPMP, but we have found distillation data to be unreliable. The data reported for DEMP and DEEP by Kosolapoff²⁸ above 10 Torr (1333 Pa) are in good agreement with our DSC data, but Kosolapoff's data are in the same temperature range that was used in our measurements. As such, none of the literature data are helpful for estimating ambient temperature vapor pressure values. The need for further work using complementary methods that are suitable for the measurement of vapor pressures in the ambient temperature range is strongly suggested by the current results.

Ideally, vapor pressure data would be measured using multiple, complementary techniques over a wide temperature range, including any specific range of interest, but this is not always an option. One of the challenges of working with meager vapor pressure data is the extrapolation of measured data to accurately predict values at untested conditions. When required, we would like to provide the best possible estimates of values in the ambient temperature range on the basis of experimental data at higher temperatures. Numerous equations

are available for correlation of measured vapor pressure data; however, the accuracy of the extrapolation of these correlations depends on a variety of factors, including data quality, breadth of the experimental temperature range, and length of the extrapolation. The Clausius–Clapeyron and Antoine equations are commonly used to correlate vapor pressure data; however, each has its limitations with respect to accurate extrapolation of high-temperature data to untested conditions.

Setting the c constant to -43 , as suggested by Thomson,²⁵ appears to work well for the extrapolation of vapor pressure data. Table 10 provides a list of compounds for which we have vapor pressure data that were measured using complementary methods, including the example compounds,¹² several related compounds from a recent report,²⁰ and the standard CWAs pinacolyl methylphosphonofluoridate (GD) and *O*-ethyl-*S*-(2-diisopropylaminoethyl) methylphosphonothiolate (VX). We fitted just the high-temperature subset of each data set using standard and modified Antoine correlations and compared the 25 °C extrapolated value to the extrapolated value from the fit of all of the data. Table 10 shows the following: (1) The extrapolations that were based on high-temperature data only and fitted with the modified Antoine equations are superior to the extrapolations of the high-temperature data only that were calculated from standard unconstrained Antoine equations. (2) The standard Antoine equations that were calculated from high-temperature data only under predict ambient vapor pressure and result in correlations with too much curvature.

An exception to the first conclusion is GD, for which the standard unconstrained Antoine correlation of the high-temperature data set gives a slightly better fit than the modified correlation. This may be due to the fairly short extrapolation of the high-temperature data to ambient temperature. As also observed in Table 10, VX is an apparent exception to the second conclusion. A standard Antoine fit to the high-temperature VX literature data yields a correlation with inappropriate positive curvature; therefore, the literature fit was constrained to a Clausius–Clapeyron correlation² (with no curvature), so this conclusion does not apply to VX.

It should be noted that two of the data sets (dicyclohexyl methylphosphonate [DCMP] and isopropyl methylphosphonic acid [IMPA]) yield unrealistically low estimates at 25 °C, based on the high-temperature data only, due to their narrow data ranges and the long extrapolations that are required.

Table 10. Comparisons of Vapor Pressure Values Calculated at 25 °C

Compound ^a	Vapor Pressure at 25 °C (Pa)			Antoine <i>c</i> Constant Based on All Data
	Based on High-Temperature Data Using Standard Antoine Equation	Based on High-Temperature Data Using Modified Antoine Equation, <i>c</i> constant = -43	Based on All Data	
DMHP ¹²	168.7	202.0	241.8	-20.0
DMMP ¹²	93.59	110.0	111.1	-51.7
DEMP ¹²	44.63	58.34	55.93	-54.2
DIMP ¹²	30.13	48.63	45.17	-50.5
DIBMP ²⁰	1.453	5.518	4.440	-60.2
DCMP ²⁰	^b	0.02352	0.03418	-59.6
IMMP ²⁰	29.43	62.85	75.89	-16.5
IMPA ²⁰	^b	0.0436	0.2466	0.0
GD ^{3,30}	49.46	61.69	53.36	-56.3
VX ¹⁵	0.4805 ^c	0.3180	0.1179	-60.2

DMHP, dimethyl phosphonate; DIBMP, diisobutyl methylphosphonate; IMMP, isopropyl methyl methylphosphonate.

^aLiterature reference number included.

^bCalculated value is $<10^{-10}$ due to excessive curvature of the correlation.

^cBased on Clausius–Clapeyron equation, reference 2.

Table 11 provides the calculated entropies of vaporization for the title compounds and for the compounds listed in Table 10. Trouton’s rule specifies a value of ~ 90 J/mol-K for the entropy of vaporization, which is calculated by dividing the enthalpy of vaporization at the normal boiling point by the normal boiling point. For the phosphonate compounds except IMPA and DCMP, the entropy of vaporization is between 100 and 109 J/mol-K. Both IMPA and DCMP required long extrapolations to their respective normal boiling points. Additionally, IMPA was constrained to a Clausius–Clapeyron fit, which likely caused a significant underestimation of its normal boiling point and an overestimation of its entropy of vaporization. IMPA also has the possibility of hydrogen bonding, which is associated with positive deviations from Trouton’s rule. The consistency of the entropies of vaporization for the remaining compounds suggests the possibility of structure-related positive deviations from Trouton’s rule, which may be the result of the polarity of these materials. Further work should be done to investigate this observation using other classes of materials.

Table 11. Normal Boiling Points and Enthalpies and Entropies of Vaporization for Title Compounds, Related Phosphonates, and GD and VX

Compound	Normal Boiling Point		ΔH_{vap} at Normal Boiling Point (kJ/mol)	ΔS_{vap} (J/mol-K)
	(°C)	(K)		
CMMP	255.45	528.6	54.8	103.7
DPMP	270.55	543.7	55.3	101.7
DMEP	184.85	458.0	49.8	108.7
DEEP	200.45	473.6	49.5	104.5
DMHP	170.45	443.6	44.6	100.5
DMMP	180.55	453.7	46.0	101.4
DEMP	192.25	465.4	47.9	102.9
DIMP	189.65	462.8	50.1	108.2
DIBMP	235.95	509.1	54.3	106.7
DCMP ^a	314.45	587.6	66.8	113.6
IMMP	186.65	459.8	49.7	108.1
IMPA ^a	277.25	550.4	69.9	127.0
GD	197.75	470.9	47.0	99.8
VX	291.55	564.7	64.1	113.5

^aNarrow experimental range and long extrapolations to normal boiling points.

The second derivative (curvature) of the Antoine equation with respect to $1/T$, shown in eq 6, is consistent with our empirical observations, that is, negative at all temperatures when c is negative and $c + T$ is positive. For all of our data sets that were measured using complementary methods, the observed c values range from -16 to -88 . At all temperatures of practical interest (-40 to 60 °C), $c + T > 0$ when $T > 100$ K. In practice, the Antoine equation begins to fail as $c + T$ approaches 0, which is of no practical interest unless extrapolation far beyond the experimental range is required. In that case, caution should be exercised.²⁹

$$d^2[\ln(P)] / d(1/T)^2 = 2bc \times [T/(c + T)]^3 \quad (6)$$

The correlation curvature and enthalpy of vaporization implications that are based on the Antoine equation for possible values of c and $c + T$ are summarized in Table 12.

It is incumbent on the researcher to measure vapor pressure over the widest range possible and to maximize the use of complementary methods that will minimize the need for long extrapolations. The use of complementary methods that produce consistent data will greatly enhance the confidence in the combined data set and relieve or minimize the necessity of extrapolating data. When it is impossible to measure data in the desired range, selection of the c constant, as recommended by Thomson, is the best approach for accurately extrapolating high-temperature data to ambient temperature.

Table 12. Correlation Curvature and Enthalpy of Vaporization Trends, Based on the Antoine Equation for Possible Values of c and $c + T$

c	$c + T$	Result
Negative	Positive	Standard case. Antoine equation has negative curvature on standard plot. Enthalpy of vaporization decreases as temperature increases.
Negative	Negative	Positive curvature. Enthalpy of vaporization increases as temperature increases. Not expected based on thermodynamic principles. Suggests large experimental error.
Positive	Positive	Positive curvature. Enthalpy of vaporization increases as temperature increases. Not expected based on thermodynamic principles. Suggests large experimental error.
Positive	Negative	Physically impossible because $T > 0$.
0	Positive ($T > 0$)	No curvature. Clausius–Clapeyron equation.

It is also desirable to specify the experimental uncertainties associated with each data set as quantitatively as possible to inform future researchers concerning analysis of the data. An example where this process was not done well is provided by the National Institute for Standards and Technology (NIST; Gaithersburg, MD) Webbook³¹ entry for DEEP, shown in Figure 10, in which all of the source data were used to determine the correlation, even though the author of the original report stated that selected low-pressure values were unreliable.²⁸ Our vapor pressure data and correlations contained herein for DMEP and elsewhere¹² for DMMP and DIMP suggest that similar erroneous analyses are contained in the NIST Webbook for these compounds. In addition, the DMMP correlation in the NIST Webbook appears to have a transcription error in the Antoine c constant and should be near -225 instead of -245 , as listed.

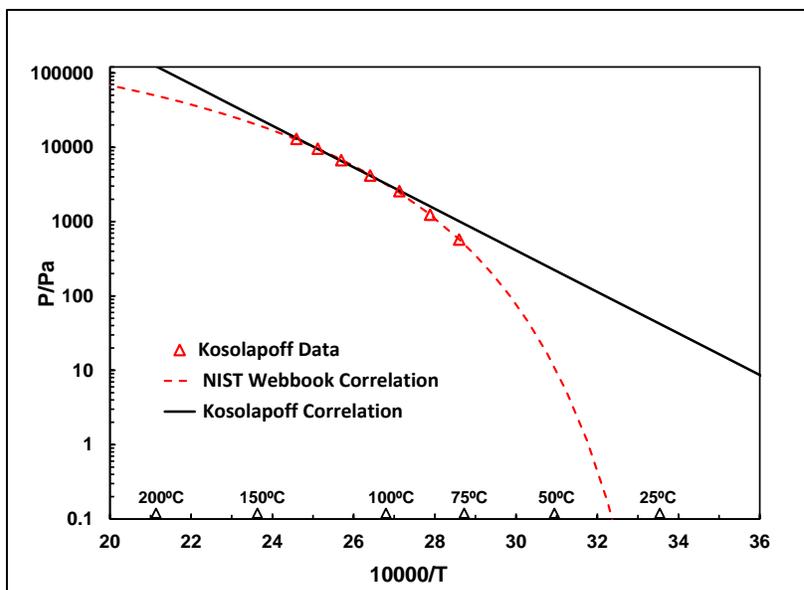


Figure 10. DEEP vapor pressure correlation from NIST Webbook compared to literature data and correlation.

Figure 11 shows a comparison of the vapor pressure correlations that were determined in this work for the title compounds. These determinations were made using Thomson's approximation and bounded by correlations that were based on a wide range of experimental data for classical CWAs, isopropyl methylphosphonofluoridate (GB),¹¹ and VX.¹⁵ All are shown with their experimental ranges as solid lines and extrapolations as dotted lines. The similarity of the slopes of these curves gives us confidence in extrapolation of the high-temperature data to ambient temperature, based on Thomson's observation. We recommend that estimates of ambient range vapor pressure, for compounds with high-temperature data only, be made based on an Antoine equation fit with the c constant constrained to a value of -43 ± 10 .

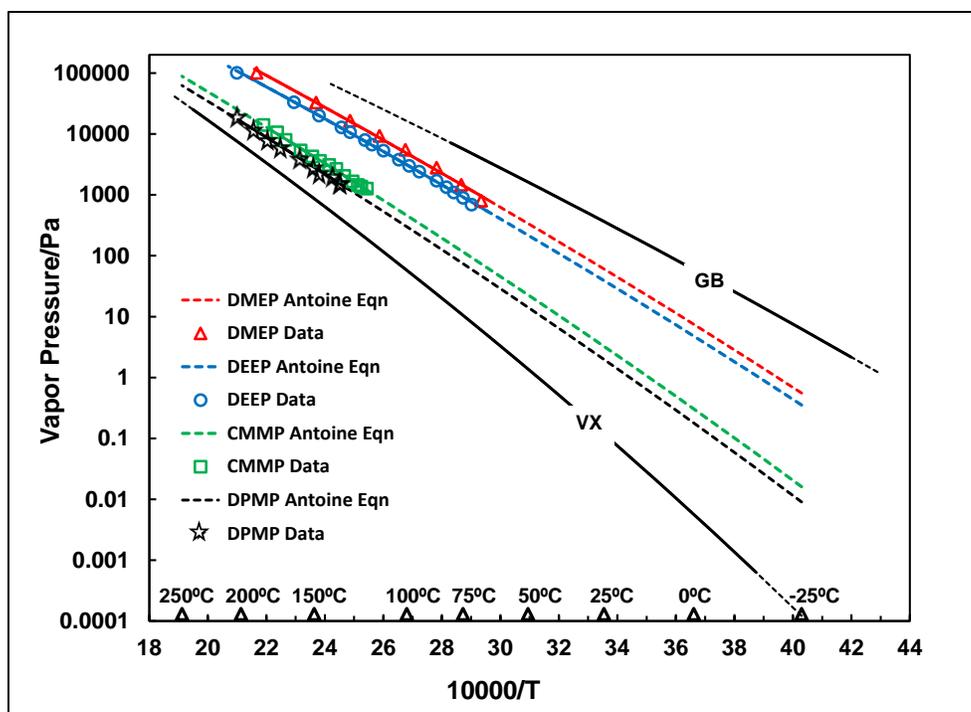


Figure 11. Data and vapor pressure curves for DMEP, DEEP, CMMP, and DPMP compared to those of GB and VX. Solid lines indicate experimental ranges, and dotted lines indicate extrapolations.

5. CONCLUSIONS

Vapor pressure measurements were completed using DSC at high temperatures on four organophosphorus compounds of interest, CMMP, DPMP, DMEP, and DEEP. None of these compounds have complementary vapor pressure data available in the ambient temperature range. Complementary data sets measured over wide temperature ranges using different methodologies not only reduce the length of extrapolations, but also enhance the confidence in each data set when multiple data sets are in agreement. In the absence of measured data at ambient temperatures, the challenge becomes performing accurate extrapolation to that range.

The data presented in this report are limited in range and measured using only one method (DSC). We examined methodology that was based on the recommendation of Thomson to predict values in the ambient temperature range using high-temperature data. For the compounds reported herein, an analysis of data from closely related materials revealed that the best estimates may be derived using Thomson's approximation with the Antoine equation c constant assigned a value of -43 . We have measured complementary data for 30 compounds, which resulted in a mean c value of -56 , with a standard deviation of 18. This result is consistent with that of Thomson and suggests that a more quantitative approximation of the c constant, based on chemical structure or polarity, should be investigated.

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ACRONYMS AND ABBREVIATIONS

ΔH_{vap}	enthalpy of vaporization
ΔS_{vap}	entropy of vaporization
CAS	Chemical Abstracts Service
CMMP	cyclohexyl methyl methylphosphonate
C_{sat}	saturation concentration or volatility
CWA	chemical warfare agent
DCMP	dicyclohexyl methylphosphonate
DEEP	diethyl ethylphosphonate
DEMP	diethyl methylphosphonate
DIBMP	diisobutyl methylphosphonate
DIMP	diisopropyl methylphosphonate
DMEP	dimethyl ethylphosphonate
DMHP	dimethyl phosphonate
DMMP	dimethyl methylphosphonate
DPMP	dipinacolyl methylphosphonate
DSC	differential scanning calorimetry
GB	isopropyl methylphosphonofluoridate
GD	pinacolyl methylphosphonofluoridate
IMMP	isopropyl methyl methylphosphonate
IMPA	isopropyl methylphosphonic acid
MW	molecular weight
NBPt	normal boiling point
NIST	National Institute for Standards and Technology
P	pressure (Pascal)
p	pressure (Torr)
P_{calc}	calculated vapor pressure
P_{exptl}	experimental vapor pressure
R	gas constant
T	temperature (Kelvin)
t	temperature (Celsius)
VX	<i>O</i> -ethyl- <i>S</i> -(2-diisopropylaminoethyl) methylphosphonothiolate

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