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## CHEMICAL BIOLOGICAL CENTER

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### VAPOR PRESSURE OF 2-CHLOROVINYL DICHLOROARSINE (LEWISITE)

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## EXECUTIVE SUMMARY

Previous vapor pressure data for the vesicant chemical warfare agent 2-chlorovinyl dichloroarsine (Lewisite) was acquired from the 1920s to 1940s. The temperature ranges included in the data varied widely. Investigators frequently extrapolated well outside of the range of the measured values to compute the vapor pressure in the ambient temperature range. The currently accepted values for the compound at 20 and 25 °C were computed from empirical data that was acquired down to only 50 °C. We have acquired new data in the range of 2 to 24 °C. By combining these data points with the older historical data, it has been possible to extend usefulness of the Antoine equation for calculating the vapor pressure of Lewisite from 0 to 193 °C. The calculated vapor pressure of Lewisite at 20 °C is 0.391 Torr.

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## PREFACE

The work described in this report was performed under the direction of the Detection Capability Officer, Defense Threat Reduction Agency Joint Science and Technology Office. This work was started and completed in July 2008.

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# VAPOR PRESSURE OF 2-CHLOROVINYL DICHLOROARSINE (LEWISITE)

## 1. INTRODUCTION

Lewisite has the Chemical Abstracts Service (CAS) Registry Number 541-25-3 and is indexed under the name, arsonous dichloride, (2-chloroethenyl). The molecular formula is  $C_2H_2AsCl_3$ , and it has a molecular weight of 207.35. Other synonyms for the compound include dichloro-(2-chlorovinyl)arsine, chlorovinylarsine dichloride, Lewisite I, L1 or L I, and EA-1034. Historical names for the compound include  $\beta$ -chlorovinyl chloroarsine and M1. Lewisite is a vesicant chemical warfare (CW) agent that was first synthesized in 1918 although not employed in combat during WWI.

Lewisite can exist as either *trans*-2-chlorovinyl dichloroarsine (Figure 1) or as the *cis* isomer. Researchers with the University of Liverpool and the University of Cambridge were the first to confirm the identity of the two isomers and show that the *trans* configuration is normally produced in larger amounts during synthesis.<sup>1</sup> Several physical parameters of *cis*-Lewisite were shown to differ significantly from those of the predominant *trans* isomer.<sup>2</sup> Several of the parameters that Whiting reported are shown in Table 1. The presence of 1-chlorovinyl dichloroarsine, also known as *geminal* Lewisite, in a sample of the agent was reported in 1993 in a study in which the *cis* and *geminal* forms were found to be minor products.<sup>3</sup>

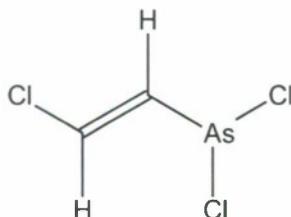


Figure 1. Structure of *trans*-2-Chlorovinyl Dichloroarsine (Lewisite).

Table 1. Thermophysical Parameters of Lewisite Reported by Whiting<sup>2</sup>

Parameter	Value	
	<i>cis</i> -Lewisite	<i>trans</i> -Lewisite
Freezing point/ °C	-44.7	-1.2
Vapor pressure/ Torr 25 °C	1.562	0.40 <sup>a</sup>
Boiling temperature/760 Torr °C	169.8	196.6
$\Delta H_{vap}^{25^\circ}$ /cal·mol <sup>-1</sup>	11,220 <sup>b</sup>	15,150 <sup>c</sup>

<sup>a</sup>0.563 Torr found in our work

<sup>b</sup>Système International d'Unités (SI): 46.9 kJ·mol<sup>-1</sup>

<sup>c</sup>SI: 63.4 kJ·mol<sup>-1</sup>. 52.6 kJ·mol<sup>-1</sup> found in our work.

The vapor pressure of the Lewisite I has been reported a number of times since the 1920's, including in a number of publications in the open literature by Green and Price,<sup>4</sup> Lewis and Perkins,<sup>5</sup> Mann and Pope,<sup>6</sup> Mohler and Pólya<sup>7</sup> and Gibson and Johnson.<sup>8</sup> Klosky and Stricker compiled and summarized some of the earliest physicochemical data of Lewisite and several related compounds for the Chemical Warfare Service Technical Command in 1921.<sup>9</sup>

In addition to the data from Lewis and Perkins,<sup>5</sup> the report included vapor pressure data from Baxter, Keyes, Lewis, Conant, and Miller, along with brief descriptions of the experimental methods. Klosky and Stricker<sup>5</sup> did not give first names or initials of the researchers, and we were unable to locate the original reports. The temperature range for the data in ref 9 was as low as 0 °C. In 1941, Sumner, Woodward, and Owens investigated the vapor pressures of arsenic trichloride and Lewisite I in a study covering the range 50 to 150 °C.<sup>10</sup> In 1944, Redemann et al. published a study of the vapor pressures of a variety of compounds obtained using a gas saturation method, including Lewisite.<sup>11</sup> Finally in 1983, Samuel et al. compiled the physical properties of a number of CW agents and related compounds, including Lewisite.<sup>12</sup> Samuel cited S.O./R/561<sup>10</sup> as the source of the data used to compute coefficients for the Antoine equation for Lewisite in which the measured points range from  $T = (50 \text{ to } 150) \text{ } ^\circ\text{C}$ . The authors do not explain their reasons for not using any experimental data from other researchers to derive their Antoine coefficients.

Recently, Bizzigotti et al. published a review of physical parameters for evaluating fate and transport of CW agents in marine environments.<sup>13</sup> In the case of Lewisite, the authors calculated a Clausius-Clapeyron equation yielding a vapor pressure of 0.710 Torr at 298.15 K. The following values used to calculate the fit were included: (1) Whiting's<sup>2</sup> publication. The Clausius-Clapeyron equation, as well as the vapor pressure and boiling temperatures, are identical to those reported in a previous publication.<sup>10</sup> The lowest and highest values that Bizzigotti et al.<sup>13</sup> used to do the fit were themselves fitted values, extrapolated 25 K outside of the measured data for the value reported at 298.15 K and 46.6 K in the case of the boiling point. (2) Banks et al.,<sup>14</sup> reported that during the fractional distillation of the reaction products of phenyl dichloroarsine and acetylene, 2-chlorovinyl dichloroarsine was separated at 4 Torr at a temperature of 303.15 to 308.15 K. The Clausius-Clapeyron equation<sup>14</sup> gives a vapor pressure of 1.29 Torr at 308.15 K, only 1/3 that reported by Banks et al.,<sup>14</sup> even at the highest point of the range given for the Lewisite fraction of the distillate.

Until recently, the primary field manual (FM 3-9) used by the war fighter reported a vapor pressure for Lewisite of 0.394 Torr at 20 °C, with no reference given.<sup>15</sup> In 2005, using the data in the Samuel report,<sup>12</sup> the vapor pressure values were updated in FM 3-11.9 to 0.0271 Torr at 0 °C and 34.6 Torr at 25 °C.<sup>16</sup> Because the value reported by Samuel was 0.35 Torr at 25 °C, the datum in the field manual was almost certainly transcribed incorrectly, and we reported an erratum to the proponent. Furthermore, the data used to generate the Antoine equation in the report by Samuel<sup>12</sup> report included no observations below 50 °C, and the values in the field manual and Samuel's report<sup>12</sup> were extrapolated as much 50 °C outside of the experimental range. The American Society for Testing and Materials (ASTM) standard test method for vapor pressure recommends avoiding extrapolation over a range larger than 10 °C.<sup>17</sup>

We recently measured the vapor-pressure of Lewisite in the range of 2 to 24 °C. By combining our data with that obtained by the earlier researchers, it has been possible to show that the currently accepted vapor pressure of the compound, based on Sumner et al.,<sup>10</sup> significantly underestimates the vapor pressure of the compound.

## 2. EXPERIMENTAL PROCEDURES

### 2.1 Apparatus and Method

The system used to generate our vapor pressure data is similar to that developed at the U.S. Army Edgewood Chemical Biological Center for measuring the vapor pressures and volatility of CW agent related compounds<sup>18,19</sup> that was later adopted for the ASTM method.<sup>9</sup> The saturator cell method passes a stream of nitrogen carrier gas, obtained in our laboratory from the boil off of a bulk liquid nitrogen tank, across an alumina wicking mechanism in a glass holder filled with the analyte (Figure 2). A saturated vapor-liquid equilibrium of the analyte is obtained on the downstream side of the saturator cell with the concentration of the analyte determined by the temperature of the liquid phase.

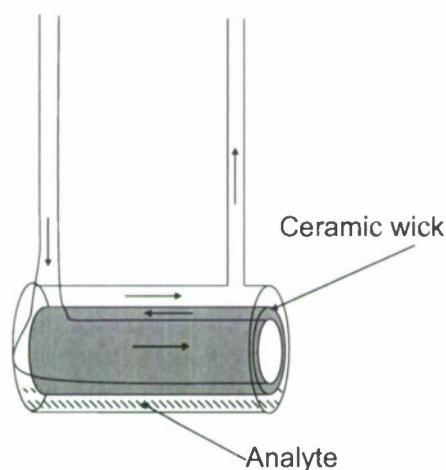


Figure 2. Schematic of Saturator Cell, Used to Generate Continuous Vapor Streams of Compounds for Determining Vapor Pressure. The arrows indicate the direction of flow of the nitrogen carrier gas.

By suspending the saturator cell in a constant temperature bath and using a known flow rate of carrier gas, the mass loss of the compound from the saturator cell is maintained at a constant rate, and the vapor pressure of the compound can be calculated using eq 1:

$$P = P_{sat} \frac{n_{analyte}}{n_{carrier} + n_{analyte}} \quad (1)$$

where  $P$  is the pure compound saturation pressure at the pressure of the saturator cell,  $P_{sat}$  is the pressure in the saturator cell,  $n_{analyte}$  is the number of moles of the analyte, and  $n_{carrier}$  is the number of moles of carrier gas. The number of moles of nitrogen ( $n_{carrier}$ ) was obtained using the ideal gas law from the carrier rate and time. The number of moles of the compound ( $n_{analyte}$ ) for eq 2 was obtained from the mass loss of the compound, which was determined by weighing the saturator cell at the beginning and end of the experiment and the formula weight of Lewisite: 207.35.

We used a Brooks (Hatfield, PA) Model 5850S mass flow controller to control the flow of carrier gas to the saturator cell, which was obtained from Glassblowers.com (Turnersville, NJ). Linearity of the S series mass flow controllers is adjusted using a second order polynomial, resulting in uncertainties of approximately 1% or better of a flow rate of  $\geq 25$  % of full scale. The constant temperature bath was a Julabo (Allentown, PA) Model F25 with a precision of 0.05 °C. The bath temperature was verified using a National Institute of Standards and Technology (NIST) traceable liquid-in-glass thermometer with an uncertainty of  $\pm 0.02$  °C. The saturator cell masses were determined using a Sartorius (Goettingen, Germany) BP211D analytical balance with a precision of  $\leq 0.1$  mg and a linearity of  $\leq 0.2$  mg. Before recording masses, the balance was checked at points above and below the mass of the saturator cell with weights traceable to NIST. After finishing an experiment, the saturator cell was dried with a lint-free paper towel and allowed to equilibrate to room temperature for a minimum of 2 hr. Prior to placing the saturator cell in the weighing chamber, we passed it across a deionizing bar (Haug, Mississauga, ON, Model EN-C). This step has proven useful even at relative humidities as high as 40 to 50 %, eliminating the slow drift in the measured mass before stabilization was achieved. We then recorded at least four readings and calculated the mean. Ambient pressure was recorded with an Omega Engineering (Stamford, CT) DPI 740 digital barometer. All flow, temperature, and mass devices and instruments were verified periodically in accordance with the U.S. Army calibration guidance.

In the past, we have successfully measured the vapor pressures of a variety of compounds, including benzene, diethyl disulfide, and 2-chloroethyl ethyl sulfide, with temperatures ranging from -12 to 23 °C.<sup>20</sup> In the case of the above three compounds, deviations from the literature values were  $< 1$  %.<sup>21</sup>

## 2.2 Feedstock

The material used to generate the vapor streams for the experiments was purified by fractional distillation to maximize the concentration of the *trans*-2-chlorovinyl isomer. The purity was determined to be  $\geq 99$  % by  $^1\text{H}$  and  $^{13}\text{C}$  nuclear magnetic resonance spectroscopy.

## 3. RESULTS AND DATA TREATMENT

### 3.1 Results

A total of five vapor pressure experiments were run at temperatures ranging from 275.05 to 297.05 K. Individual runs ranged from as short as 4 hr at the highest temperatures to as long as 25 hr for the lowest temperatures to obtain a minimum delta mass of 0.125 g. The carrier gas flow rates ranged from 75 to 100  $\text{cm}^3 \cdot \text{min}^{-1}$  (referenced to 294.26 K and 101325 Pa). The data from the trials have been summarized in Table 2. The measured vapor pressure ( $P$ ) has been provided in Torr (to be consistent with FM 3-11.9 and the historical data) and Pascal, the accepted SI unit.

Table 2. Experimental Data from Vapor Pressure Measurements of Lewisite in Our Laboratory

Temperature		Carrier rate* cm <sup>3</sup> ·min <sup>-1</sup>	Time (minutes)	Δ Mass (g)	P	
°C	K				Torr	Pa
1.9	275.05	100	1532	0.1561	0.08726	11.63
9.9	283.05	80	1424	0.2233	0.1746	23.28
14.9	288.05	75	937	0.2117	0.2675	35.66
20.9	294.05	100	261	0.1270	0.4278	57.04
23.9	297.05	100	243	0.1476	0.5361	71.47

\*Referenced to 294.26 K and 101325 Pa

### 3.2 Data Treatment

In addition to the five data points in this work, we incorporated as many of the historical vapor pressure measurements as possible. Among the historical data, S.O./R/561<sup>10</sup> provided the largest single source of vapor pressure data. The authors reported that they used a “constant boiling point method.” The lowest points were recorded to only two significant digits and appeared to be biased at the lower end of the range. We considered excluding several of the points showing the largest deviations from the computed line. The availability of multiple experimental values in the range of 0 to 50 °C from other researchers, however, rendered the problem moot when we found that including all of the data from Sumner, et al.<sup>10</sup> made little difference in the Antoine equation. Furthermore, the detailed explanation of their measurement method, including drawings of their experimental apparatus appeared to lend credence to the data.

Klosky and Stricker provided sixteen data points in their review. The sources of data<sup>4,5</sup> from the open literature were primarily concerned with the synthesis of the materials and reported reduced pressure boiling points without additional comment. Nevertheless, we were reluctant to reject individual data points without careful consideration. Klosky and Stricker reported that Baxter “and co-workers” measured the vapor pressure of Lewisite by “the air bubbling loss in weight method.”<sup>9</sup> This was likely to have been a gas saturation method similar in principle to that used in our work. Klosky and Stricker did not give experimental methods for the data points by Conant, Lewis, and Keyes.<sup>9</sup> In the case of Keyes, the temperatures of the two lowest data points were stated as having been “approximate.” We did not, however, exclude these two points from our computations.

Concerning the atmospheric pressure boiling temperature, there has been some disagreement. Herbst reported it to be ca. 203 °C.<sup>22</sup> Totalling 32 pages, the review article contains extensive physical data on 87 compounds, a description of methods of measuring the physical parameters, and methods of treating the data. Despite the length and breadth of the article, however, there are no references for any of the physical data on the compounds. Whiting<sup>2</sup> reported 196.6 °C, although this appears to have been taken from Sumner et al.,<sup>10</sup> which was extrapolated from a maximum temperature of 150 °C. Klosky and Stricker reported that Miller obtained a boiling temperature (using fractional distillation), of 190 °C at 760 Torr.<sup>9</sup> This matched the values attributed to Conant and Lewis, who reported data points at other temperatures and pressures as well.<sup>9</sup> Lewis and Perkins provided a Clausius-Clapeyron equation and four boiling temperatures at what appeared to be round values of pressure (760, 30 15, and

10 Torr), attributing the data to a report by G. P. Baxter in Chemical Warfare Communications.<sup>5</sup> If data from Lewis and Perkins<sup>5</sup> are plotted the Clausius-Clapeyron equation given is not reproduced, which predicts a boiling temperature of 172.5 °C at 760 Torr, vis-à-vis the atmospheric temperature boiling temperature of 190 °C that appeared in the article. It appeared likely, therefore, that the value reported by Miller, Conant, and Baxter,<sup>9</sup> and Lewis and Perkins<sup>5</sup> were obtained experimentally, and the boiling temperature of Lewisite at 101325 Pa is at or close to 190 °C. The measurement was included in the pooled data that we used to compute the vapor pressure curve.

The experimental values of vapor pressure and their sources are compiled in Table 3. Pressure is stated in Torr to be consistent with that reported by the original authors and to avoid in a number of cases a precision not necessarily implicit in the data (i.e., 2.3 Torr  $\approx$  306.6 Pa).

The data points shown in Table 2 were combined into matrix form and MatLab was then used to do the least squares fit of the Antoine equation (2):

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

where  $T$  is in K. Table 4 gives the values of the constants in the Antoine equation derived from the least squares fit of the data in Table 2, as well as the parameters for calculating the vapor pressure in Pascal. Figure 3 is a plot of the experimental data points, indicated by source, as well as the fitted line from the least squares fit of the data, with the pressure in Torr. Figure 4 is a plot of the “best fit” line with the pressure in Pascal.

Table 3. Data Used to Derive Antoine Vapor Pressure Coefficients for Lewisite

T/K	Our work	Sumner	Baxter	Price	Keyes	P/Torr Lewis	Conant	Redemann	Mohler	Mann	Gibson
273.15			0.087								
275.05	0.08726										
283.05	0.1746										
288.05	0.2675										
288.15			0.289								
293.15								0.393			
294.05	0.4278										
297.05	0.5361										
298.15			0.613		0.78						
308.15			1.233								
313.15								1.60			
323.15		2.3									
328.15		3.4									
330.15					2.8						
333.15		4.6									
338.15		6.2									
343.15		8.1									
348.15		10.6									
349.25											10
349.65										12.5	
353.15		13.9									
355.15										16.5	
357.15							20				
358.15		17.9									
363.15		22.8									
366.15				26, 30					26		
368.15		28.8									
369.15					24.3						
371.15						30					
373.15		36.1									
378.15		45.1									
383.15		55.7									
388.15		67.5									
393.15		81									
398.15		96.3									
403.15		113.7									
408.15		136.9									
413.15		163.2									
418.15		194.1									
423.15		228									
459.15									724		
463.15						760	760				

Table 4. Values of the Constants in the Antoine Equation for Calculating the Pressure of Lewisite in Torr and Pascal

Antoine Constant	Value of the Constant in the Indicated Pressure Units	
	Torr	Pa
a	17.7447	22.6375
b	4711.9425	4498.9425
c	-40.9426	-40.9426

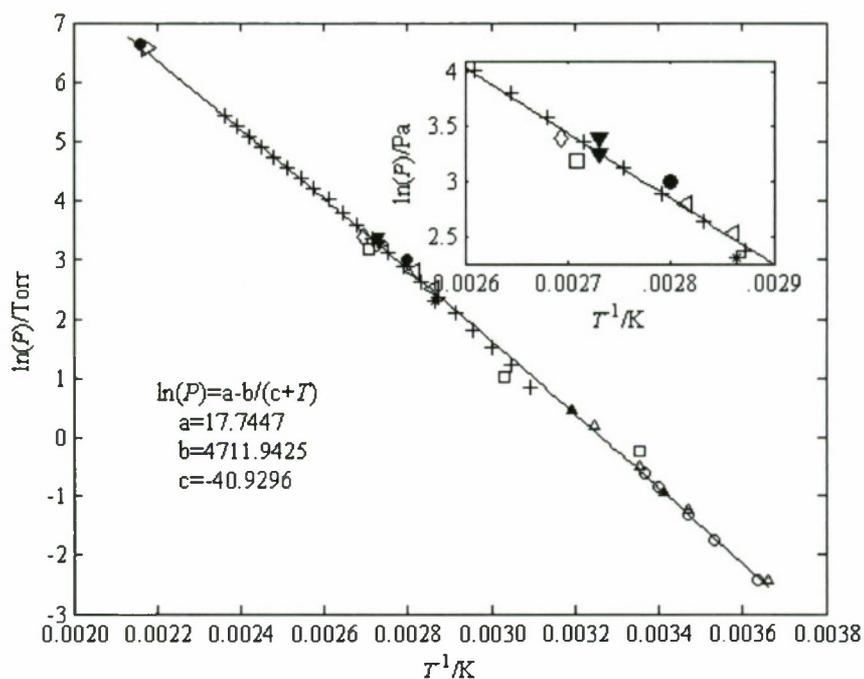


Figure 3. Vapor Pressure of Lewisite I from Multiple Sources: Conant, ●; Sumner, +; Lewis, ◇; Keyes, □; Price, ▼; Baxter, △; Redemann, ▲; Mohler, ◁; Mann, ▷; Gibson, \*; this work, ○; and best fit, —. The inset shows the region between  $T \approx 345$  to  $385$  K.

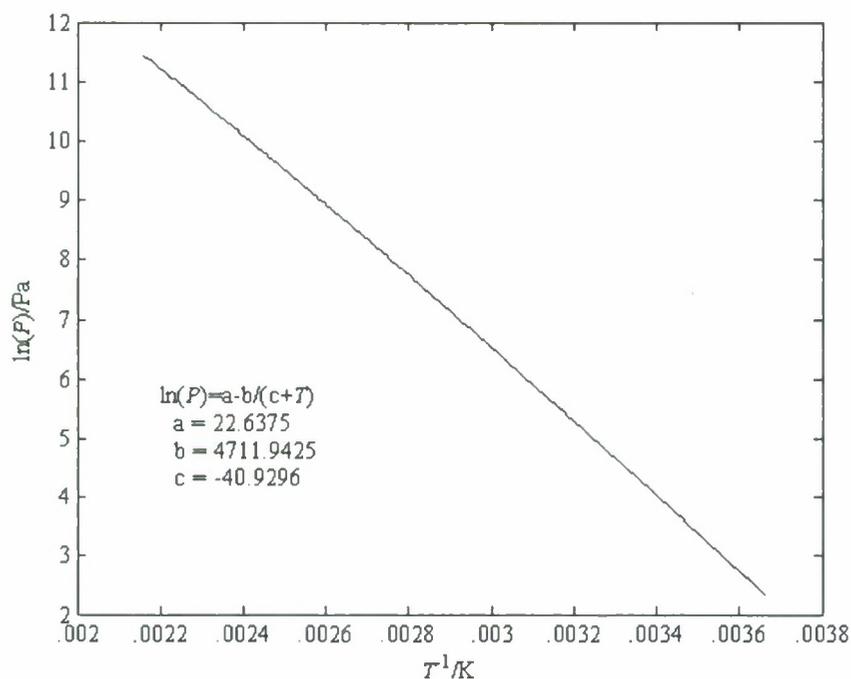


Figure 4. Vapor Pressure of Lewisite I and Values of the Constants for the Antoine Equation for Pressure in Pascal

Measured and calculated values of the vapor pressure of Lewisite from our work, as well as the fractional deviations from the calculated values, are shown in Table 5. Table 6 gives calculated values of the vapor pressure of Lewisite from the Antoine constants derived from this report vis-à-vis the calculated values using the constants from the Samuel report.

Table 5. Measured and Calculated Values of the Vapor Pressure of Lewisite and Fractional Deviations

T/K	P/Torr		$(P_{meas} - P_{calc}) / P_{calc} \times 100$
	Measured	Calculated	
275.05	0.08726	0.09231	-5.48
283.05	0.1746	0.1795	-2.74
288.05	0.2675	0.2661	0.52
294.05	0.4278	0.4182	2.29
297.05	0.5361	0.5202	3.06

Table 6. Calculated Values of the Vapor Pressure of Lewisite I at Several Temperatures. The last column shows the values of the vapor pressure derived from the equation in the Samuel report.<sup>12</sup>

<i>T</i> /K	<i>t</i> / °C	<i>P</i> /Pa (This work)	<i>P</i> /Torr (This work)	<i>P</i> /Torr (Samuel)
273.15	0	10.35	0.0783	0.0271
293.15	20	52.40	0.391	0.22
298.15	25	75.47	0.563	0.35
465.01*	191.86	101335	760.06	**

\*Calculated boiling point

\*\*Estimated boiling point 195.9 °C

#### 4. CONCLUSIONS

The physical properties data of the vesicant chemical warfare Lewisite currently disseminated to the war fighters significantly underestimates the vapor pressure of the compound in the ambient temperature range. The vapor pressure of 2-chlorovinyl dichloroarsine (Lewisite I) was measured at five points between 1.9 and 23.9 °C using a saturator cell method. By combining our experimental values with data obtained by earlier researchers, we have been to update the Antoine constants used to predict the vapor pressure of Lewisite, thus improving the accuracy of the predictions of its volatility for vapor generation in the laboratory and hazard predictions in the tactical environment. The calculated vapor pressure of Lewisite is 52.4 Pa at 20 °C and 75.47 Pa at 25 °C.

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