



# EDGEWOOD CHEMICAL BIOLOGICAL CENTER

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## VAPOR PRESSURE OF METHYL SALICYLATE AND N-HEXADECANE

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## PREFACE

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# VAPOR PRESSURE OF METHYL SALICYLATE AND N-HEXADECANE

## 1. INTRODUCTION

Methyl salicylate (MeS) and n-hexadecane are of potential interest to the chemical warfare defense community as simulants for the chemical warfare agents, bis(2-chloroethyl) sulfide (HD) and O-ethyl-S-(2-diisopropylaminoethyl) methylphosphonothiolate (VX), respectively. Vapor pressure similarities make these materials potential simulants for filter testing and environmental persistence studies.

Original vapor pressure data for MeS were reported as preliminary by Ramsay and Young at temperatures between 68.7 and 222.4 °C, corresponding to vapor pressures between 300 and 101500 Pa.<sup>1</sup> Later, Matthews et al. published an extensive data set for MeS between 81.0 and 220.5 °C that, although a few percent higher than the data of Ramsay and Young, agree substantially with the earlier data.<sup>2</sup> Based on the regularity of their deviation from correlated values, the vapor pressure values reported by Guenther between 78 and 225 °C do not appear to be experimental data.<sup>3</sup> To our knowledge, no data has been published for values lower than Ramsay's lowest value near 300 Pa. However, a recent compilation extrapolates MeS data to as low as 1 Pa.<sup>4</sup>

Vapor pressure data for n-hexadecane have been reported by a number of workers at temperatures between 22.1 and 287.5 °C, corresponding to vapor pressures between 0.3 and 101325 Pa.<sup>5-10</sup> The literature data for n-hexadecane are consistent over this very wide range. This report extends the experimental data range for both compounds to lower values of pressure and temperature.

This report provides new vapor pressure correlation equations for liquid MeS between its normal boiling and melting points and for solid and liquid n-hexadecane. Heats of vaporization are calculated over the experimental temperature range for both compounds in the liquid state, and heats of sublimation and fusion are derived for solid n-hexadecane.

## 2. EXPERIMENTAL

MeS [Chemical Abstracts Service (CAS) no. 119-36-8, >99%] and n-hexadecane (CAS no. 544-76-3, >99%) were purchased from Aldrich Chemical Co., Inc. (Milwaukee, WI) and used without purification. Vapor saturation methodology and data analysis techniques have been described in detail previously.<sup>11</sup> The only variation used in the present work was to heat-trace the saturator effluent lines to allow measurement of data at temperatures as high as 70 °C. Saturator data were measured using the Dyna-Therm Corporation (Houston, TX) model 900 purge and trap and Hewlett-Packard Company (Palo Alto, CA) model 5890 gas chromatographic (GC) equipment and methodology, and as before, the GC was equipped with a flame-ionization detector. Saturator calibration and data collection and analysis methodology were the same as used previously. The vast majority of the present saturator data were obtained using a flow rate of 10 standard cubic centimeters per minute (sccm) through the saturator tube.

Saturator flow rates as high as 300 sccm were also investigated and had no apparent effect on the amount of analyte sampled by the analysis system, confirming steady-state operation. The insensitivity of the data to flow rates verifies that the data were obtained at conditions within the range of liquid-vapor equilibrium of the analyte under the present conditions.

Carrier gas used in this work was oil-free house air with a dew point of  $\leq 50$  °C. As before, the mass flow controllers were calibrated using a calibrator standard and are believed to be accurate to less than 1% of the full-scale value. No purity corrections were made for either compound, principally due to their initial high purity. It has also been observed that the Raoult's Law correction used previously for liquids nullifies itself when the same sample is used to calibrate and measure saturator vapor pressure data, as was done in the present work.

### 3. RESULTS

#### 3.1 Methyl Salicylate

Vapor pressure data measured in this work for MeS are listed in Table 1 and plotted in Figure 1 along with selected literature values. The lowest value reported here is about 1 °C below the freezing point of MeS, and it is not clear whether the data should be considered as a sub-cooled liquid or solid phase data point. Since the point is so close to the freezing point, it makes little difference, however that data point has not been used to correlate the data. Antoine correlation equations were derived in two common formats based on the data of Ramsay and Young and the new data presented in this report. These equations are provided in Table 2. Temperature-dependent values for the vapor pressure, volatility or saturation concentration, and heat of vaporization of MeS at selected temperatures are listed in Table 3. The extrapolated normal boiling point based on these data and the correlation is 220.91 °C.

Table 1. Experimental Vapor Pressure Data for Methyl Salicylate

| T     |       | Experimental VP |         | Calculated VP/Pa |          | Difference <sup>†</sup> |
|-------|-------|-----------------|---------|------------------|----------|-------------------------|
| °C    | K     | Pa              | Torr    | Pa               | Torr     | %                       |
| -9.6* | 263.5 | 0.543           | 0.00407 | 0.5039           | 0.003780 | 7.76                    |
| 0.4   | 273.5 | 1.57            | 0.0118  | 1.501            | 0.01126  | 4.60                    |
| 10.4  | 283.5 | 4.09            | 0.0307  | 4.043            | 0.03032  | 1.17                    |
| 20.4  | 293.5 | 9.79            | 0.0734  | 9.980            | 0.07486  | -1.91                   |
| 30.4  | 303.5 | 21.7            | 0.163   | 22.83            | 0.1712   | -4.95                   |

\*Data Measured Below the Melting Point; Excluded from Correlation

<sup>†</sup> $100 \cdot (P_{\text{expt}} - P_{\text{calc}}) / P_{\text{calc}}$

Note: Calculated values for liquid phase data were obtained using Antoine Coefficients shown in Table 2.

Table 2. Antoine Correlation Equations for MeS in Two Common Units Systems

|   |          |
|---|----------|
| $\ln(P)/\text{Pa} = a - b/(c + T_K)$                  |          |
| a   | 21.7510  |
| b   | 4323.80  |
| c   | -71.1907 |
| $\log(P)/\text{Torr} = A - B/(C + T_C)$               |          |
| A   | 7.32143  |
| B   | 1877.80  |
| C   | 201.959  |
| $T_K = 265 \text{ to } 493; T_C = -8 \text{ to } 220$ |          |

Table 3. Calculated Vapor Pressure, Volatility ( $C_{\text{sat}}$ ), and Heat of Vaporization for MeS at Selected Temperatures

| $T_C$  | VP<br>(Pa) | VP<br>(Torr) | $C_{\text{sat}}$<br>( $\text{mg}/\text{m}^3$ ) | $\Delta H_{\text{vap}}$<br>(kJ/mole) |
|--------|------------|--------------|--|--------------------------------------|
| -8     | 0.5820     | 0.004365     | 40.17  | 67.18                                |
| 0      | 1.407      | 0.01056      | 94.29  | 65.76                                |
| 10     | 3.864      | 0.02899      | 249.7  | 64.15                                |
| 20     | 9.688      | 0.07266      | 604.7  | 62.71                                |
| 25     | 14.88      | 0.1116       | 913.3  | 62.04                                |
| 30     | 22.44      | 0.1683       | 1354   | 61.40                                |
| 40     | 48.48      | 0.3636       | 2833   | 60.22                                |
| 50     | 98.52      | 0.7390       | 5579   | 59.13                                |
| 60     | 189.7      | 1.423        | 10420  | 58.14                                |
| 70     | 348.0      | 2.610        | 18560  | 57.23                                |
| 80     | 611.7      | 4.588        | 31690  | 56.40                                |
| 100    | 1689       | 12.67        | 82820  | 54.90                                |
| 120    | 4111       | 30.83        | 191300   | 53.61                                |
| 140    | 9016       | 67.63        | 399400   | 52.48                                |
| 160    | 18130      | 136.0        | 766000   | 51.48                                |
| 180    | 33890      | 254.2        | 1369000  | 50.60                                |
| 200    | 59530      | 446.5        | 2302000  | 49.81                                |
| 220    | 99110      | 743.4        | 3678000  | 49.10                                |
| 220.91 | 101325     | 760          | 3753000  | 49.07                                |

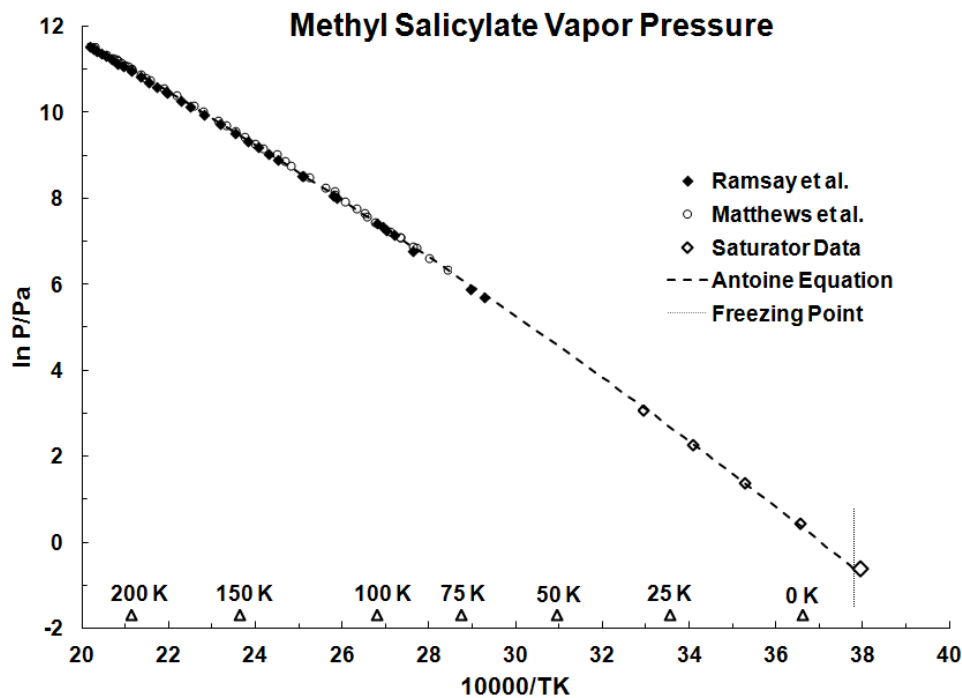


Figure 1. Vapor pressure data for MeS.

Note: Filled diamonds, Ref. 1; open circles, Ref 2; open diamonds, this work. Large open diamond is below the freezing point of MeS.

### 3.2 n-Hexadecane

The vapor pressure data measured in this work using the saturation method for n-hexadecane are listed in Table 4 and plotted in Figure 2 along with selected data from previous literature. Antoine correlation equations were derived in two common formats based on the literature data<sup>5-10</sup> and the new data listed in Table 4. These equations are provided in Table 5. Table 6 lists the Clausius-Clapeyron equations for n-hexadecane based on the two data points below the freezing point and the vapor pressure at the freezing point based on the liquid phase data. These values should be considered preliminary due to the sparseness of the data. Temperature-dependent values for the vapor pressure, volatility or saturation concentration, and heat of vaporization of MeS are listed in Table 7.

Table 4. Experimental Vapor Pressure Data for n-Hexadecane

| Temperature (°C) | Experimental VP (Pa) | Calculated VP (Pa) | Difference (%) |
|------------------|----------------------|--------------------|----------------|
| 0.4*             | 0.0028               | 0.00847            | NA             |
| 11.6*            | 0.029                | 0.0380             | NA             |
| 22.1             | 0.142                | 0.135              | 4.9            |
| 31.2             | 0.366                | 0.366              | 0.00           |
| 41.6             | 1.06                 | 1.05               | 0.96           |
| 51.5             | 2.44                 | 2.62               | 7.4            |
| 60.9             | 5.57                 | 5.84               | 5.0            |
| 70.4             | 11.4                 | 12.4               | 9.3            |

\*Data Measured Below Freezing Point; Data not used in Correlation.

Note: Calculated values for liquid phase data were obtained using Antoine Coefficients shown in Table 5.

Table 5. Antoine Correlation Equations for n-Hexadecane in Two Common Units Systems

|   |          |
|---|----------|
| $\ln(P)/\text{Pa} = a - b/(c + T_K)$                  |          |
| a   | 22.1703  |
| b   | 5005.5   |
| c   | -87.9567 |
| $\log(P)/\text{Torr} = A - B/(C + T_C)$               |          |
| A   | 7.5035   |
| B   | 2173.86  |
| C   | 185.193  |
| $T_K = 291 \text{ to } 558; T_C = 18 \text{ to } 285$ |          |

Table 6. Preliminary Clausius-Clapeyron Equations for Solid n-Hexadecane in Two Common Units Systems

|   |         |
|---|---------|
| $\ln(P)/\text{Pa} = a - b/(c + T_K)$                |         |
| a   | 50.0411 |
| b   | 15286.8 |
| c   | 0       |
| $\log(P)/\text{Torr} = A - B/(C + T_C)$             |         |
| A   | 19.6077 |
| B   | 6638.98 |
| C   | 273.15  |
| $T_K = 273 \text{ to } 291; T_C = 0 \text{ to } 18$ |         |

Table 7. Calculated Vapor Pressure, Volatility ( $C_{\text{sat}}$ ), and Heat of Vaporization for n-Hexadecane at Selected Temperatures

| $T_c$  | VP<br>(Torr) | VP<br>(Pa) | $C_{\text{sat}}$<br>( $\text{mg}/\text{m}^3$ ) | $\Delta H_{\text{vap}}$<br>(kJ/mole) |
|--------|--------------|------------|--|--------------------------------------|
| 20     | 0.0008116    | 0.1082     | 10.05  | 84.94                                |
| 25     | 0.001450     | 0.1933     | 17.66  | 83.74                                |
| 30     | 0.002521     | 0.3362     | 30.20  | 82.59                                |
| 40     | 0.007083     | 0.9444     | 82.13  | 80.48                                |
| 50     | 0.01822      | 2.430      | 204.8  | 78.57                                |
| 60     | 0.04341      | 5.788      | 473.2  | 76.83                                |
| 70     | 0.09662      | 12.88      | 1022   | 75.25                                |
| 80     | 0.2024       | 26.99      | 2081   | 73.80                                |
| 90     | 0.4019       | 53.59      | 4019   | 72.47                                |
| 100    | 0.7606       | 101.4      | 7401   | 71.25                                |
| 120    | 2.402        | 320.3      | 22190  | 69.06                                |
| 140    | 6.587        | 878.2      | 57890  | 67.18                                |
| 160    | 16.07        | 2142       | 134700   | 65.53                                |
| 180    | 35.56        | 4740       | 284900   | 64.08                                |
| 200    | 72.44        | 9658       | 555900   | 62.79                                |
| 220    | 137.6        | 18340      | 1013000  | 61.65                                |
| 240    | 246.0        | 32790      | 1741000  | 60.62                                |
| 260    | 417.4        | 55650      | 2843000  | 59.69                                |
| 280    | 676.9        | 90240      | 4443000  | 58.84                                |
| 285.06 | 760          | 101325     | 4944000  | 58.64                                |

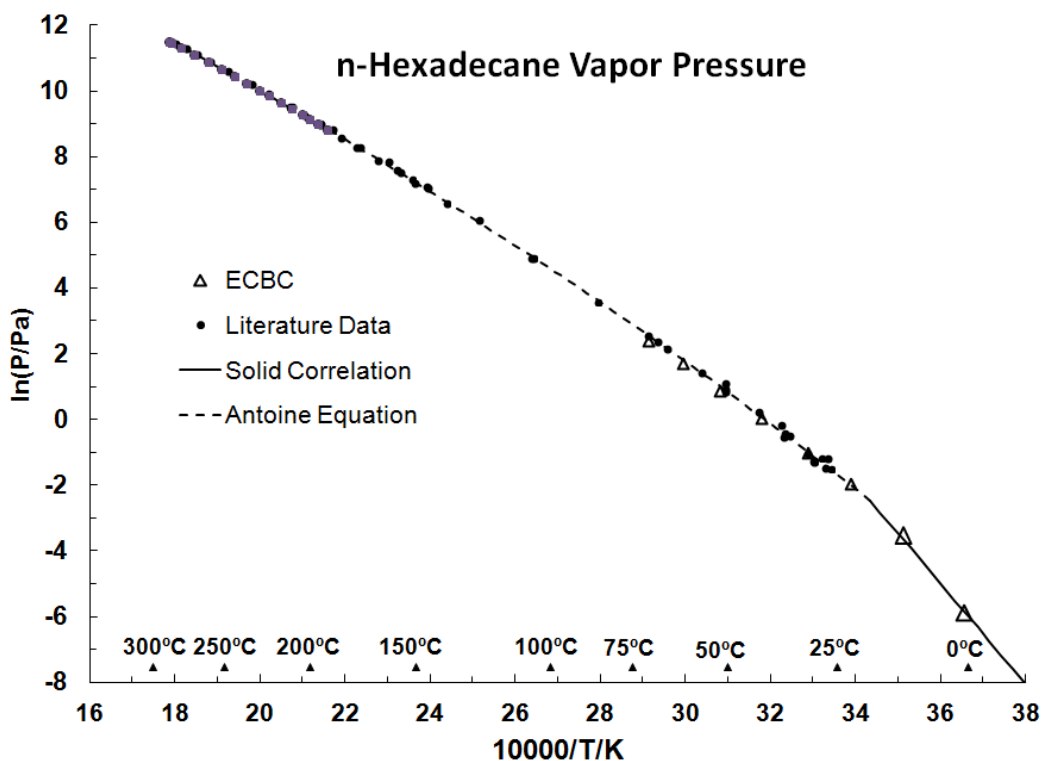


Figure 2. Vapor pressure data for n-hexadecane.

Note: U.S. Army Edgewood Chemical Biological Center (ECBC). Filled circles, Refs 5-10; open triangles, this work) and Antoine correlation determined from liquid phase data shown and Clausius-Clapeyron correlation determined from solid phase data.

#### 4. DISCUSSION

Respiratory protection against medium- and low-volatility nerve agents such as HD and VX is not a significant concern for personnel wearing standard activated-carbon-based military respiratory protection devices or inside citadels (e.g., armored vehicles, shelters) equipped with collective protection systems due to the extremely efficient filtration characteristics of those systems, particularly for materials with physical properties similar to these chemical warfare agents. Qualification of advanced individual and collective protection filtration technology systems (e.g., advanced adsorbents, catalytic oxidation, and pressure-swing adsorption (PSA), requires validation that the advanced filtration systems provide the required level of protection while operating within the constraints of host systems and do not lead to other safety of use issues. For reaction-based technologies (e.g., catalytic oxidation), it is difficult to identify surrogate chemicals to use for validation, and the accepted approach has been to perform studies using chemical agents only in the very early stages of lab-scale development, giving way to surrogates in later testing that might be performed under full-scale conditions. For adsorption-based processes (e.g., PSA), the use of surrogate chemicals is more suitable since the relationship

between physical properties, principally vapor pressure and solubility, and filtration performance is well understood. For the latter, it becomes advantageous to have vapor pressure data to select appropriate surrogates for validation studies. The current work is aimed at identifying suitable surrogate chemicals for validation studies by measuring vapor pressure data in the ambient temperature range.

Literature data for MeS is limited to temperatures above 68 °C. Extrapolation of high-temperature data to lower temperatures is frequently performed, but can lead to errors, especially as the extrapolation lengthens. The liquid phase saturator data listed in Table 1 were combined with the data of Ramsay and Young and the data of Matthews et al. to derive the Antoine equation correlation shown in Table 2. The resulting correlation accurately describes all of the liquid phase data, producing an average difference between experimental and calculated values of less than 1.8% with no single variance exceeding 5.6%. The data of Matthews et al. are quite similar to those of Ramsay and Young, although 3.7–8.1% higher than estimated based on a correlation of Ramsay and Young's data for 40 of the 43 data points listed.

The lowest data point measured for MeS in the current work was just below its freezing point and was not used for correlation purposes. The experimental vapor pressure value for that point was higher than the correlated value, suggesting that the data point is appropriate for super-cooled liquid rather than the solid phase, however, we were unable to verify that supposition. The vapor pressures of MeS and HD in the ambient temperature range are the same within current experimental error.<sup>12</sup> The extrapolated normal boiling point for HD is 217.8 °C, which is 3.1 °C lower than the estimated value of MeS.

It is informative to compare MeS vapor pressure values predicted using the literature sources to the ambient temperature data. We have found that the correlation proposed by Matthews agrees within experimental error with the current ambient temperature data, while an Antoine correlation based solely on Ramsay and Young's data predicts values for all of the ambient temperature data that far exceed the error limits of our measured data. For example, the value at 0.4 °C predicted by correlating Ramsay and Young's data (0.95 Pa) is about 60% of our experimental value (1.57 Pa) and is clearly outside the current error limits for that point. This value is compared to that predicted using Matthews' correlation, 1.488 Pa at 0.4 °C, which is within 5.5% of our experimental measurement. The Antoine equation fit to the saturator data above the melting point and the data presented by previous workers<sup>1,2</sup> has been performed, and the results are shown in Figure 1. The average difference between the saturator data and the Antoine correlation predictions is less than 5%. The residual differences between measured and calculated error for the saturator data are scattered above and below the calculated values indicating a random error, most likely attributable to the temperature stability of the apparatus used to obtain these measurements.

n-Hexadecane was chosen for evaluation based on its vapor pressure similarity to VX, however, no data are available in the literature below 28 °C, owing to its low volatility. The present work extends the range of measured vapor pressure data for n-hexadecane by over two



orders of magnitude to lower pressure and covers the entire liquid phase range and a majority of the ambient temperature range. The vapor pressure of n-hexadecane is approximately twice that of VX over the liquid range; this difference is slightly less when the comparison is made on the basis of saturation concentration (or volatility,  $\text{mg/m}^3$ ) instead of vapor pressure owing to the higher molecular weight of VX.

Comparison of the Antoine equation derived using new saturator data in combination with data from references 5-10 to the correlation proposed by Camin et al. based on data measured between 190–287 °C reveals that the equation proposed by Camin significantly underestimates the vapor pressure values at lower temperatures, by more than a factor of 2 in several cases. On the other hand, the current Antoine equation reproduces the values measured by Ruan et al. at temperatures between 28–70.5 °C with an average difference of about 6%.

The two lowest temperature data points for n-hexadecane were below the freezing point and have been used in combination with the extrapolated vapor pressure of liquid n-hexadecane at the freezing point to derive a Clausius-Clapeyron correlation for the solid phase vapor pressure. This correlation enables estimation of the heat of fusion of n-hexadecane by the difference of the heat of evaporation of the liquid and heat of sublimation of the solid at the melting point from the change in slope of the standard vapor pressure plot shown in Figure 2. The heat of sublimation estimated from the solid phase correlation is 127.10 kJ/mole. The heat of vaporization at the melting temperature for liquid MeS is 85.45 kJ/mole, and the resulting heat of fusion is 41.65 kJ/mole.

## 5. CONCLUSIONS

New vapor pressure data have been measured in the ambient temperature range for n-hexadecane and MeS using vapor saturation methodology.

The data reported here extend the range of measured data for MeS into the ambient temperature range and nearly three orders of magnitude to lower pressure. The vapor pressure of MeS is the same as that of HD within the limits of current experimental error.

The vapor pressure of n-hexadecane reported here extends the experimental range by more than two orders of magnitude to lower pressure than previously reported. The vapor pressure of n-hexadecane is about twice that of VX over the liquid range. By measuring data for solid n-hexadecane, we have been able to calculate its heats of vaporization, sublimation, and fusion.

The ambient temperature data are consistent with previously reported data for both compounds and confirm the validity of both.

Based on current data, MeS and n-hexadecane can be considered as potential non-reactive vapor pressure simulants for HD and VX, respectively.

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## ACRONYMS AND ABBREVIATIONS

|      |   |
|------|---|
| CAS  | Chemical Abstracts Service                                  |
| ECBC | U.S. Army Edgewood Chemical Biological Center               |
| GC   | gas chromatograph   |
| HD   | sulfur mustard, bis(2-chloroethyl) sulfide                  |
| MeS  | methyl salicylate   |
| NMR  | nuclear magnetic resonance                                  |
| PSA  | pressure-swing adsorption                                   |
| sccm | standard cubic centimeters per minute                       |
| VX   | O-ethyl-S-(2-diisopropylaminoethyl) methylphosphonothiolate |





