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VAPOR PRESSURE MEASUREMENTS OF SOME CHEMICAL AGENTS USING DIFFERENTIAL THERMAL ANALYSIS. PART III

Frederic Belkin, et al

Edgewood Arsenal
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O,O'-Diethyl methylphosphonothioate	Dimethyl trisulfide	GA
Heat of vaporization	Volatility	GD

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Vapor pressure data were obtained for GA, GD, EA 3580B, dimethyl trisulfide, and O,O'-diethyl methylphosphonothioate by use of a modified differential thermal analysis (DTA) method. The data were fitted to the Antoine vapor pressure equation and volatilities and heats of vaporization were calculated.

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PREFACE

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VAPOR PRESSURE MEASUREMENTS OF SOME CHEMICAL AGENTS USING DIFFERENTIAL THERMAL ANALYSIS. PART III

I.   INTRODUCTION.

During the use of common isothermal vapor-pressure methods such as the isoteniscope, it is difficult to measure vapor pressure for many chemical compounds at elevated temperatures because many of these compounds are too unstable to withstand elevated temperatures for the several minutes to hours required for the measurements.

Previous reports[1-5] on vapor pressure measurements using differential thermal analysis (DTA) showed the method to be reliable for obtaining vapor pressure data. Experiments[1,2] have shown that the DTA method could be used successfully for measuring the vapor pressures of a variety of chemical agents at higher experimental temperatures than with other methods. This report presents vapor pressure data for a series of compounds measured using the DTA method.

In order to attain some insight into the effect of impurities on the boiling point, as measured by this technique, work was performed with solutions having ideal solvent properties. This was accomplished by use of mixtures of benzene and toluene.

II.   PROCEDURES.

A.   Experimentation.

The apparatus previously described[1,2] is a modified Model 900 differential thermal analyzer.* The experimental procedures were very similar to those used for normal operation of the DTA apparatus[6] except for control and measurement of the cell pressure. For pressures above 15 torr, a Cartesian Diver manostat regulated the pressure while measurement was accomplished with a Wallace and Tiernan Model FA 187 manometer. Lower pressures were controlled using an adjustable continuous-leak valve and cell pressure was measured using a size "D" McLeod gage (pressure range 0 to 15 torr).

An electronic manometer was used in place of both the mercurial manometer and McLeod gage for studies with compounds GA and GD. This manometer** was also used to measure pressures below 20 torr during studies with compound EA 3580. All other pressures were measured with the mercury manometer.

The electronic manometer is accurate to ±0.02% of the reading plus 0.03% of full scale on the 0 to 1000-torr scale, which is used for all readings above 300 torr. The accuracy is ±0.1% of the reading plus 0.03% of the full scale on all other scales.

To test the effect of the presence of high- and low-boiling impurities on the measured boiling point, mixtures of reagent grade benzene and toluene were used. A number of solutions of up to 19 mole percent of each component in the other were prepared gravimetrically. Each mixture was run in duplicate on the DTA apparatus to determine the boiling point of the mixture at atmospheric pressure. All results were then corrected to a pressure of 760 torr and compared to published data for the system.

B.   Sample Preparation.

The samples of GA and GD were purified by vacuum distillation. The GA was distilled at 0.35 torr with a head temperature of 49° to 52°C. GD was distilled at a pressure of 1.7 torr with a head temperature of 46° to

*E. I. DuPont de Nemours and Company, Wilmington, Delaware.

**Datametrics, Inc., Waltham, Massachusetts.

48.7°C. The EA 3580 was purified by triple recrystallization from hexane. The remaining compounds were used without further purification.

C.   Calculations.

Using a computer program developed by Penski and Latour,[7] and modified to be compatible with the Univac 1108, the experimental data obtained for each compound were fitted to the Antoine vapor pressure equation

$$\log P = A - B/(C + t)$$

where

P = vapor pressure in torr

t = temperature in degrees centigrade

A, B, C = constants

From the vapor pressure data, other physicochemical values were calculated. The computer was programmed to provide the heat of vaporization and volatility for each compound.[1] The standard deviation was calculated for each Antoine equation.[1,2,7]

III.   RESULTS.

The chemical purities of the compounds studied were obtained and the results of the analyses are presented in table 1.

Table 1.   Chemical Purity of the Samples Studied

Compound	Purity	Method of analysis
	%*	
GA	92.1	Wet method
	96	Nuclear magnetic resonance
GD	92.4	Wet method
	97	Nuclear magnetic resonance
EA 3580	99.7	Wet method
Me_2S_3	96	Nuclear magnetic resonance
$MePS(OEt)_2$	97.1	Gas chromatography

*NMR-atom %, wet chemical-wt %.

NOTE: In this and other tables, Me is used to mean CH_3 and Et is used to mean C_2H_5.

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Table 2 provides a compilation of the constants for the Antoine equations for the compounds measured. In addition, the experimental temperature range, as well as the normal boiling point is provided. The boiling point was obtained by an extrapolation using the Antoine equation. Also tabulated are the standard deviations of the experimental data from values calculated using the Antoine equation. Line plots constructed from the equations are shown in figure 1. Volatilities and heats of vaporization were calculated and these values are provided at selected temperatures in table 3.

Table 2. Vapor Pressure Data

Compound	Antoine constants			Experimental range	Boiling point*	Standard deviation, $\times 10^{-2}$
	A	B	C			
				°C		log (torr)
GA	7.2569	1990.30	211.23	90–152	244	2.1
GD	6.9623	1595.25	190.78	68–190	200	0.8
FA 3580	6.9436	2128.23	145.23	208–286	379	0.9
Me$_2$S$_3$	7.0408	1662.57	223.93	60–175	176	0.5
MePS(OEt)$_2$	7.6088	1993.86	229.98	82–190	192	1.6

*The temperature calculated from the Antoine equation at P = 760 torr.

Table 3. Calculated Physicochemical Properties of the Samples Studied

| Compound	Temperature	Vapor pressure	Volatility	Heat of vaporization
	°C	torr	gm/cu m	Kcal/mole
GA	50*	0.43	3.50	13.94
	100	7.28	50.8	13.09
	150	55.87	343.6	12.50
	200*	261.3	1437.0	12.06
GD	50*	2.17	19.6	13.15
	100	29.93	234.3	12.02
	150	191.0	1319.0	11.26
FA 3580	150*	0.54	5.6	20.01
	200*	6.01	55.9	18.30
	250	36.20	304.4	17.07
	300*	145.7	1118.0	16.14
Me$_2$S$_3$	25*	2.30	15.6	10.92
	50*	9.37	58.7	10.59
	100	83.97	439.4	10.10
	150	393.2	1882.0	9.74
MePS(OEt)$_2$	50*	3.07	25.6	12.16
	100	36.85	266.4	11.67
	150	229.9	1466.0	11.32

*Extrapolated values.
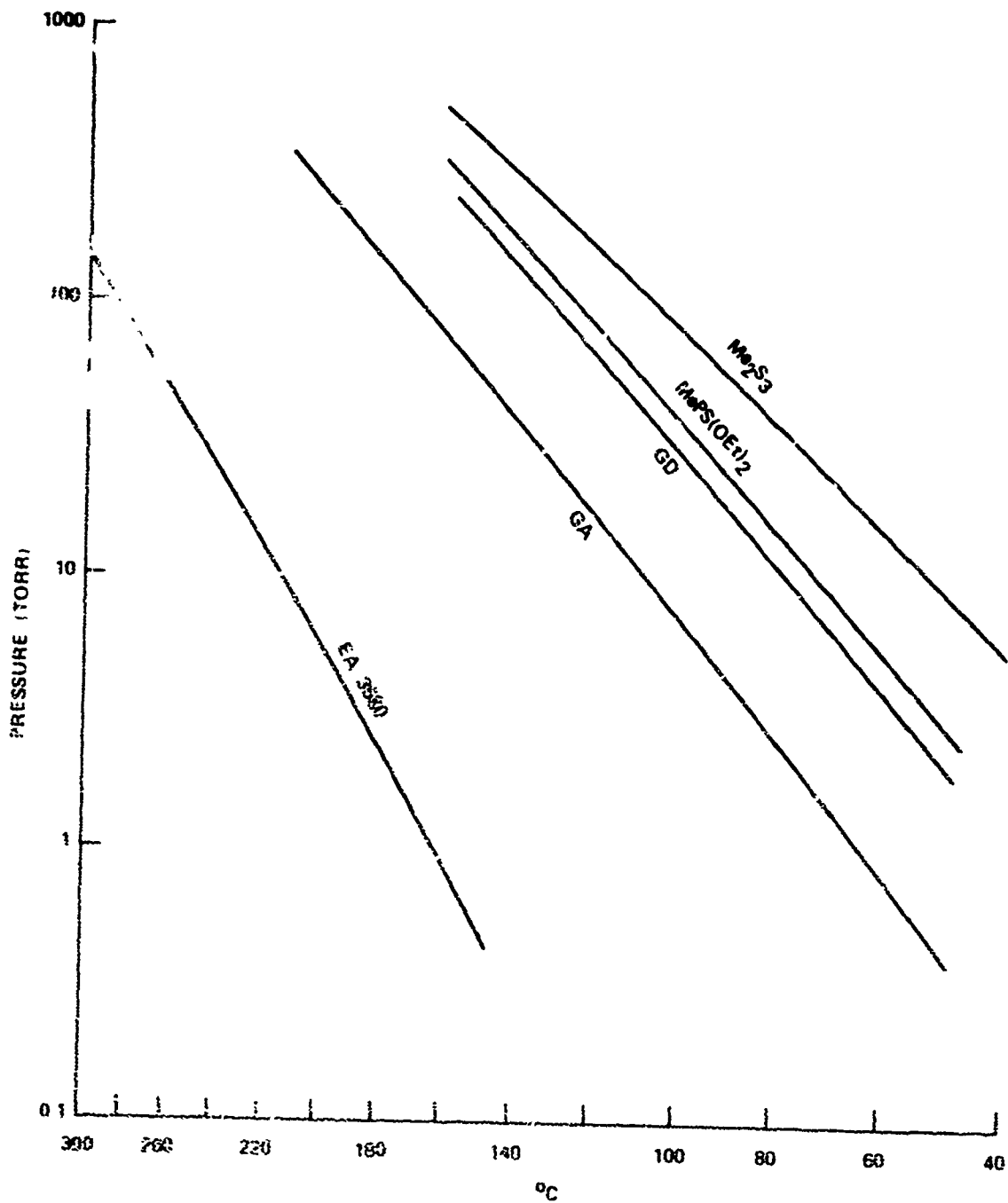
Figure 1. Log P Versus 1/T Curves for Data Given in Table 4

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Vapor pressure determinations by various methods have been reported in the literature for the five compounds listed in this report. There is an overlap of four GD vapor-pressure points between 68° and 95°C with a vapor pressure study by Fielder.* Comparison of his data with those obtained by this method shows a maximum deviation of 3.7% between the two sets of results. The extrapolated DTA value for GA, 0.60 torr at 55°C, is in good agreement with the value of 0.53 ±0.04 torr obtained from the transference method.[8]

Two sets of vapor pressure data exist for EA 3580B**[9] as a liquid. In both studies, 90°C was the highest temperature of vapor pressure measurement. The extrapolated-DTA vapor pressure value for EA 3580B at 90°C is 7.9 microns (this report) versus 7.8 and 11.7 microns for the other sets of vapor pressures obtained by the Knudsen method.

There is one vapor pressure point reported in the literature for MePS(OEt)$_2$. This value,[10] 5 torr at 57° to 59°C, is in good agreement with the calculated DTA value of 58.6°C at 5 torr.

The vapor pressure of methyl trisulfide has been previously measured by other workers[11,12] during vacuum distillations. At 15 torr, the distillation temperature was 58.4° to 59°C compared to 59.6°C for the DTA value. Another distillation value at 13 torr was 56° to 57°C which is in good agreement with the calculated DTA value of 56.6°C.

The boiling point data obtained on the mixtures of benzene and toluene are provided in table 4 and a plot of the experimental data points versus the calculated solution boiling points (solid line) provided by Todd[13] at 760 torr is shown in figure 2.

Table 4. Measured Boiling Points of Benzene-Toluene
Solutions by the DTA Method

Toluene in benzene	Measured boiling point	
	Run No. 1	Run No. 2
mole %	°C	
0.75	80.0	80.0
2.7	79.8	79.8
4.1	80.8	80.5
9.4	82.0	81.8
13.4	82.0	83.0
19.4	84.3	—
82.8	108.5	108.0
88.0	109.3	109.0
93.1	109.0	110.3
96.0	109.5	110.5
97.6	110.5	110.5
98.5	110.8	—

*Fielder, D. The Vapor Pressure and Mass Spectrum of Purified GD (U). In preparation.

**Neumann, J. E. Notebook 7389. pp 39-44. April 1956. CONFIDENTIAL Notebook.
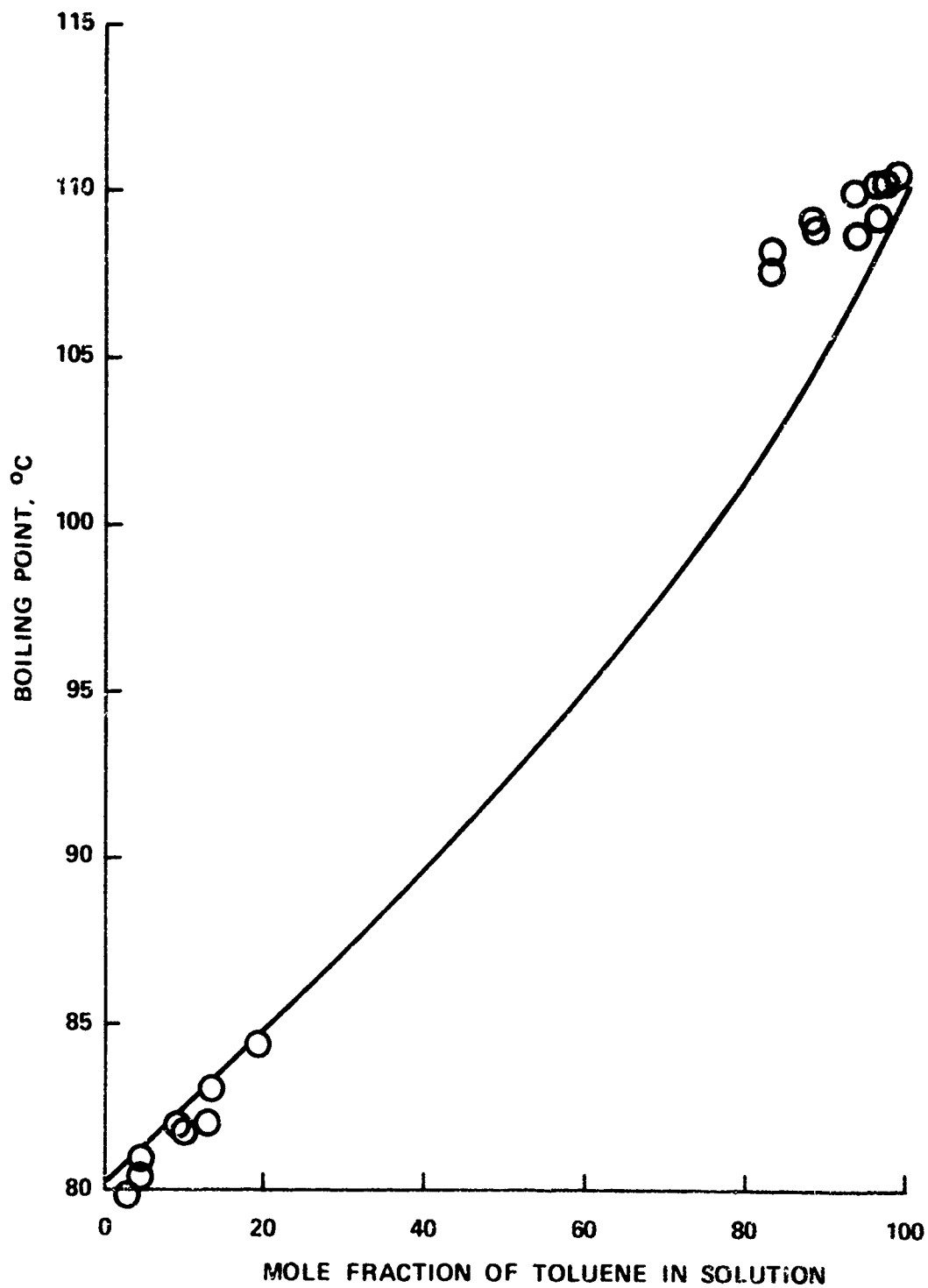
Figure 2.   Temperature — Composition at Constant Pressure for
Benzene-Toluene Mixtures

The toluene solutions with benzene as a low-boiling impurity produced experimental temperatures much closer to the normal boiling point of the solvent than was predicted by ebulliometric measurements. For example, the solution with 12-mole-percent benzene in toluene should have a boiling point of 105°C according to Todd.[13] Experimental temperatures measured were 109.3° and 109.0°C by the DTA method. This can be explained if some of the lower boiling benzene is distilled off first leaving a partially purified solvent to be measured. The benzene solutions with toluene as a high-boiling impurity produced experimental data that had much better agreement with predicted values. In this case, the partial purification could not occur to any great extent due to the large bulk of benzene present. In either case, the data indicate that a true vapor-liquid equilibria is not established in the DTA method. This, however, could be an advantage when vapor pressure data is obtained by the DTA method on relatively impure samples.

IV. DISCUSSION.

The features of the DTA method of vapor pressure measurement were previously described in detail. The DTA method enables vapor pressures to be measured at higher temperatures than standard isothermal methods for compounds that decompose at temperatures below their normal boiling point. The method is relatively rapid, requires only between 1 and 3 μl of sample for each vapor pressure-temperature determination, and does not subject the material under test to high temperatures for extended periods.

V. CONCLUSIONS.

A modified differential thermal analyzer apparatus was used to generate vapor pressure data for: GA, GD, EA 3580B, dimethyl trisulfide, and O,O'-diethyl methylphosphonothioate. Vapor pressure-temperature relations were determined using a computer program to reduce the experimental data and fit it to an Antoine vapor pressure equation. In addition, volatility and heat of vaporization were calculated for each compound over selected temperature ranges. The DTA method enables vapor pressure measurement at higher temperatures than standard isothermal methods for compounds that decompose below their normal boiling point.

The effect on measured boiling points of ideal low- and high-boiling impurities gave experimental boiling points much closer to the normal boiling point of the solvent than would be predicted by ebulliometric measurements. On the other hand, solutions containing high-boiling impurities showed boiling points much closer to the predicted values. The feature of partial purification during measurement adds to the value of the procedure.

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