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**EDGEWOOD ARSENAL
TECHNICAL REPORT**

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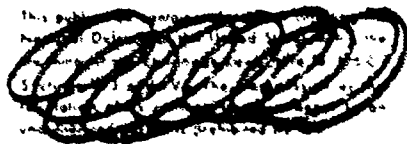
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**VAPOR PRESSURE MEASUREMENTS OF
SOME CHEMICAL AGENTS
USING DIFFERENTIAL THERMAL ANALYSIS
PART I. (U)**

by

**Frederic Belkin
Harry A. Brown, Jr.
Chemical Laboratory**

March 1973



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EDGEWOOD ARSENAL TECHNICAL REPORT

EATR 4710

VAPOR PRESSURE MEASUREMENTS OF SOME CHEMICAL AGENTS
USING DIFFERENTIAL THERMAL ANALYSIS. Part I (U)

by

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Harry A. Brown, Jr.
Chemical Research Division
Chemical Laboratory

March 1973

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FOREWORD

The work described in this report was authorized under Project 1T061101A91A, In-House Laboratory Independent Research Program (U). This work was started in February 1970 and completed in May 1971. The experimental data are recorded in notebooks 8343 and 8337.

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DIGEST

A method for determining vapor pressure-temperature relations for chemical agents has been developed using a modified differential thermal analysis (DTA) apparatus. Vapor pressure data for 10 compounds have been generated. These compounds are: GF, VX, EA 1356, EA 2222, EA 2223, EA 4923, EA 5365, EA 5403, EA 5414, and EA 5488. A computer program was used to reduce the experimental data and fit it to the Antoine vapor pressure equation. In addition, volatility and heat of vaporization were calculated for each compound over selected temperature ranges.

The DTA method permits vapor pressure measurements to be made of relatively unstable compounds at higher temperatures than can be made with the Knudsen cell or the isoteniscope. Significantly smaller amounts of material are required for the DTA method. The technique is presently useable at pressures between approximately 1 and 760 torr, at temperatures above 35° to 40°C.

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(C) VAPOR PRESSURE MEASUREMENTS OF SOME CHEMICAL AGENTS USING DIFFERENTIAL THERMAL ANALYSIS

I. (U) INTRODUCTION.

The measurement of vapor pressures of some chemical agents has been, in the past, limited to relatively low temperatures with respect to their normal boiling points, since many of these compounds are thermally unstable and will decompose more rapidly at elevated temperatures. The methods presently in use in our laboratory, such as the isoteniscope and the Knudsen cell techniques, compound the problems because they require that the material remain at constant temperature for times ranging from several minutes to several hours. These isothermal methods cannot, therefore, be used at temperatures where appreciable decomposition of the compound may occur.

A method of vapor pressure measurement was sought which would have advantages over the standard methods. Desirable features would include: (1) elimination of the necessity to subject the compound under study to high temperatures for extended periods; (2) rapid acquisition of data; (3) small sample requirements for each experimental determination; (4) also, it would be available commercially, requiring only minimal modification to provide adequate performance.

There are several reports which describe the use of differential thermal analysis (DTA) methods for the determination of boiling points of pure organic liquids¹ and for the determination of vapor pressures.²⁻⁴ The initial experiments presented here with model compounds showed that DTA methods could be successfully used for measuring the vapor pressures of a variety of chemical agents at temperatures where the isothermal methods could not be used.

II. (U) APPARATUS.

The apparatus used for the experimental determinations was a modified version of the Calorimeter Cell.* Modifications introduced included: (1) substitution of a standard DTA block for the Boersma-type air cell, (2) rewiring of electrical connections to obtain negative 'y' axis deflection for endothermic reactions, (3) attachment of flow and pressure controls to the base of the cell, and (4) a modified version of the bell jar to allow measurement of cell pressure close to the sample location.

Ancillary equipment included two types of vacuum systems. For pressures between 15 and 760 torr, a vacuum pump was connected to the system through a manostat, a 25-liter ballast tank, and a cold trap filled with dry-ice-acetone mixture. The system pressure is controlled by the

¹ Vassalo, D.A., and Harden, J.C. Precise Phase Transition Measurements of Organic Materials by Differential Thermal Analysis. *Anal. Chem.* **34**, 132 (1962).

² Krawetz, A.A., and Tovrog, T. Determination of Vapor Pressure by Differential Thermal Analysis. *Rev. Sci. Instrum.* **33**, 1465 (1962).

³ Barrall, E.M., Porter, I.S., and Johnson, J. Microboiling Point Determination at 30 to 760 Torr by Differential Thermal Analysis. *Anal. Chem.* **37**, 1053 (1965).

⁴ Kemme, H.R., and Kreps, S.I. Vapor Pressure Determination by Differential Thermal Analysis. *Anal. Chem.* **41**, 1869 (1969).

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manostat and measured by a precision mercurial manometer connected to the system through a port in the bell jar. A diagram of this system is shown in figure 1. For pressures below 15 torr, the manostat, the ballast tank, and the manometer were removed from the system. Pressure in the cell was regulated by using an adjustable continuous-leak valve attached to the cell base. Cell pressure was measured with a size "D" McLeod gauge (pressure range 0 to 15 torr) mounted directly on the bell jar.

The cell was connected to a Model 900 DTA apparatus.* This unit provided temperature control of the pressure cell and a means of recording the experimental data.

III. (U) PROCEDURES.

A. (U) Experimentation.

Experimental procedures were very similar to those used for normal operation of the DTA apparatus except for control and measurement of cell pressure. Between 1- and 5-microliters of the liquid sample was placed on 100 to 140 mesh glass beads contained in either a standard 2-mm sample tube or a 4-mm-diameter by 28-mm-long sample tube. The tube was generally filled to a depth of 2 mm with glass beads. The reference sample consisted of a similar amount of glass beads. The reference and the sample tubes were placed in the DTA heating block, the sensing thermocouples were inserted into the tubes, and the bell jar was put in place. After the vacuum pump was started and the desired pressure was established in the cell, the run was started. Linear heating rates of between 10° and 20°C/min were generally used.

The thermogram obtained for each experimental run exhibited an endothermic peak at the temperature where the sample boiled at the experimentally fixed pressure. The boiling point temperature was determined by extrapolation of the foreslope of the peak back to the baseline.⁵ For each run, the boiling point could be determined to an accuracy of $\pm 0.5^\circ\text{C}$. Figure 2 shows typical thermograms for pure and impure compounds.

Vapor pressures below 15 torr were measured with a "D" scale McLeod gauge accurate to $\pm 3\%$. Higher pressures were measured in initial experiments using a Wallace & Tiernan Model FA 135 manometer, accurate to ± 0.25 torr. This manometer was subsequently replaced with a Wallace & Tiernan Model FA 187 manometer, accurate to ± 0.15 torr. The Model FA 187 manometer was used in vapor pressure measurements of agents EA 2222, EA 4923, EA 5403, and EA 5488.

B. (U) Calculations.

Using a computer program and plotting techniques developed by Penski and Latour,⁶ the experimental data obtained for each compound were fitted to the Antoine vapor pressure equation

* Manufactured by E. I. duPont de Nemours & Co.

⁵ Smothers, W. J., and Chiang, Y. *Differential Thermal Analysis: Theory and Practice*, p 45. Chemical Publishing Co., Inc., New York, New York, 1958.

⁶ Penski, E. C., and Latour, L.J. EATR 4491. *Conversational Computation Method for Fitting the Antoine Equation to Vapor Pressure-Temperature Data*. February 1971. UNCLASSIFIED Report.

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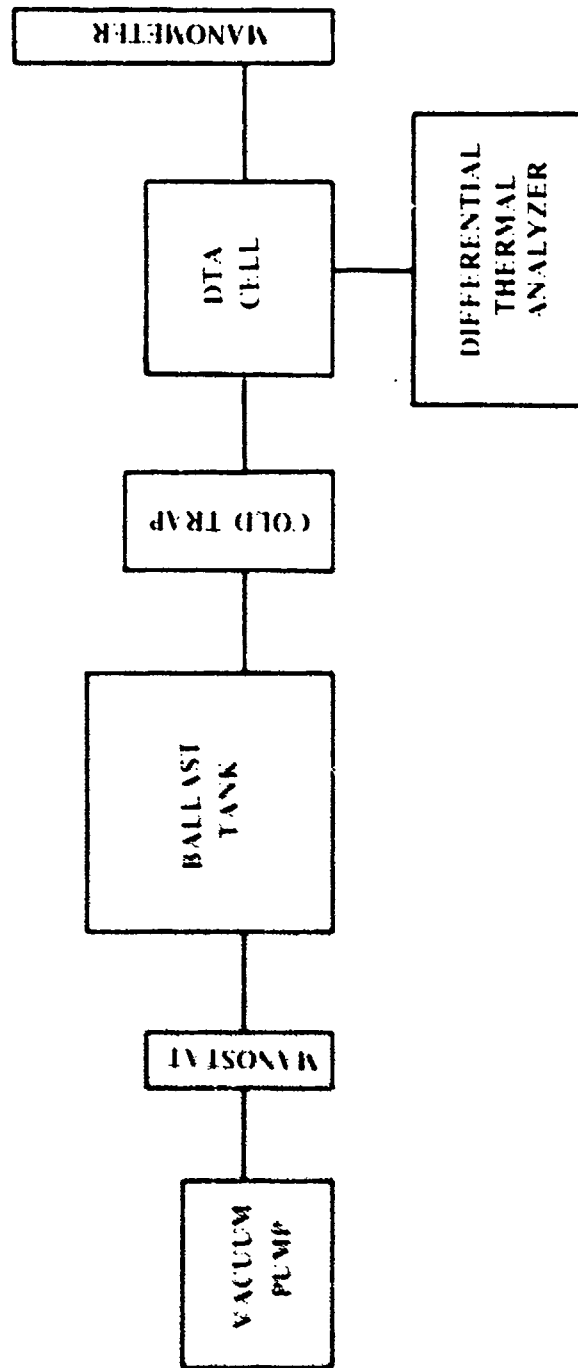


Figure 1 (U). Block Diagram of the Vapor Pressure Apparatus

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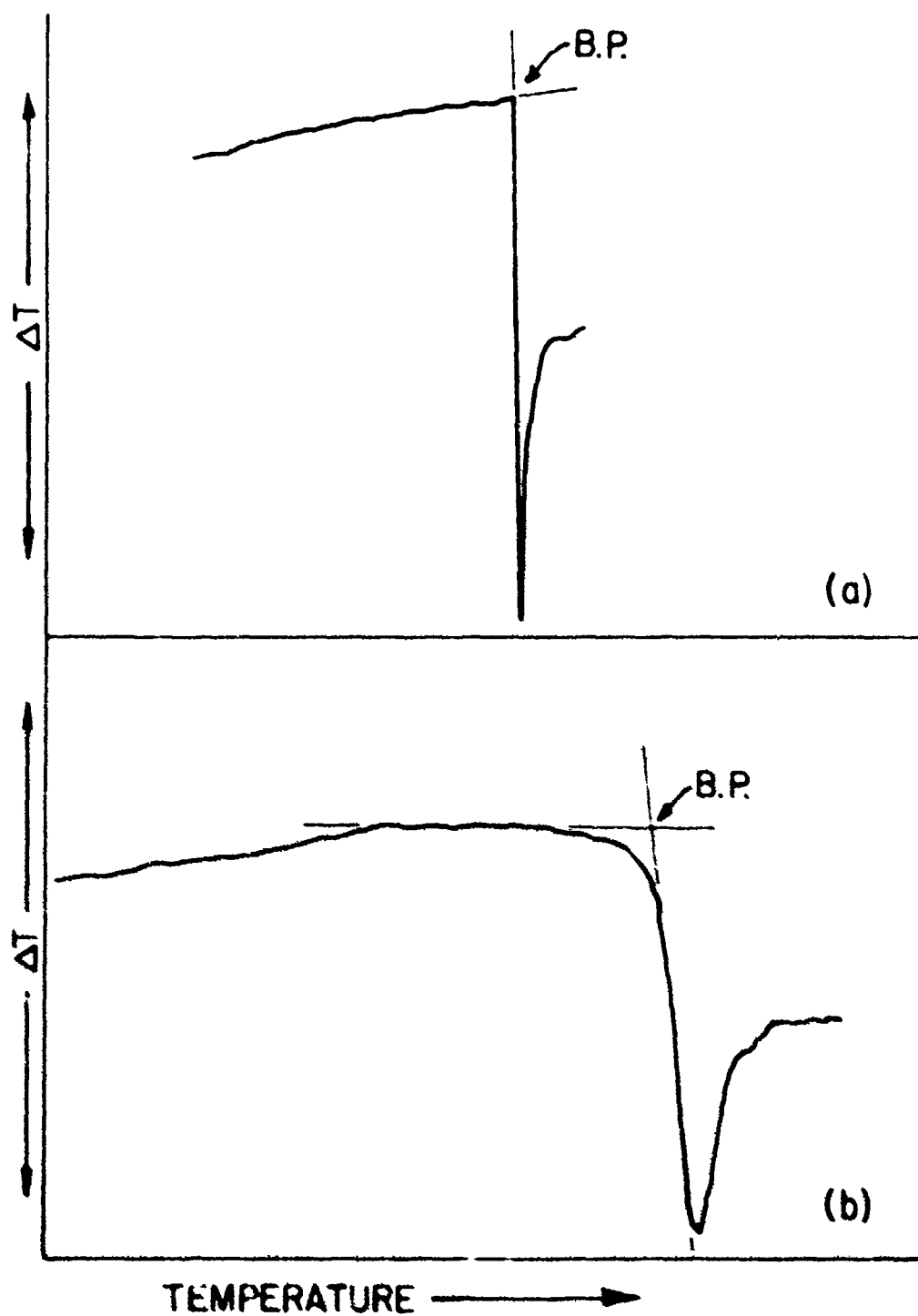


Figure 2 (U) Typical Boiling Endotherms
(a) Pure Compound. (b) Impure Compound

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$$\log P = A - B/(C + t) \quad (1)$$

where

P = vapor pressure in torr
t = temperature in degrees centigrade
A, B, C = constants

The Antoine equation has advantages over other vapor pressure-temperature equations because of the small number of constants required, and the extrapolations are believed to be more reliable than for other equations.^{7,8}

From the vapor pressure data, other physicochemical values can be calculated. The computer was programmed to calculate the heat of vaporization (Kcal/mole) and the volatility (gm/cu m) for each compound from the following equations

$$\text{heat of vaporization} = \frac{(4.5766 \times 10^{-3})BT^2}{(C + t)^2} \quad (2)$$

$$\text{volatility} = \frac{PM \times 10^3}{0.082053T} \quad (3)$$

where

B and C = Antoine constants

t = temperature in degrees centigrade

T = temperature in degrees Kelvin

P = vapor pressure in atmospheres

M = molecular weight

⁷ Reid, R. C., and Sherwood, J. K. *The Properties of Gases and Liquids*, p 135. McGraw-Hill New York, New York 1966.

⁸ Thomson, G. W. *The Antoine Equation for Vapor-Pressure Data*. *Chem. Rev.* 15, 1(1946)

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Substitution into the Antoine formula permits the vapor pressure to be calculated at any desired temperature. The standard deviation (SD) was calculated for each Antoine equation using the following equation:

$$SD = \left(\frac{S}{n-1} \right)^{1/2} \quad (4)$$

where

$$S = \sum (\log P_{\text{calc}} - \log P_{\text{exp}})^2$$

Using the logarithmic values prevents excess weighting of the higher values.⁶

IV. (C) RESULTS.

A. (U) Model Compound.

Aniline was used as a model compound to aid in the development of the DTA method for determining vapor pressure. Stull's data⁹ were used to develop an Antoine equation for this compound.

$$\log P = 6.5605 - 1264.69 / (158.03 + t)$$

The vapor pressure of Reagent Grade, A.C.S. aniline was experimentally determined at temperatures between 44°C and its normal boiling point. The calculated vapor pressures obtained from the Antoine equation for the literature values were correlated with experimental values. The maximum error between these results was about 5%, which is the expected maximum error for the Antoine equation.⁷

B. (U) Sample Analysis.

Chemical purities of the compounds used in this study were determined by personnel of the Analytical Chemistry Branch. The results of the analyses are presented in tables I and II. The structures and nomenclature for these compounds are presented in the Glossary.

C. (C) Vapor Pressure Data.

(U) The vapor pressure of two samples of EA 2223 having different purities were measured and compared. Since comparable data were obtained with the two samples of EA 2223, the data were combined and treated as one data set.

⁹ Stull, D. R. Vapor Pressure of Pure Substances. *Ind. and Eng. Chem.* **39**, 517 (1947).

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Table I (U). Chemical Purity of Agent Samples

Compound	Purity	Method of analysis
VX	91.9%	Hydrolytic
GF	84.4% 44 mg H ⁺ /100 gm	Hydrolytic
EA 1356	85.6% 10 mg H ⁺ /100 gm	Hydrolytic
EA 2222	90.6% 91.4% One peak	Thiono content Hydrolytic Gas chromatography
EA 2223 Sample 1	87.6% 2 mg H ⁺ /100 gm	Hydrolytic
EA 2223 Sample 2	94.0% <1 mg H ⁺ /100 gm	Hydrolytic
EA 5365	88% 98%	Base hydrolysis Acid hydrolysis
EA 5403	95.5% See table II	Total amine Elemental analysis
EA 5414	See table II	Elemental analysis
EA 5488	98% 95% Trace impurity See table II	Titrimetric Hydrolytic Gas chromatography Elemental analysis
EA 4923	84.9% 4.7% EA 4922 1.5% Unknown 8.9% Not eluted	Gas chromatography

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Table II (C). Elemental Analysis of EA 5403, EA 5414, and EA 5488 (U)

Element	EA 5403		EA5414		EA5488	
	Calculated	Found	Calculated	Found	Calculated	Found
C	39.6	40.1	39.6	39.9	45.8	45.8
H	8.6	8.7	8.6	8.8	7.7	8.0
F	8.95	8.35	8.95	8.51	8.04	*
N	13.2	12.1	13.2	12.9	11.9	11.8
O	15.08	*	15.08	*	12.45	*
P	14.60	14.13	14.6	14.5	13.11	13.06

* Not determined.

(U) Table III provides a compilation of the constants for the Antoine equations for the chemical agents studied. Table III also provides the experimental range over which the data were obtained, as well as the boiling point as calculated from the Antoine equation for each agent. The standard deviation of the experimental data from the Antoine equation, which was calculated using equation (4), is also presented in table III. The appendix provides line plots constructed from the Antoine equation. Volatilities and heats of vaporization were calculated using equations (2) and (3); these values are provided at selected temperatures in table IV.

(U) The calculated value for C in the Antoine equation is often found to be less than 273. The dependence of C on the experimental data points is rather sensitive; and if there are deviations in the data or if the data range is too narrow, a value of C may be calculated which is not realistic (i.e., less than 100 or over 300). Therefore, if C was found to be outside this range, the value 273.15 was used. This converts the Antoine equation to the Clausius-Clapeyron equation.

V (U). DISCUSSION.

The method of vapor pressure measurement described in this report has several important advantages over the standard methods. It is a dynamic method which does not subject the material to high temperatures for extended periods. The method is relatively rapid, requiring only small amounts of material for each experimental determination. An apparatus is available on the commercial market which requires only minor modifications to be used for these determinations. These modifications, however, do not preclude use of the instrument for its primary purpose -- differential thermal analysis.

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Table V provides a comparison of the normal operating parameters for the DTA method with those of the isoteniscope¹⁰ and the Knudsen¹¹ methods. It should be noted that the comparisons made are general in nature and that any of the methods may be useable, under certain circumstances, outside of the listed ranges.

Comparing the vapor pressure determinations performed by Lafferty¹² (from 60° to 140°C) on EA 2223 with this work, there is a maximum difference of less than 6% between the calculated vapor pressures of the two determinations. In another vapor pressure study, by Link,¹³ the maximum difference between the overlapping curves (from 60° to 90°C) was about 1%. Lafferty's sample had a purity of 91.3% and that of Link, 84%.

Table III (U). Agent Vapor Pressure Data

Agent	Antoine constants			Experimental range	Boiling point*	Standard deviation 10 ⁻²
	A	B	C			
				°C	°C	log (torr)
GF	6.5679	1516.31	171.81	55-170	239.4	4.11
VX	8.7840	3247.39	273.15**	110-235	293.9	2.52
EA 1356	6.3580	1384.13	157.34	60-225	240.7	4.58
EA 2222	7.1814	1482.28	222.64	40-120	122.0	1.00
EA 2223	7.9819	2485.60	260.70	60-225	226.6	2.17
EA 4923	7.7754	2030.91	241.67	65-175	173.3	1.12
EA 5365	8.8125	2877.64	260.38	60-150	224.8	2.61
EA 5403	8.8879	2947.07	269.72	60-150	220.7	2.48
EA 5414	9.7060	3320.35	262.36	80-155	224.1	2.30
EA 5488	8.4629	3226.38	273.15**	130-215	304.8	2.09

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

** C is taken as 273.15°C.

¹⁰ Smith, A., and Menzies, A.W.C. Studies in Vapor Pressure III. A Static Method for Determining the Vapor Pressures of Solids and Liquids. *J. Am. Chem. Soc.* **32**, 1412 (1910).

¹¹ Thomson, G.W. *Physical Methods of Organic Chemistry*, Part I. A. Weissberg, ed. p 193 Interscience Publishers, New York, New York, 1949.

¹² Lafferty, J.P. Notebook 6955, pp 6-8, February 1963. CONFIDENTIAL Notebook.

¹³ Link, R. Notebook 6355 p 42, August 1960. CONFIDENTIAL Notebook.

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Table IV (C). Calculated Physicochemical Properties of Some Chemical Agents (U)

Agent	Temperature	Pressure	Volatility	Heat of vaporization
	°C	torr	gm/cu m	Kcal/mole
GF	25*	0.073	0.71	15.92
	50*	0.34	4.82	14.73
	100	9.76	75.55	13.08
	150	71.80	490.19	12.00
	200*	308.84	1885.7	11.24
VX	100*	0.65	7.48	15.32
	150	7.47	75.7	15.32
	200	51.20	464.0	15.32
	250*	242.91	1990.8	15.32
FA 1356	50*	0.48	4.64	15.38
	100	9.54	79.58	13.32
	150	71.52	526.3	12.01
	200	305.12	2008.4	11.10
FA 2222	25*	15.69	108.0	9.83
	50	55.53	352.8	9.53
	100	386.43	2126.3	9.07
FA 2223	50*	0.96	9.34	12.30
	100	12.32	103.9	12.17
	150	85.06	632.5	12.07
	200	386.01	2567.0	12.00
FA 4923	50*	6.49	39.35	11.41
	100	67.81	356.0	11.08
	150	389.14	1801.6	10.85
FA 5365	50*	0.35	3.42	14.27
	100	6.72	57.2	14.12
	150	63.15	474.3	14.00
FA 5403	50*	0.47	4.96	13.77
	100	8.31	75.76	13.73
	150	73.92	694.4	13.70
FA 5414	50*	0.12	1.25	16.26
	100	3.49	31.82	16.11
	150	45.06	362.4	16.00
FA 5488	100*	0.66	6.65	14.76
	150	6.89	61.68	14.76
	200	44.05	352.7	14.73

*Extrapolated values.

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Table V (U). Comparison of Methods for the Measurement of Vapor Pressure

Experimental parameter	DTA method	Knudsen method	Isotenoscope method
Sample required for a series of vapor pressure points (gm)	0.05	0.1 to 0.5	1 to 10
Sample required for a single vapor pressure determination (gm)	0.005	0.05	1 to 10
Pressure range (torr)	1 to 760	0.001 to 0.7	5 to 760
Temperature range (°C)	40 to 400	-40 to 150	-40 to 200
Time the sample is exposed to elevated temperatures	Few minutes	Few hours	Few hours
Time the sample is exposed to the specific test temperature	Seconds	Minutes	Minutes

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For EA 4923, there was an overlap of 1 vapor pressure point with another vapor pressure study.¹⁴ The vapor pressure from this study was 18.4 torr versus 18.2 torr for the vapor pressure determined by the DTA method at 70°C.

Vapor pressure data are available for GF,^{15,16} VX,^{16,17} EA 1356¹⁸ and EA 5365.¹⁷ All of the literature data were obtained over a temperature range lower than the vapor pressure reported here. The extrapolated DTA datum was compared with the vapor pressure data point at the highest reported temperature. Extrapolating our GF data to 30°C shows a deviation of 7% from the literature data point.¹⁵ There is about a 29% difference between the extrapolated DTA data point for VX and the vapor pressure measured at 100°C by Savage.¹⁷ This discrepancy may be due to a difference in sample purity. There is a 17% difference between the calculated vapor pressure for EA 1356 at 25°C and a data point measured by Fielder.¹⁸ The correlation between the EA 1356 data is satisfactory, considering the long extrapolation of the DTA data and the fact that samples of different purities were used. An excellent correlation exists between the extrapolated DTA data and the data for EA 5365 measured by Savage¹⁷ at 45°C. There is about a 4% difference between the two results.

Kemme and Kreps¹⁹ noted that discrepancies in vapor pressure data reported in other studies appear to be due more to differences in purity than to differences in experimental methods. Extremely high chemical purity could not be obtained on the agents investigated in this study because of the lack of chemical and thermal stability, small sample size, and difficulty involved in the purification of samples. The presence of soluble high-boiling impurities generally causes a decrease in vapor pressure. Impurities which have a higher vapor pressure than the pure sample has could increase the vapor pressure of a sample.

With pure samples, the DTA method will produce a vertical foreslope for the boiling endotherm indicative of a constant boiling point. If the sample is not pure (less than 99.5 mole percent),⁴ there will be a deviation from the vertical foreslope, as the boiling range is no longer constant. An increase in the foreslope, as vapor pressure is measured at higher pressures and higher temperatures, generally indicates the presence or generation of an impurity. The DTA method, therefore, has an advantage over other methods since it allows estimation of the purity and thermal stability of the sample at the moment the vapor pressure is being determined.

¹⁴Snyder, A.D., et al. Monsanto Research Corp. Final Report. Contract DAAA 15-68-C-0316. Physical and Colloid Chemical Research on Agents (U). December 1970. CONFIDENTIAL Report.

¹⁵Neale, E. PTP 341. The Vapor Pressures of Some Organic Phosphorus Compounds (U). April 1953. UNCLASSIFIED Report.

¹⁶Melanson, B.M. Suffield Technical Note No. 49. Physical Properties of Some Toxic Agents and Simulants (U). March 1963. SECRET Report.

¹⁷Savage, J.J. Notebook 8080. pp 49-52. April 1971. CONFIDENTIAL Notebook.

¹⁸Fielder, J. Notebook 7318. p 109. December 1968. CONFIDENTIAL Notebook.

¹⁹Kemme, J.L., and Kreps, S.I., Vapor Pressure of Primary n-Alkyl Chlorides and Alcohols. J. Chem. and Eng. Data. 10, 98 (1969).

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From the generally good correlation of our data for both the agents and the standard compounds with that of the literature values, it appears that the accuracy of our experimental method is comparable to standard methods of vapor pressure determination.

The range over which the experimental data were obtained varied widely for different compounds, as can be seen in table III. The utility of the technique at low pressures is limited by the accuracy of the pressure-measuring apparatus and the ability to maintain and control a specific low pressure. At present, pressure measurements cannot be determined accurately below about 1 torr. Mechanical problems in cooling the cell below room temperature have, thus far, limited the useable range to temperatures above approximately 35°C to a maximum of about 500°C. The highest temperatures at which reliable data could be obtained was limited to the temperature at which decomposition of the sample in the cell became significant. Initial sample purity is also a factor affecting the upper temperature limit at which a useable endotherm can be generated. In all cases the upper temperature limit for the DTA method is above that for the isothermal techniques.

It should be noted that some of the data presented in table IV are values calculated above and below the experimental range. Thus, values outside of this experimental range are, of necessity, extrapolated values with a loss of accuracy corresponding to the degree of extrapolation. For this reason, the data as presented have been rounded-off to a degree consistent with the accuracy of the experimental technique.

VI. (U) CONCLUSIONS.

A method for determining vapor pressure-temperature relations for chemical agents has been developed using a modified differential thermal analysis (DTA) apparatus. Vapor pressure data for 10 compounds have been generated. These compounds are: GF, VX, EA 1356, EA 2222, EA 2223, EA 4923, EA 5365, EA 5403, EA 5414, and EA 5488. A computer program was used to reduce the experimental data and fit it to the Antoine vapor pressure equation. In addition, volatility and heat of vaporization were calculated for each compound over selected temperature ranges. The method permits vapor pressure measurements at higher temperatures and pressures than afforded by conventional methods, such as the Knudsen cell and the isoteniscope. The dynamic nature of the technique reduces problems of agent decomposition, and the method provides reliable data. Only small amounts of sample are needed to determine a vapor pressure curve.

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LITERATURE CITED

1. Vassallo, D. A., and Harden, J. C. Precise Phase Transition Measurements of Organic Materials by Differential Thermal Analysis. *Anal. Chem.* 34, 132 (1962).
2. Krawetz, A. A., and Tovrog, T. Determination of Vapor Pressure by Differential Thermal Analysis. *Rev. Sci. Instrum.* 33, 1465 (1962).
3. Barrall, E. M., Porter, E. S., and Johnson, J. Microboiling Point Determination at 30 to 760 Torr by Differential Thermal Analysis. *Anal. Chem.* 37, 1053 (1965).
4. Kemme, H. R., and Kreps, S. I. Vapor Pressure Determination by Differential Thermal Analysis. *Anal. Chem.* 41, 1869 (1969).
5. Smothers, W. J., and Chiang, Y. *Differential Thermal Analysis: Theory and Practice.* p 45. Chemical Publishing Co., Inc., New York, New York. 1958.
6. Penski, E. C., and Latour, L. J. EATR 4491. Conversational Computation Method for Fitting the Antoine Equation to Vapor Pressure-Temperature Data. February 1971. UNCLASSIFIED Report.
7. Reid, R. C., and Sherwood, T. K. *The Properties of Gases and Liquids.* p 135. McGraw-Hill, New York, New York. 1966.
8. Thomson, G. W. The Antoine Equation for Vapor Pressure Data. *Chem. Rev.* 38, 1 (1946).
9. Stull, D. R. Vapor Pressure of Pure Substances. *Ind. and Eng. Chem.* 39, 517 (1947).
10. Smith, A., and Menzies, A. W. C. Studies in Vapor Pressure: III. A Static Method for Determining the Vapor Pressures of Solids and Liquids. *J. Am. Chem. Soc.* 32, 1412 (1910).
11. Thomson, G. W. *Physical Methods of Organic Chemistry.* Part I. A. Weissberger, ed. p 193. Interscience Publishers, New York, New York. 1949.
12. Lafferty, J. P. Notebook 6955. pp 6-8. February 1963. CONFIDENTIAL Notebook.
13. Link, R. Notebook 6355. p 42. August 1960. CONFIDENTIAL Notebook.
14. Snyder, A. D., et al. Monsanto Research Corp. Final Report. Contract DAAA 15-68-C-0316. Physical and Colloid Chemical Research on Agents (U). December 1970. CONFIDENTIAL Report.

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15. Neale, E. PTP 341. The Vapor Pressures of Some Organic Phosphorous Compounds (U). April 1953. UNCLASSIFIED Report.
16. Melanson, B. M. Suffield Technical Note No. 49. Physical Properties of Some Toxic Agents and Simulants (U). March 1963. SECRET Report.
17. Savage, J. J. Notebook 8080. pp 49-52. April 1971. CONFIDENTIAL Notebook.
18. Fielder, D. Notebook 7318. p 109. December 1968. CONFIDENTIAL Notebook.
19. Kemme, H. R., and Kreps, S. I. Vapor Pressure of Primary n-Alkyl Chlorides and Alcohols. J. Chem. and Eng. Data. 14, 98 (1969).

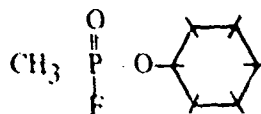
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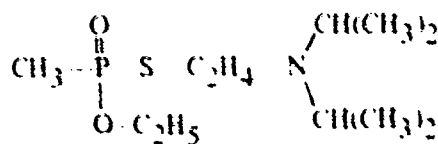
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(C) STRUCTURE AND NOMENCLATURE FOR COMPOUNDS
DISCUSSED IN THIS REPORT (U)

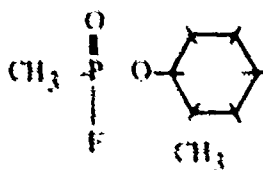
(U) GF - cyclohexyl methylphosphonofluoridate



(U) VX - diisopropylaminoethylethoxy methylphosphonothioate



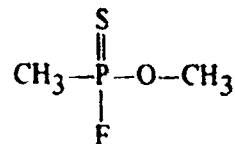
(C) EA 1356 - 2-methylcyclohexyl methylphosphonofluoridate



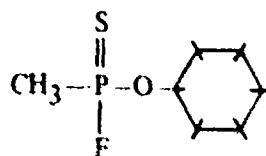
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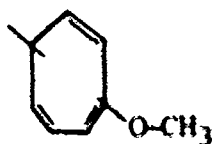
(C) EA 2222 - O-methyl methylphosphonofluoridothioate



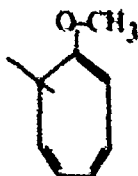
(C) EA 2223 - O-cyclohexyl methylphosphonofluoridothioate



(C) EA 4922 - 3-methoxy cycloheptatriene



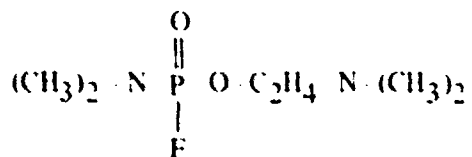
(C) EA 4923 - 1-methoxy cycloheptatriene



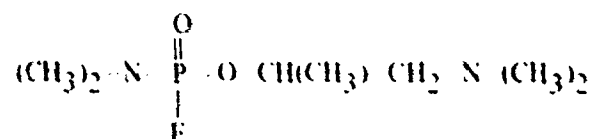
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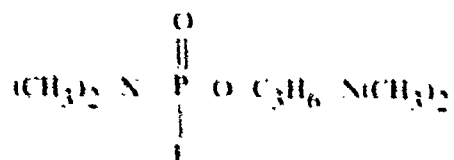
(C) EA 5365 - dimethylaminoethyl N,N-dimethylphosphoramidofluoridate



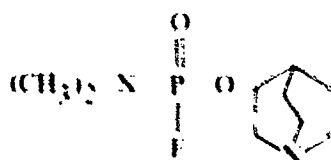
(C) EA 5403 - 1-dimethylamino-2-propyl N,N-dimethylphosphoramidofluoridate



(C) EA 5414 - 3-dimethylaminopropyl N,N-dimethylphosphoramidofluoridate



(C) EA 5488 - 3-quinuclidyl N,N-dimethylphosphoramidofluoridate



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APPENDIX

LINE PLOTS CONSTRUCTED FROM THE ANTOINE EQUATION

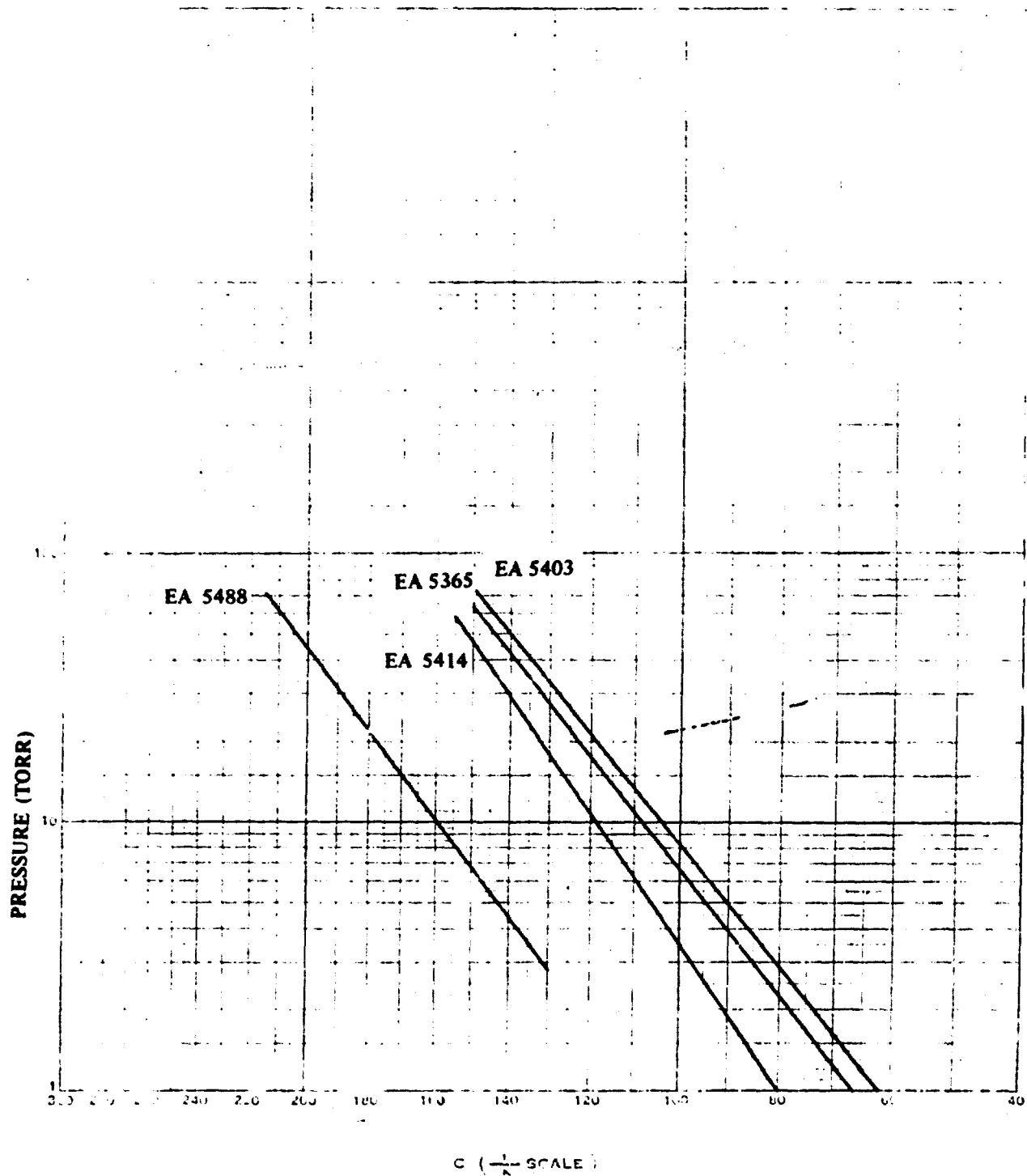


Figure A-1 (U). Log p Versus 1/T Curves for Selected Agents Described in Table IV

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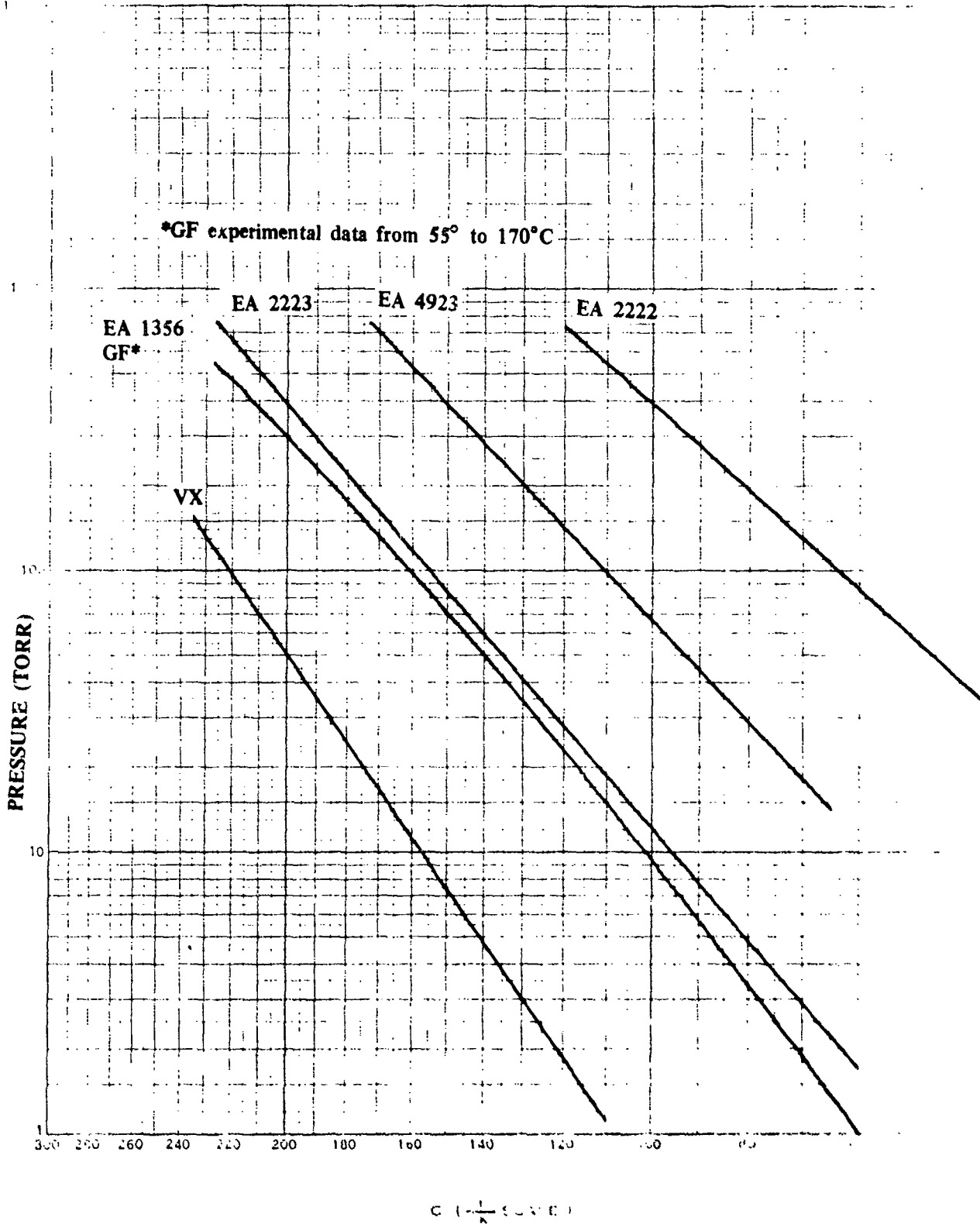


Figure A-2 (U). Log p Versus 1/T Curves for Selected Agents Described in Table IV

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13. ABSTRACT (U) A method for determining vapor pressure-temperature relations for chemical agents has been developed using a modified differential thermal analysis (DTA) apparatus. Vapor pressure data for 10 compounds have been generated. These compounds are: GF, VX, EA 1356, EA 2222, EA 2223, EA 4923, EA 5365, EA 5403, EA 5414, and EA 5488. A computer program was used to reduce the experimental data and fit it to the Antoine vapor pressure equation. In addition, volatility and heat of vaporization were calculated for each compound over selected temperature ranges. The method permits vapor pressure measurements at higher temperatures and pressures than afforded by conventional methods, such as the Knudsen cell and the isoteniscope. The dynamic nature of the technique reduces problems of agent decomposition, and the method provides reliable data. Only small amounts of sample are needed to determine a vapor pressure curve.			
14. KEYWORDS			
DTA		EA 2222	
Vapor pressure		EA 2223	
Volatility		EA 4923	
Heat of vaporization		EA 5365	
Differential thermal analysis		EA 5403	
GF		EA 5414	
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