AD NUMBER
AD881829
LIMITATION CHANGES
TO: **Approved for public release; distribution is unlimited.**
FROM: **Distribution authorized to DoD only; Administrative/Operational Use; FEB 1971. Other requests shall be referred to Edgewood Arsenal, ATTN: SMUEA-TSTI-T, Edgewood Arsenal, MD 21010.**
AUTHORITY
ECBC memo dtd 27 Oct 2016

EDGEWOOD ARSENAL
TECHNICAL REPORT

EATR 4491

CONVERSATIONAL COMPUTATION METHOD FOR FITTING THE ANTOINE EQUATION TO VAPOR PRESSURE-TEMPERATURE DATA

by

Elwin C. Penski

Leo J. Latour, Jr., SP4

February 1971

DEPARTMENT OF THE ARMY
EDGEWOOD ARSENAL
Research Laboratories
Chemical Research Laboratory
Edgewood Arsenal, Maryland 21010

Distribution Statement

Each transmittal of this document outside the Department of Defense must have prior approval of the Commanding Officer, Edgewood Arsenal, ATTN: SMUEA-TSTI-T, Edgewood Arsenal, Maryland 21010.

Disclaimer

The findings in this report are not to be construed as an official Department of the Army position unless so designated by other authorized documents.

Disposition

Destroy this report when no longer needed. Do not return it to the originator.

JCP-I, DPG

EDGEWOOD ARSENAL TECHNICAL REPORT

EATR 4491

CONVERSATIONAL COMPUTATION METHOD FOR FITTING THE ANTOINE EQUATION TO VAPOR PRESSURE-TEMPERATURE DATA (U)

by

Elwin C. Penski
Leo J. Latour, Jr. SP4 E4

Physical Chemistry Department

February 1971

Project 1B062116AD10

DEPARTMENT OF THE ARMY
EDGEWOOD ARSENAL
Research Laboratories
Chemical Research Laboratory
Edgewood Arsenal, Maryland 21010

FOREWORD

The work described in this report was authorized under Project 1B062116AD10, Search for Potential Chemical Agents (U). This work was started in March 1969 and completed in October 1970. The data are recorded in notebook 8463.

Acknowledgment

The authors wish to acknowledge helpful discussions with Philip B. Coulter, Materials Engineering Laboratory Branch, Physical Chemistry Department, during the early planning stages of this effort.

DIGEST

A least-squares technique has been developed for determination of the constants of the Antoine equation. The method involves use of the procedure of search by golden section. A conversational FORTRAN program is provided with results of sample runs utilizing data from the open literature. The method gives accurate fits, though the constants calculated differ slightly from the literature constants because the method described is for fitting data that have a relatively constant percentage error rather than a constant absolute error. The former is usually more appropriate when values are measured over a wide range of temperatures. Plots are provided automatically through the use of a teleplotter.

CONTENTS

CONVERSATIONAL COMPUTATION METHOD FOR FITTING THE ANTOINE EQUATION TO VAPOR PRESSURE-TEMPERATURE DATA

I. INTRODUCTION.

The vapor pressure of a pure compound is a unique function of temperature. It is a property required for many calculations in physical chemistry, chemical engineering, and numerous other disciplines. Equations relating to vapor pressure and temperature are required to summarize vapor pressure data; to permit the use of the data in computer programs; and for smoothing, interpolation, extrapolation, and determining heats of vaporization. One of the most widely used equations for fitting vapor pressure-temperature data is the Antoine equation,[1] the use of which has been reviewed by Thomson.[2]

In addition to fitting vapor pressure data, the Antoine equation may be used to fit densities, fugacities of liquids, kinematic viscosities, relative vapor pressures, and other types of data. The Antoine equation, which has its basis in the well-known Clapeyron equation (see any elementary physical chemistry text), is*

$$\frac{dP}{dT} = \frac{\Delta H_v}{T \Delta V} \tag{1}$$

where

P = vapor pressure
T = absolute temperature
ΔHv = heat of vaporization
ΔV = change in volume associated with vaporization

If the molar volume of the liquid is negligible compared with that of the vapor and the vapor is a perfect gas, then the Clausius-Clapeyron equation is applicable.

$$\frac{d \ln P}{d(1/T)} = -\frac{\Delta H_v}{R} \tag{2}$$

This equation may be integrated, if ΔH_v is constant, to give

$$\log P = A - B/T \tag{3}$$

where A and B are parameters. The equation also may be written as follows:

$$\log P = A - \mathrm{B}/(t + 273.16) \tag{4}$$

where t is temperature in °C.

The Antoine equation results from replacing the value 273.16 in equation (4) with a parameter C.

*All terms are defined in the glossary at the end of the text.

$$\log P = A - B/(t + C) \tag{5}$$

This equation has been found to be adequate, except for data of very high precision, over the range from the triple point to reduced pressures of 0.75.[2]

The advantages of the Antoine equation include the following: small number of constants required, temperature may be made the dependent variable by a simple inversion, and extrapolations are believed to be more reliable than for other equations.[3]

The value for C is usually found to be lower than 273.15 and has often been taken arbitrarily as 230.[4] The latter value has been found to be typical for organic compounds that are liquids at room temperature. Because calculating the best value for C is a time-consuming task without a computer, the value $C = 230$ frequently is found in the literature.

Equations (2) and (5) can be combined to give the heat of vaporization

$$\Delta H_v = 2.3RB\left(\frac{T}{t+C}\right)^2 \tag{6}$$

II. THEORY.

The Antoine equation [equation (5)] may be written in the form of a linear equation

$$Y = A + BX \tag{7}$$

by use of the transformations

$$Y = \log P \tag{8}$$

$$X = -1/(C+t) \tag{9}$$

A set of Y's and X's may be fitted by ordinary linear regression analysis,[5] which results in the following equations:

$$A = \left(\sum_{i=1,n} Y_i - B\sum_{i=1,n} X_i\right)/n \tag{10}$$

$$B = \frac{n\sum_{i=1,n} X_i Y_i - \left(\sum_{i=1,n} X_i\right)\left(\sum_{i=1,n} Y_i\right)}{n\sum_{i=1,n} X_i^2 - \left(\sum_{i=1,n} X_i\right)^2} \tag{11}$$

where Y_i and X_i are the ith value of Y and X, respectively, and n is the number of points being fitted. Given a set of vapor pressures with the corresponding temperatures, any value of C, A, and B may be found.

The method of standard error of estimate involves minimizing the following function,

$$\sum_{i=1,n} [Y_i \text{ (experimental)} - Y_i \text{ (calculated from eq 6)}]^2$$

which will be referred to as S. In this case, S may be considered a function of C alone because both A and B are known functions of C for a given set of experimental data. Because S may not be minimized analytically by any simple known method, values of S are calculated for varying values of C until a minimum value of S is found.

The following equation results from the above discussion:

$$S = \sum_{i=1,n} [Y_i - A - BX_i]^2 \tag{12}$$

Expansion yields

$$S = \sum_{i=1,n} (A^2 + 2ABX_i + B^2X_i^2 + Y_i^2 - 2AY_i - 2BX_iY_i) \tag{13}$$

Summing terms individually gives

$$S = nA^2 + 2AB \sum_{i=1,n} X_i + B^2 \sum_{i=1,n} X_i^2 + \sum_{i=1,n} Y_i^2 - 2A \sum_{i=1,n} Y_i - 2B \sum_{i=1,n} X_i Y_i \tag{14}$$

which is used in the computer program to determine S.

The search method used to find the best value of C involves division of a line segment by a method developed by Euclid. The method, called the search by golden section procedure and described in detail by Wilde,[6] had great mystical significance among scholars of the Renaissance. This search method was selected because it does not require advance knowledge of how many calculation steps are required. It involves division of a line segment into two unequal parts so that the ratio of the whole to the larger part is equal to the ratio of the larger to the smaller segment.

In mathematical terms this definition leads to the following two equations:

First,

$$L_j = L_{j+1} + L_{j+2}$$

where

L_j = length of a line
L_{j+1}, L_{j+2} = length of segments into which the line is divided

Second,

$$\frac{L_j}{L_{j+1}} = \frac{L_{j+1}}{L_{j+2}} \equiv Z$$

It may readily be shown from the above equations that Z must be equal to 1.6180340 and that

$$L_{j+1} = \frac{L_j}{Z} = 0.61803399\, L_j$$

After m divisions of the line (which is equivalent to dividing the original line, L_o, m times)

$$L_m = \frac{L_o}{Z^m}$$

As an example, after 24 divisions of the line, L_m is equal to 0.00000965 times the length of the original line, L_o.

The standard error of estimate provided by the program is calculated from the following equation:

$$SD = \left[\frac{S}{n-1}\right]^{1/2} \tag{15}$$

It is emphasized that the values for the logarithm of vapor pressure are used for the dependent variable in the least-squares fit; the calculated logarithms of vapor pressures are subtracted from the logarithms of the measured pressures to calculate the standard deviation. Using the data in this manner prevents excessive weighting of larger pressures in the analysis. Generally, the method tends to weight values as a fixed percentage of the measured value. If the absolute error of the measurement is constant, regardless of the magnitude of the values measured, then the method developed in this report probably will not provide the best possible fit to the data.

III. DESCRIPTION OF COMPUTER PROGRAM.

The program is quite self-explanatory; the first question the program asks is how many pairs of temperature-pressure values are to be entered. This is answered by typing the number of data pairs plus a carriage return. Next, the points are entered; as many as 100 points may be used,

but only 70 characters per line may be entered and recorded by the teletype. There must be a carriage return at the end of each line. If the points are to be entered by paper tape, at the end of each line there must be a carriage return, X-off, and rubout.

The computer queries the operator regarding the need for a data table, after which the equation constants are printed along with the calculated standard deviation and an extrapolated boiling point.* This information is followed by a printout of the experimental and calculated vapor pressure values.

An option then is provided for generating a table of vapor pressures, volatilities, and heats of vaporization over a temperature range and in temperature increments selected by the operator. This information is printed after the molecular weight of the compound is provided.

The program automatically loads the experimental and calculated values of vapor pressure into a file named EZ for plotting on a Typagraph Corporation teleplotter.[7]

Generally, when vapor pressures have been measured only over a narrow range of temperatures or the data are not very accurate, it is better to estimate a value for C and then do a standard linear least-squares fit of the data. When C is calculated and found to be greatly different from similar compounds of comparable molecular weight, one should be suspicious of the data. Thomson[2] has discussed these matters in detail.

Appendix A defines the items used in the computer program, which is given in appendix B.

IV. SAMPLE CALCULATIONS.

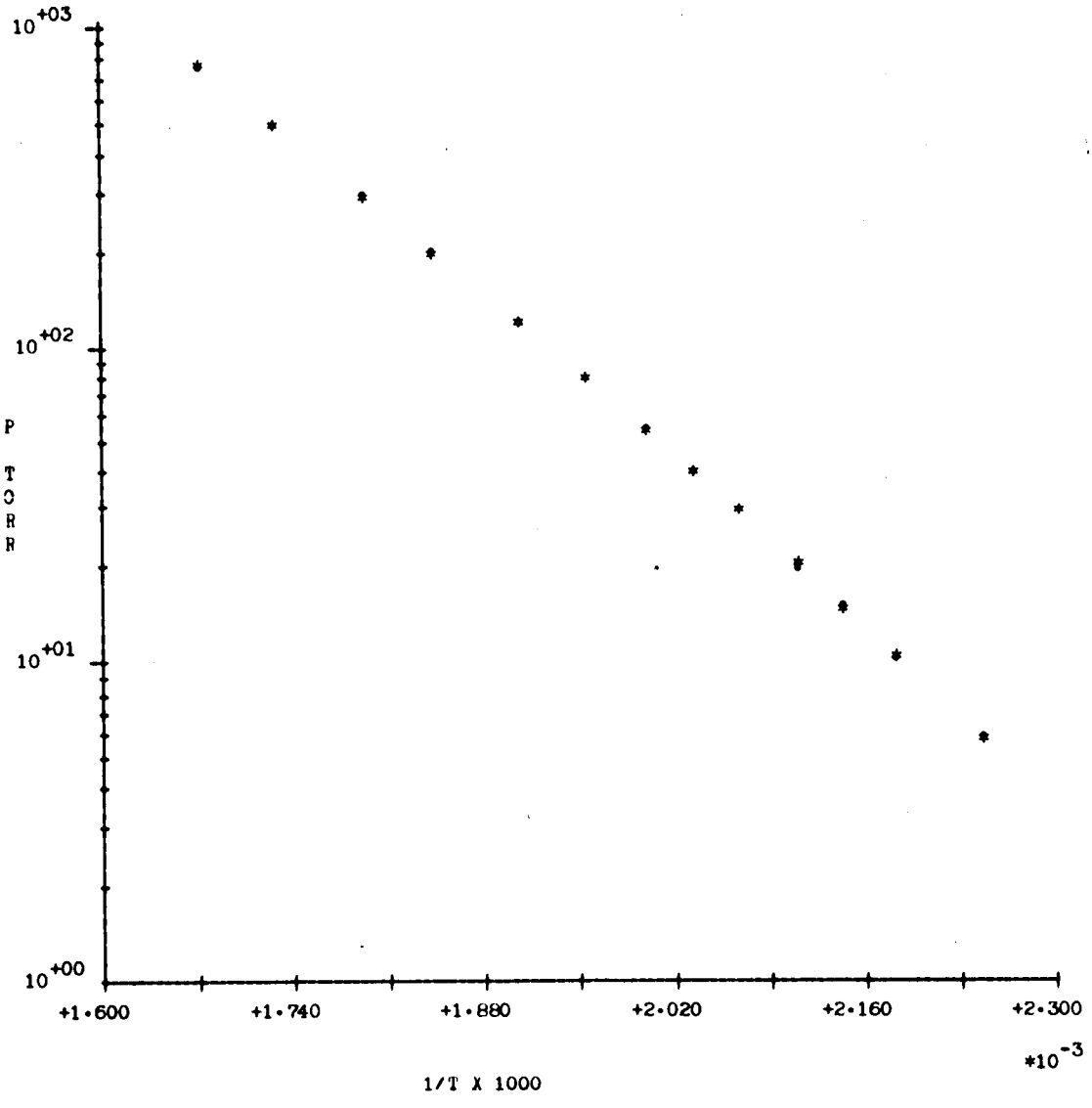
Appendix C provides two sample runs using the reported vapor pressure data of Kremme and Kreps.[8] The first sample run is for 1-hexadecanol. The vapor pressures for this compound were plotted automatically and are shown in the figure. Although Kremme and Kreps used a different method of determining the Antoine constants, they are in good agreement with the values calculated, as shown in table I. The parameters differ by 1%, and the average and maximum errors of estimate are comparable.

The second sample run is for 1-tetradecanol. This sample run demonstrates a situation in which C is found to be outside the range from 100 to 273.16. In this case, the constants differ significantly from those determined by Kremme and Kreps.[8]

It was found that the Antoine constants of Kremme and Kreps led to different errors of the estimate than were reported. Recalculation of the errors with their data and constants shows a maximum error of 11.4% instead of the reported value of 1.665%. Table II provides the results of the recalculation.

This computer program was run also with the vapor pressure data of isobutyl borate reported by Christopher and Shilman.[9] The calculated boiling point of 210.4°C agreed exactly with their value. They calculated a heat of vaporization of 12.345 kcal/mole, which compared favorably with the value of 12.33 obtained in this study.

*Caution should be exercised in using extrapolated vapor pressure values. Depending on the change in heat of vaporization with temperature and the extent of extrapolation, significant errors may result.



SYMBOL	NO.PTS.	LEGEND
•	13	-? EXPERIMENTAL
*	13	-? CALCULATED

Figure. Typagraph Plot of Vapor Pressure Versus Reciprocal Absolute Temperature for 1-Hexadecanol

Table I. Comparison of Data Fits by Kremme and Kreps* With Sample Runs

Compound	Antoine constants			Error of estimate		Calculation method
	A	*B*	*C*	Avg	Max	
				%		
1-Hexadecanol	7.04183	1880.126	127.123	1.180	3.569	Kremme & Kreps.
	7.06077	1893.76	128.406	1.189	3.536	This report.
1-Tetradecanol	6.48407	1412.907	95.368	0.793	1.665	Kremme & Kreps.
				1.6	11.4	Recalculated.
	6.21962	1244.90	75.600	2.072	5.775	This report.

*Kremme, H. R., and Kreps, S. I. J. Chem. Eng. Data *14*, 98 (1969).

Table II. Recalculated 1-Tetradecanol Data

Temp	Vapor pressure		Difference
	Exper	Calcd	
°C	*Torr*		%
151.6	5.2	5.8	11.4
163.0	10.5	10.4	-1.3
171.0	15.3	15.1	-1.1
177.0	19.9	19.8	-0.5
188.4	32.1	32.0	-0.4
199.1	48.4	48.5	0.2
213.3	80.1	80.7	0.7
225.7	120.0	121.2	1.0
243.1	202.8	204.0	0.6
257.8	302.6	304.4	0.6
277.9	501.2	499.8	-0.3
295.9	755.2	746.4	-1.2

The program, with slight modification, may be used to fit other physicochemical data; i.e., densities, fugacities of liquids, kinematic viscosities, etc.

V. CONCLUSIONS.

A conversational FORTRAN computer program is described that calculates the constants required for solution of the Antoine equation for vapor pressure-temperature data. Convenient printouts of experimental data used, calculated vapor pressure data, volatility data, heats of vaporization, and an estimated normal boiling point are provided. In addition, the standard error of estimate is calculated.

LITERATURE CITED

1. Antoine, C. Compt. Rend. *107*, 681 (1888).

2. Thomson, G. W. Chem. Rev. *38*, 1 (1946).

3. Willingham, C. B., Taylor, W. J., Pignocco, J. M., and Rossini, F. D. J. Res. Nat. Bur. Stand. *35*, 219 (1945).

4. Dreisbach, R. R., and Martin, R. A. Ind. Eng. Chem. *41*, 2875 (1949).

5. Klerer, M., and Korn, G. A. Digital Computer User's Handbook Part 3 p 43. McGraw-Hill Book Company, New York, New York. (1967).

6. Wilde, D. J. Optimum Seeking Methods. p 32. Prentice-Hall Inc., Englewood Cliffs, New Jersey. (1964).

7. Typagraph Model 3 User's Manual. Vol 1 General. Typagraph Corporation, San Diego, California. 1970.

8. Kremme, H. R., and Kreps, S. I. J. Chem. Eng. Data *14*, 98 (1969).

9. Christopher, P. M., and Shilman, A. J.Chem. Eng. Data *12*, 333 (1967).

GLOSSARY

A,B,C	Parameters of the Antoine equation
ΔH_v	Heat of vaporization
L_j	Line segments where j is number of divisions by golden section method
n	Number of data points
P	Vapor pressure
R	Ideal gas law constant
S	Sum of the squares of differences between calculated and measured values of log P
SD	Standard error of estimate
t	Temperature in °C
T	Temperature in °K
ΔV	Change in volume associated with vaporization
X	Reciprocal of $-(C + t)$
X_i	The ith value of X
Y	Logarithm of P
Y_i	The ith value of Y
Z	Ratio of successive lengths by golden section

APPENDIXES

APPENDIX A

DEFINITIONS OF TERMS IN PROGRAM

A, B	Parameters in the Antoine equation
BP	Boiling point calculated from Antoine equation
B9	Maximum allowable range of uncertainty associated with the value of parameter C
C	Parameter in the Antoine equation
C1	Log P calculated from Antoine equation
C2	P calculated from Antoine equation
D1	Controls printing of optional data table
G	Linear array of measured pressure values
GOLD	Line segment from golden section method
H	Maximum temperature used in optional output table
I	subscript
IC	Subscript to be used in sub-routine names COMP to select C
INT	Interval of temperature for calculating table
I1, J, K, K1	Subscripts
L	Subscript or lowest temperature in optional output table
L1	Subscript
N1	Number of data points
N9	Controls printing of diagnostic message
PCD	Percent difference between measured and calculated pressures
PRC	Pressure calculated from Antoine equation
RDT	Reciprocal of temperature in °K
SD	Standard error of estimate
S1	Sum of X_i's

S2	Sum of X_i^2's
S3	Sum of $(X_i * Y_i)$'s
S4	Sum of Y_i's
S5	Sum of Y_i^2's
T	Linear array of experimental temperatures in °C
T1	Temperature used for calculating optional output table
V	Linear array of successive values of S
W	Linear array of trial values of parameter C
W1	Lowest value of C used; normally 100
W2	Highest value of C used; normally 273
X	Reciprocal of -(C + t)
Y	Linear array of common logarithms of measured pressure values

APPENDIX B

PROGRAM LISTING

The language used is CALL/360: FORTRAN**. CALL/360 is a system designed to provide the enormous efficiency of fast turnaround conversational computing with immediate access to the full capabilities of a large computer, IBM 360/65 in this case, at a conveniently located remote terminal. Because a few of the features of this subset of FORTRAN may not be familiar to some readers, they are discussed below.

First, the REAL*8 specification statement establishes variables as real constants of eight locations or approximately 16.8 decimal digits of precision. The rest of the real floating point variables are about 7.2 decimal digits. Second, the percentage symbol at the end of a line replaces the continuation number commonly used with cards. Third, the "*" used in the READ commands in place of a format statement number indicates that the format to be used for data input is list directed. In this format, data items are separated by either a comma or a blank space.

**CALL/360 FORTRAN Language Reference Manual. G320-1054-0. International Business Machines Corporation, New York, New York. 1970.

```
100 "TITLE: ANTOINE
105 "PROGRAM TO FIND CONSTANTS FOR THE ANTOINE EQUATION
110      COMMON Y(100),T(100),S4,S5,A,B,W(4),V(4),N1,IC
115      DIMENSION G(100)
120      REAL*8 Y,T,S4,S5,A,B,AFL
125      CALL OPEN(1,'EZ','OUTPUT')
130 "INPUT SECTION
135      WRITE(6,100)
140 100  FORMAT(/' UNITS:  TEMPERATURE     CENTIGRADE'/%
145     *                  PRESSURE        TORR'/)
150   1  WRITE(6,10)
155  10  FORMAT('  HOW MANY POINTS?')
160      READ(5,*)N1
165      S4=0
170      XXX=1E37
175      XXL=9E37
180      S5=0
185      WRITE(6,11)
190  11  FORMAT(' DATA: T1,P1,T2,P2,.....')
195      READ(5,*)(T(I),G(I),I=1,N1)
200 "CALCULATE LOGS OF VAPOR PRESSURES, SUM OF LOGS, AND SUM
205 "OF LOGS SQUARED
210      DO 20  I=1, N1
215      RTK=1.0/(273.16+T(I))
220      WRITE(1) RTK,G(I)
225      Y(I)=ALOG10(G(I))
230      S4=S4+Y(I)
235      S5=S5+Y(I)*Y(I)
240  20  CONTINUE
245      WRITE(1) XXX,XXX
250 140  WRITE(6,12)
255  12  FORMAT('  DATA TABLE? (1=YES; 0=NO)')
260      READ(5,*) D1
265  41  FORMAT(9X'TEMPERATURE'6X'PRESSURE'/)
270      IF( D1 .LT. 0.5 ) GO TO 156
275      WRITE(6,41)
280      DO 40  I=1, N1
285      WRITE(6,87) T(I),G(I)
290  87  FORMAT(3X,1PE16.4,1PE16.3)
295  40  CONTINUE
300 "DEFINE RANGE OF SEARCH
305 156  W1=100
310      W2=273.15
315 " BEGIN SEARCH
320 160  CONTINUE
325 "SET LIMIT OF UNCERTAINTY (B9) ALLOWABLE FOR C
```

```
330      B9=0.005
335      I=1
340      J=2
345      K=3
350      L=4
355 "THE FOUR POINTS INVOLVED IN THE SEARCH ARE STORED IN
360 "      W(N), N=1,4 IN AN ORDER DETERMINED BY PROGRESS
365 "      OF SEARCH
370      W(I)=W1
375      IC=I
380      CALL      COMP
385      W(L)=W2
390      IC=L
395      CALL      COMP
400 184  GOLD=W(L)-W(I)
405      GOLD=GOLD*.61803399
410      IF(GOLD.LT.B9) GO TO 258
415      W(K)=W(I)+GOLD
420      IC=K
425      CALL      COMP
430 "IF  STATEMENTS INVOLVING V(N) DETERMINE WHICH LINE SEGMENTS
435 "TO
440      IF( V(I).GT.V(L)) GO TO 202
445      L=1
450      I=4
455 202  IF( V(K).LT.V(L)) GO TO 214
460      L=4
465      W(I)=W(K)
470      V(I)=V(K)
475      I=1
480      GO TO 184
485 214  L=4
490      I=1
495 218  GOLD=GOLD*.61803399
500      IF( GOLD.LT.B9) GO TO 258
505      W(J)=W(I)+GOLD
510      IC=J
515 226  CALL      COMP
520      IF( V(J).LT.V(K)) GO TO 248
525      I1=I
530      I=J
535      J=K
540      K=I1
545      IF( GOLD.LT.B9) GO TO 258
550      W(K)=W(I)+GOLD
555      GOLD=GOLD*.61803399
560      IC=K
565      GO TO 226
```

```
570 248 L1=L
575     L=K
580     K=J
585     J=L1
590     GO TO 218
595 "DETERMINE WHETHER C IS IN THE INITIAL RANGE
600 258 IF(W1.EQ.W2) GO TO 301
605     IC=J
610     IF( W(I).GT.W1) GO TO 266
615     IC=I
620     GO TO 356
625 266 IF( W(L).LT.W2) GO TO 300
630     IC=L
635     GO TO 362
640 301 IC=I
645 300 CONTINUE
650     C=W(IC)
655     WRITE(6,29)
660 29  FORMAT('0 LOG P=A-B/(C+T)')
665     WRITE(6,28) A,B,W(IC)
670 28  FORMAT('0  A'5X,1PE12.5/3X'B'5X,1PE12.5/3X'C'5X,1PE12.5)
675     SD=SQR1(V(IC)/(N1-1))
680     WRITE(6,27) SD
685 27  FORMAT('0 STANDARD DEVIATION'3X,1PE12.5)
690     BP=-B/(2.88081-A)-C
695     WRITE(6,26)BP
700 26  FORMAT('0 BOILING POINT     ' 4X,1PE12.5)
705     WRITE(6,38)
710 38  FORMAT('0TEMPERATURE'21X'PRESSURE'18X'PERCENT'/%
715     22X'EXPERIMENTAL'5X'CALCULATED'10X'DIFFERENCE' )
720     DO 111 I=1,N1
725     PRC=A-B/(C+T(I))
730     PRC=10.**PRC
735     PCD=(PRC-G(I))*100.0/G(I)
740 43  FORMAT(2X,F8.3,12X,F11.5,5X,F11.5,6X,F11.5)
745     RTK=1.0/(273.16+T(I))
750     WRITE(1) RTK,PRC
755 111 WRITE(6,43) T(I), G(I), PRC, PCD
760     WRITE(1) XXL,XXL
765     CALL CLOSE(1)
770 39  FORMAT('0 TABLE? GIVE: LOWEST,HIGHEST AND INCREMENT OF%
775     TEMPERATURE'/' AS INTEGERS (0,0,0 MEANS NO)')
780     WRITE(6,39)
785     READ(5,*) L,H,INT
790     IF( L.EQ.H) GO TO 387
795     WRITE(6,101)
800 101 FORMAT(/' GIVE MOLECULAR WEIGHT')
805     READ(5,*) XMOL
```

```
      WRITE(6,46)
46    FORMAT(' TEMPERATURE   VAPOR PRESSURE      VOLATILITY%
     1  HEAT OF VAPORIZATION')
      T1=L
      R=0.082053
      CON=1.9872E-3*2.3026
344   C1=A-B/(C+T1)
346   IF(T1.GT.H) GO TO 388
      C2=10.0**C1
      TK=T1+273.15
      VOL=C2*XMOL/(R*TK*760.0)*1.0E+06
      HEAT=CON*B*(TK/(T1+C))**2
      WRITE(6,59) T1, C2, VOL,HEAT
59    FORMAT(2X, F10.3,F16.5,F16.3,F16.3)
      T1=T1+IN1
      GO TO 344
356   WRITE(6,49) W(IC)
49    FORMAT('0 C LESS THAN '1PE12.5)
      GO TO 366
362   WRITE(6,48) W(IC)
48    FORMAT('0 C GREATER THAN '1PE12.5)
366   IF(N9.GT.0) GO TO 378
      N9=3
      WRITE(6,47)
47    FORMAT('0THE CONSTANT C IN LOG P=A+B/(C+T) IS ESTIMATED TO BE'/%
     1  ' OUTSIDE THE RANGE 100 TO 273.  TO CONTINUE, SPECIFY THE'/%
     2  ' ENDPOINTS OF ANOTHER RANGE.  IF BOTH ENDPOINTS ARE THE'/%
     3  ' SAME, THE CALCULATION WILL BE DONE USING THAT VALUE FOR'/%
     4  ' C.  0,0  WILL STOP THE ANALYSIS.')
378   CONTINUE
      READ(5,*) W1,W2
      IF( W1.EQ.0) GO TO 387
      GO TO 160
388   WRITE(6,390)
390   FORMAT(/' UNITS: VOLATILITY        MILLIGRAMS/CUBIC METER'/%
     1  '         HEAT OF VAPORIZATION   KCAL/MOLE'//)
387   WRITE(6,389)
389   FORMAT (' MORE DATA? ( 1=YES, 0=NO )')
      READ(5,*)D1
      IF (D1 .LT. 0.5) GO TO 999
      WRITE (6,391)
391   FORMAT(' NEW FILE NAME ')
      READ (5,*) AFL
      CALL OPEN (1,AFL,'OUTPUT')
      GO TO 1
999   END
```

```
1050      SUBROUTINE      COMP
1055      COMMON Y(100),T(100),S4,S5,A,B,W(4),V(4),N1,IC
1060      REAL*8 Y,T,S1,S2,S3,S4,S5,A,B,X
1065      S1=0
1070      S2=0
1075      S3=0
1080      DO 50 K1=1, N1
1085      X=-1.0/(T(K1)+W(IC))
1090      S1=S1+X
1095      S2=S2+X*X
1100      S3=S3+Y(K1)*X
1105 50   CONTINUE
1110      B=(N1*S3-S1*S4)/(N1*S2-S1*S1)
1115      A=(S4-B*S1)/N1
1120      V(IC)=N1*A**2+2.0*A*B*S1+B*B*S2+S5-2.0*A*S4-2.0*B*S3
1125      RETURN
1130      END
```

APPENDIX C

SAMPLE RUNS

```
RUN

ANTOINE      11:34    10/27/70  TUESDAY     LEA


UNITS:  TEMPERATURE     CENTIGRADE
        PRESSURE        TORR

 HOW MANY POINTS?
? 13

DATA: T1,P1,T2,P2,.....
? 172.1,5.9,  185.3,10.3,  193.4,15.1,  201.0,19.8

? 211.0,30.1,  218.6,40.4,  227.3,55.3,  238.7,80.3

? 251.6,120.3,  269.3,200.5,  285.0,302.1,  305.9,502.4,  325.1,759.2

 DATA TABLE? (1=YES; 0=NO)
? 1

        TEMPERATURE       PRESSURE

        1.7210D+02        5.900E+00
        1.8530D+02        1.030E+01
        1.9340D+02        1.510E+01
        2.0100D+02        1.980E+01
        2.1100D+02        3.010E+01
        2.1860D+02        4.040E+01
        2.2730D+02        5.530E+01
        2.3870D+02        8.030E+01
        2.5160D+02        1.203E+02
        2.6930D+02        2.005E+02
        2.8500D+02        3.021E+02
        3.0590D+02        5.024E+02
        3.2510D+02        7.592E+02

 LOG P=A-B/(C+T)

  A       7.06077D+00
  B       1.89376D+03
  C       1.28406E+02

 STANDARD DEVIATION     7.08865E-03

 BOILING POINT          3.24650E+02
```

TEMPERATURE	PRESSURE		PERCENT
	EXPERIMENTAL	CALCULATED	DIFFERENCE
172.100	5.90000	5.73942	-2.72167
185.300	10.30000	10.56907	2.61235
193.400	15.10000	14.99629	-0.68683
201.000	19.80000	20.50014	3.53603
211.000	30.10001	30.27901	0.59469
218.600	40.39999	40.11848	-0.69681
227.300	55.30000	54.55376	-1.34945
238.700	80.30000	79.82768	-0.58819
251.600	120.30000	119.47359	-0.68696
269.300	200.50000	199.09674	-0.69988
285.000	302.10010	301.92554	-0.05778
305.900	502.39990	501.58472	-0.16226
325.100	759.19995	767.27490	1.06361

TABLE? GIVE: LOWEST,HIGHEST AND INCREMENT OF TEMPERATURE
AS INTEGERS (0,0,0 MEANS NO)
? 150,350,10

GIVE MOLECULAR WEIGHT
? 242.45

TEMPERATURE	VAPOR PRESSURE	VOLATILITY	HEAT OF VAPORIZATION
150.000	1.81390	0.17E+05	20.018
160.000	3.12226	0.28E+05	19.546
170.000	5.18220	0.45E+05	19.110
180.000	8.32321	0.71E+05	18.708
190.000	12.97603	0.11E+06	18.334
200.000	19.69006	0.16E+06	17.987
210.000	29.15074	0.23E+06	17.663
220.000	42.19601	0.33E+06	17.361
230.000	59.83130	0.46E+06	17.078
240.000	83.24406	0.63E+06	16.812
250.000	113.81445	0.85E+06	16.562
260.000	153.12517	0.11E+07	16.327
270.000	202.96800	0.15E+07	16.105
280.000	265.34741	0.19E+07	15.896
290.000	342.48364	0.24E+07	15.698
300.000	436.80786	0.30E+07	15.510
310.000	550.96069	0.37E+07	15.332
320.000	687.78735	0.45E+07	15.163
330.000	850.32446	0.55E+07	15.002
340.000	1041.79248	0.66E+07	14.848
350.000	1265.58472	0.79E+07	14.702

UNITS: VOLATILITY MILLIGRAMS/CUBIC METER
HEAT OF VAPORIZATION KCAL/MOLE

MORE DATA? (1=YES, 0=NO)
? 0

STOP

```
UNITS:  TEMPERATURE     CENTIGRADE
        PRESSURE        TORR

 HOW MANY POINTS?
? 12

DATA: T1,P1,T2,P2,.....
? 151.6,5.2, 163.0,10.5, 171.0,15.3, 177.0,19.9, 188.4,32.1

? 199.1,48.4, 213.3,80.1, 225.7,120.0, 243.1,202.8

? 257.8,302.6, 277.9,501.2, 295.9,755.2

 DATA TABLE? (1=YES; 0=NO)
? 0


 C LESS THAN  1.00000E+02

THE CONSTANT C IN LOG P=A+B/(C+T) IS ESTIMATED TO BE
OUTSIDE THE RANGE 100 TO 273.  TO CONTINUE, SPECIFY THE
ENDPOINTS OF ANOTHER RANGE.  IF BOTH ENDPOINTS ARE THE
SAME, THE CALCULATION WILL BE DONE USING THAT VALUE FOR
C.  0,0  WILL STOP THE ANALYSIS.
? 50,100


 LOG P=A-B/(C+T)

  A       6.21961D+00
  B       1.24490D+03
  C       7.55994E+01

 STANDARD DEVIATION     1.16157E-02

 BOILING POINT          2.97258E+02

TEMPERATURE                     PRESSURE                        PERCENT
                        EXPERIMENTAL      CALCULATED            DIFFERENCE
   151.600                   5.20000         5.49919             5.75361
   163.000                  10.50000        10.04831            -4.30181
   171.000                  15.30000        14.83733            -3.02398
   177.000                  19.89999        19.55545            -1.73137
   188.400                  32.10001        31.92149            -0.55611
   199.100                  48.39999        48.72598             0.67353
   213.300                  80.10001        81.37863             1.59629
   225.700                 120.00000       122.41991             2.01659
   243.100                 202.80000       205.79420             1.47643
   257.800                 302.60010       305.95801             1.10968
   277.900                 501.19995       498.85498            -0.46787
   295.900                 755.19995       738.93457            -2.15378

 TABLE? GIVE: LOWEST,HIGHEST AND INCREMENT OF     TEMPERATURE
AS INTEGERS (0,0,0 MEANS NO)
? 0,0,0
```

DISTRIBUTION LIST 4

Agency	Copies
EDGEWOOD ARSENAL	
Associate Technical Director, ATTN: SMUEA-TD-A	1
Record Copy, ATTN: SMUEA-AGAR	1
Authors Copy, Chemical Research Laboratory	2
Mail Room, Research Laboratories	1
Director, Research Laboratories	1
Chief, Medical Research Laboratory	1
ATTN: SMUEA-RM(3)	7
Chief, Veterinary Medicine Department	2
Chief, Clinical Research Department	3
Chief, Toxicology Department	1
Chief, Biophysics Laboratory	1
Chief, Industry Liaison Office	1
Chief, Chemical Research Laboratory	1
Chief, Analytical Chemistry Department	1
Chief, Organic Chemistry Department	1
Chief, Physical Chemistry Department	1
Chief, Physical Research Laboratory	1
Chief, Dissemination Research Department	1
Technical Support Directorate	
Chief, Field Evaluation Division	1
Technical Information Division	
ATTN: SMUEA-TSTI-TP	2
ATTN: SMUEA-TSTI-TR	1
ATTN: SMUEA-TSTI-TL	10
Director, DDEL	
ATTN: SMUEA-DPP	1
ATTN: SMUEA-DDW	1
Director, WDEL	
ATTN: SMUEA-W	1
ATTN: SMUEA-WCP	1
Systems Analysis Office, ATTN: SMUEA-OS	1
Patent Advisor, Office of Counsel	1
Foreign Intelligence Office, ATTN: SMUEA-POF	3
Director, USAMUCOM, Operations Research Group	1
Commanding Officer, US Army Technical Escort Center	1
CO, Quality Assurance Directorate, ATTN: SMUEA-QAE	1
DEPARTMENT OF DEFENSE	
Defense Documentation Center Cameron Station Alexandria, Virginia 22314	20

DISTRIBUTION LIST 4 (Contd)

Agency	Copies
Defense Intelligence Agency ATTN: DIAAP-7E Washington, D.C. 20301	1
DEPARTMENT OF THE ARMY	
Department of the Army Office, Chief of Research & Development ATTN: OCRD-CRDNCB Washington, D.C. 20310	1
Headquarters Department of the Army OACSFOR ATTN: FOR CM SR Washington, D.C. 20310	1
Director of CBR and Nuclear Operations, OACSFOR Department of the Army ATTN: Tech Coordinator (C) Washington, D.C. 20310	1
Commanding Officer US Army Limited War Laboratory ATTN: CRDLWL-7C ATTN: CRDLWL-7A Aberdeen Proving Ground, Maryland 21005	 1 1
Commanding General US Army Weapons Command Future Wpns Systems Division Rock Island, Illinois 61201	1
USA FSTC AMXST-AB2 Federal Office Building 220 7th Street N.E. Charlottesville, Virginia 22901	1
Commanding General First US Army ATTN: AHABC-N Fort Meade, Maryland 20755	1
HQ USAREUR & Seventh Army ODCSOPS, Doc & Sys Div ATTN: AEAGC-SB APO New York 09403	1
Chief of Research & Development ATTN: Life Sciences Division Department of the Army Washington, D.C. 20310	1

DISTRIBUTION LIST 4 (Contd)

Agency	Copies
Commanding Officer Technical Library ATTN: STEAP-TL Aberdeen Proving Ground, Maryland 21005	1
Commanding General Sixth US Army ATTN: AMOPT-N Presidio of San Francisco, California 94129	1
OFFICE OF THE SURGEON GENERAL	
The Surgeon General Department of the Army ATTN: MEDPS-P Washington, D.C. 20315	1
Commanding General US Army Medical Research & Development Command ATTN: MEDDH-RNC Main Navy Building Washington, D.C. 20315	1
Commander & Director USA Institute of Surgical Research Brooke Army Medical Center Fort Sam Houston, Texas 78234	1
US ARMY MATERIEL COMMAND	
Commanding General US Army Materiel Command ATTN: AMCSF ATTN: AMCRD-BC ATTN: AMCMA-WM Washington, D.C. 20315	 1 1 1
Commanding General US Army Test and Evaluation Command ATTN: AMSTE-NB Aberdeen Proving Ground, Maryland 21005	1
Commanding Officer Rocky Mountain Arsenal ATTN: SMURM-DOF Denver, Colorado 80240	1
Commanding General Deseret Test Center ATTN: Technical Library Dugway, Utah 84022	1

DISTRIBUTION LIST 4 (Contd)

Agency	Copies
Commanding General Deseret Test Center ATTN: STEPD-PA-RA(S) Building 100, Soldier's Circle Fort Douglas, Utah 84113	1
Senior Standardization Representative US Army Standardization Group, UK ATTN: CRDSGU-H65 FPO, New York 09510	1
Senior Standardization Representative US Army Standardization Group Canadian Forces Headquarters Ottawa 4, Ontario, Canada	1
US ARMY MUNITIONS COMMAND	
Commanding General US Army Munitions Command	
ATTN: AMSMU-RE-R	1
ATTN: AMSMU-RE-C	1
ATTN: AMSMU-LB	1
ATTN: AMSMU-LM Dover, New Jersey 07801	1
Commanding Officer Pine Bluff Arsenal ATTN: SMUPB-C-MU Pine Bluff, Arkansas 71601	1
CONARC	
Commandant US Army Chemical Center and School ATTN: AJMCL-A Fort McClellan, Alabama 36201	1
President US Army Armor & Engineer Board ATTN: STEBB-AD-L Fort Knox, Kentucky 40121	1
Commandant US Army Medical Field Service School Brooke Army Medical Center ATTN: CDCO Fort Sam Houston, Texas 78234	1

DISTRIBUTION LIST 4 (Contd)

Agency	Copies
COMBAT DEVELOPMENTS COMMAND	
Commanding General US Army Combat Developments Command ATTN: CDCMR-U Fort Belvoir, Virginia 22060	1
Commanding Officer USA CDC Maintenance Agency ATTN: CDCMA-E Aberdeen Proving Ground, Maryland 21005	1
Commanding Officer USA CDC CBR Agency Fort McClellan, Alabama 36201	1
Commanding Officer USA CDC Infantry Agency Fort Benning, Georgia 31905	1
Commanding General Institute of Land Combat ATTN: Technical Library Fort Belvoir, Virginia 22060	1
Commanding Officer USA CDC Field Artillery Agency ATTN: CAGFA-OS Fort Sill, Oklahoma 73503	1
Commanding Officer USA CDC Institute of Land Combat ATTN: Technical Library 2461 Eisenhower Ave Alexandria, Virginia 22314	1
Commanding Officer USACDC MP Agency ATTN: CDCMPA-O&D Fort Gordon, Georgia 30905	1
DEPARTMENT OF THE NAVY	
Chief, Bureau of Medicine & Surgery Department of the Navy ATTN: Code 723 Washington, D.C. 20390	1

DISTRIBUTION LIST 4 (Contd)

Agency	Copies
Commanding Officer Naval Explosive Ordnance Disposal Facility ATTN: Army Chemical Office Indian Head, Maryland 20640	1
Commander US Naval Weapons Laboratory ATTN: FC ATTN: FX4 Dahlgren, Virginia 22448	1 1
Office of the Chief of Naval Operations OP-342J Navy Department Washington, D.C. 20350	2
Commanding Officer Naval Scientific and Technical Intelligence Center (ATTN: STIC-22) Naval Observatory, Bldg 52 Washington, D.C. 20390	1
Commander Naval Ordnance Systems Command ATTN: ORD-035D1 Department of the Navy Washington, D.C. 20360	1
Commander Naval Air Systems Command Department of the Navy ATTN: Code AIR-350E Washington, D.C. 20360	1
Commander (Code 753) Naval Weapons Center ATTN: Technical Library China Lake, California 93555	1
DEPARTMENT OF THE AIR FORCE	
ADTC (ADAM) Eglin AFB, Florida 32542	1
HQ, USAF ATTN: AFRDDA Washington, D.C. 20330	1
HQ, USAF ATTN: AFMSPG Washington, D.C. 20333	1

DISTRIBUTION LIST 4 (Contd)

Agency	Copies
Commander, USAFSAM ATTN: SMSL (Aeromedical Library) Brooks AFB, Texas 78235	1
Commander Tech Tng Center (TSOP) Lowry AFB, Colorado 80230	1
Commander Headquarters, AFSC ATTN: SCTSW Andrews AFB Washington, D.C. 20331	1
Air Force Armament Labs Chief, Non-Explosive Munitions Division (ATM) Eglin AFB, Florida 32542	1
Commanding Officer OOAMA	
ATTN: OONEC	1
ATTN: OOYIB	1
ATTN: OONNOP Hill AFB, Utah 84401	1
US MARINES	
Headquarters US Marine Corps Office of the Deputy Chief of Staff (Air) ATTN: Code AAW Washington, D.C. 20380	1
Commanding General Fleet Marine Force, Pacific ATTN: Ordnance Section c/o FPO San Francisco, California 96610	1
Development Center Marine Corps Development & Education Command ATTN: NBC Branch, Fire Support Division Quantico, Virginia 22134	1

DISTRIBUTION LIST 4 (Contd)

Agency	Copies
OUTSIDE AGENCIES	
Battelle Memorial Institute Remote Area Conflict Information Center 505 King Avenue Columbus, Ohio 43201	1
PHS/AMC Liaison Officer Fort Detrick Frederick, Maryland 21701	2
Institute for Defense Analyses 400 Army-Navy Drive ATTN: Classified Library Arlington, Virginia 22202	1
Technical Services Division National Library of Medicine 8600 Rockville Pike Bethesda, Maryland 20014	1
National Aeronautics & Space Administration Aerospace Safety Research & Data Institute Lewis Research Center Cleveland, Ohio 44135	1
CONTRACTOR	
The RAND Corporation ATTN: Library D 1700 Main Street Santa Monica, California 90406	1

DISTRIBUTION LIST FOR DD 1473's

Chief of of Research and Development Headquarters, Department of the Army ATTN: Director of Army Technical Information Washington, D.C. 20310	3
Technical Support Directorate	
ATTN: SMUEA-TSTD	1
ATTN: SMUEA-TSTI-TR	1
ATTN: SMUEA-TSTI-TL	2

JCP-I, DPG

UNCLASSIFIED

Security Classification

DOCUMENT CONTROL DATA - R & D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY (Corporate author)	2a. REPORT SECURITY CLASSIFICATION
CO, Edgewood Arsenal ATTN: SMUEA-RCRP (3) Edgewood Arsenal, Maryland 21010	UNCLASSIFIED 2b. GROUP NA

3. REPORT TITLE

CONVERSATIONAL COMPUTATION METHOD FOR FITTING THE ANTOINE EQUATION TO VAPOR PRESSURE-TEMPERATURE DATA

4. DESCRIPTIVE NOTES (Type of report and inclusive dates)

This work was started in March 1969 and completed in October 1970.

5. AUTHOR(S) (First name, middle initial, last name)

Elwin C. Penski and Leo J. Latour, Jr., SP4 E4

6. REPORT DATE	7a. TOTAL NO. OF PAGES	7b. NO. OF REFS
February 1971	41	9

8a. CONTRACT OR GRANT NO.	9a. ORIGINATOR'S REPORT NUMBER(S)
b. PROJECT NO. 1B062116AD10	EATR 4491
c.	9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report)
d.	

10. DISTRIBUTION STATEMENT

Each transmittal of the document outside the agencies of the US Government must have prior approval of the Commanding Officer, Edgewood Arsenal, ATTN: SMUEA-TSTI-T, Edgewood Arsenal, Maryland 21010.

11. SUPPLEMENTARY NOTES	12. SPONSORING MILITARY ACTIVITY
Chemical agents	NA

13. ABSTRACT

A least-squares technique and a search method are combined for determination of the constants of the Antoine equation for vapor pressure data. The method is designed for fitting data that have a relatively constant percentage error rather than a constant absolute error. A conversational FORTRAN program is provided with results of sample runs utilizing data from the open literature. The calculation also provides estimates of heats of vaporization and normal boiling point. Plots of the data are provided automatically through the use of a teleplotter.

14. KEYWORDS

Vapor pressure
Antoine equation
Conversational computation
Least squares
Boiling point
Heat of vaporization
Computer program
Volatility
Physical chemistry
Plotting

DD FORM 1 NOV 68 1473 REPLACES DD FORM 1473, 1 JAN 64, WHICH IS OBSOLETE FOR ARMY USE.

UNCLASSIFIED

Security Classification

DEPARTMENT OF THE ARMY
US ARMY RESEARCH, DEVELOPMENT AND ENGINEERING COMMAND
EDGEWOOD CHEMICAL BIOLOGICAL CENTER
5183 BLACKHAWK ROAD
ABERDEEN PROVING GROUND, MD 21010-5424

REPLY TO
ATTENTION OF

RDCB-DSR-S

OCT 27 2016

MEMORANDUM THRU Director, Edgewood Chemical Biological Center, (RDCB-D/Dr. Joseph L. Corriveau), 5183 Blackhawk Road, Aberdeen Proving Ground, Maryland 21010-5424

FOR Defense Technical Information Center (DTIC), 8725 John J. Kingman Road, Ft Belvoir, VA 22060-6218

SUBJECT: Request for Change in Distribution

1. This action is in response to an Edgewood Chemical Biological Center (ECBC) internal request for a Change in Distribution for the below listed document:

Penski, E.C.; Latour, L.J.; *Conversational Computation Method for Fitting the Antoine Equation to Vapor Pressure-Temperature Data*, Edgewood Arsenal, Aberdeen Proving Ground, MD, 01 February 1971, Distribution E. **CBRNIAC-CB-001954**

2. The above listed document has a current distribution statement prohibiting further release without permission from the proponent office. ECBC Subject Matter Experts have reviewed the document and deemed it suitable for the change in distribution to read "Distribution Statement A: Approved for public release; distribution unlimited."

3. The point of contact is Adana Eilo, ECBC Security Specialist, (410) 436-2063 or adana.l.eilo.civ@mail.mil.

RONALD L. STAFFORD
Security Manager