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Note

A NUMERICAL PROCEDURE FOR CALCULATING CONSTANTS FOR THE ANTOINE EQUATION BY THE FIXED POINT METHOD

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The representation of the vapor pressure of a liquid as a function of temperature is a frequently encountered problem [1]. Although a number of different equations are used, the Antoine equation

$$\log p = A - \frac{B}{C+t} \tag{1}$$

where A, B, and C are constants, is perhaps the best of the three parameter equations for fitting vapor pressure data [1–5]. Furthermore, the constants A, B, and C are useful in calculating other thermodynamic quantities. However, determining the values for the constants is not a simple procedure and several methods have been discussed [3,4]. While the most accurate method is a nonlinear least squares approach, it is mathematically the most complex to perform. The least desirable method is to use the vapor pressures at three temperatures and solve the three equations for A, B, and C. Thompson [3] described a graphical method based on choosing one (p,t) point as being without error. While this might at first seem to be a gross approximation, it is not always so since the boiling point is usually accurately known. Thus, the method of Thompson can provide values for A, B, and C that are nearly as accurate as those from least squares methods. Furthermore, the graphical method of Thompson is easily implemented numerically using a programmable calculator of medium capacity. We describe here the procedure for this numerical evaluation of the Antoine constants.

METHOD

For simplicity, we begin by letting $y = \log p$. If it is assumed that the exact data pair is (y_0, t_0), then

$$y_0 = A - \frac{B}{C+t_0} \tag{2}$$

All the other data are represented by

$$y_i = A - \frac{B}{C + t_i} \tag{3}$$

from which

$$B = -(y_i - A)(C + T_i)$$

Then

$$y_i - y_0 = (y_i - A)(C + t_i)\left[\frac{1}{C + t_i} - \frac{1}{C + t_0}\right] \tag{4}$$

or

$$y_i - y_0 = y_i - A - \frac{(y_i - A)(C + t_i)}{(C + t_0)} \tag{5}$$

Equation (5) simplifies to

$$y_i - y_0 = \frac{(t_0 - t_i)(y_i - A)}{(C + t_0)} \tag{6}$$

which is then placed in the form for computation as [3]

$$\frac{y_i - y_0}{t_i - t_0} = \frac{A}{C + t_0} - \frac{y_i}{C + t_0} \tag{7}$$

If we let $F_i = (y_i - y_0)/(t_i - t_0)$, a linear relationship exists between F_i and y_i with a slope of $-1/(C + t_0)$ and an intercept of $A/(C + t_0)$. Thus, A and C can be evaluated. However, a better way of calculating A and B is from eqn. (3) by using linear regression of y_i and t_i when the value of C has been obtained. Thus, a linear relationship exists between y_i and $1/(C + t_i)$ for which the slope is $-B$ and the intercept is A.

The program

In order to handle N data pairs, $2N$ registers are required. Additionally, most programmable calculators utilize six data registers for linear regression. Thus, $(2N + 6)$ registers are required in addition to some sort of loop control. The program described here for the Texas Instruments TI-59 calculator can load 20 (p_i, t_i) data pairs without repartitioning.

To program the analysis, it is necessary that linear regression be performed twice. The first case uses F_i and y_i. For N data pairs, there will be $(N - 1)$ values of F_i and y_i. In performing the second linear regression, all the data are used with y_i vs. $1/(C + t_i)$ so that there are N data pairs. Thus, the loop control must be changed during program execution. A data counter is built into the data storage routine and the loop control is changed as required during processing.

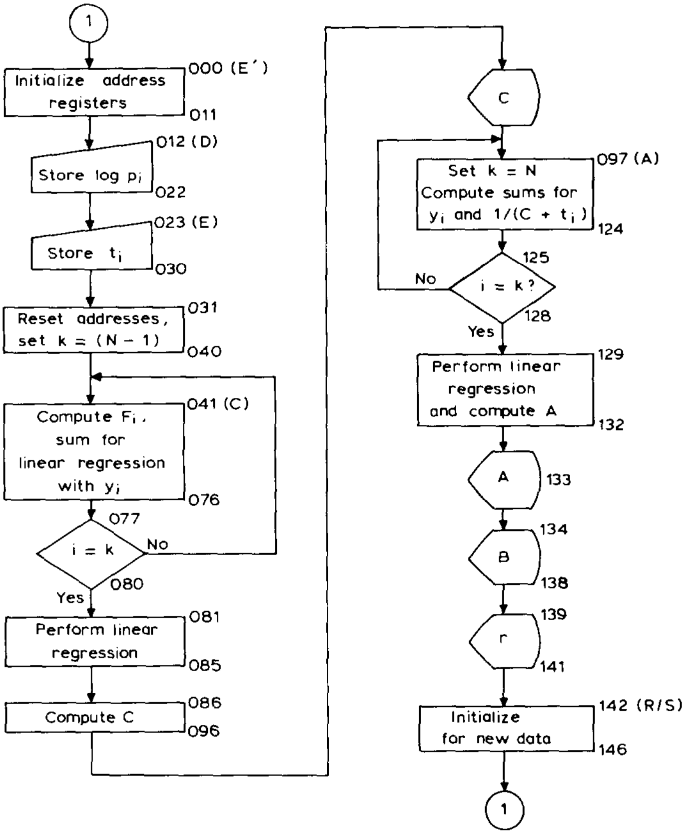

Fig. 1. Flowchart for computing Antoine constants. Numbers refer to steps in the program and letters refer to program labels.

The initialization consists of clearing memories (CMS) and pressing key E′, a label to execute a subroutine to set initial address registers. Next, the p_i values are entered pressing key D after each. They are converted to log p_i and stored. Finally, the t_i values are entered pressing key E after each. Computation begins by pressing key C which results in the value of C being displayed. Pressing key A causes the computation of A and pressing key B causes the computation of B. Pressing key R/S computes the value of the correlation coefficient for the fit of the data to eqn. (1). Pressing the R/S key again clears the register holding the number of data pairs and initializes the address registers for a new data set. Figure 1 shows a flowchart of the computation and a complete program listing is given in the Appendix.

RESULTS

In order to determine the accuracy of the program, vapor pressure data for several types of compounds were studied [6–9]. In each case, the entire

TABLE 1

Antoine constants for several compounds

Compound	Calculated using the program[a]				Published values			
	A[b]	B	C	r[c]	A[b]	B	C	Ref.
Cycloheptane	5.8584	1334.75	216.753	0.9(7)619	5.8568	1333.78	216.644	6
Cyclodecane	5.9879	1683.03	207.918	0.9(7)629	5.9813	1679.01	207.557	6
Cyclohexene	5.8663	1218.38	222.760	0.9(8)09	5.8724	1221.90	223.172	7
Propyl acetate	6.0196	1284.49	208.840	0.9(8)31	6.0199	1284.67	208.860	8
Methyl acetate	6.0304	1135.21	216.691	0.9(7)340	6.0876	1165.80	220.246	8
Butyronitrile	6.1461	1462.88	225.354	0.9(7)678	6.1291	1452.08	224.186	7

[a] Using the vapor pressure data given in the refs. No data points were omitted.

[b] Computed using vapor pressure in the same units as originally reported (kPa, mm Hg, cm Hg).

[c] Number in parentheses is the number of nines following the decimal point. 0.9(7)619 is actually 0.9999999619, etc.

set of data was used as reported with no attempt being made to remove data which were less accurate. In all cases, the highest (p,t) pair listed was assigned as (p_0,t_0). For other data sets for which the calculated results are not shown, it was frequently found that selecting a different pair as (p_0, t_0) improved the accuracy of the results. The results of the computations are shown in Table 1. For most purposes, the accuracy of ± 0.005 in A, $+0.5$ in C, and ± 1.0 in B is sufficient [3]. The results shown in Table 1 indicate that the calculator program implementing the numerical equivalent of Thompson's graphical method provides a sufficient level of accuracy. The computation is completed in a total computing time of 50 sec (for a set of 10 data pairs) and the computed constants enable data to be presented using the Antoine equation rather than the usual $\log p = A + B/T$ form.

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APPENDIX

TI-59 Program for computing Antoine constants

```
000   76   LBL      037   01   1        074   54   )        111   85   +
001   10   E'       038   95   =        075   54   )        112   43   RCL
002   02   2        039   42   STO      076   78   Σ+       113   16   16
003   00   0        040   00   00       077   97   DSZ      114   54   )
004   42   STO      041   36   PGM      078   00   00       115   35   1/X
005   10   10       042   01   01       079   00   00       116   32   X ≷ T
006   04   4        043   71   SBR      080   45   45       117   73   RC*
007   00   0        044   25   CLR      081   60   OP       118   10   10
008   42   STO      045   01   1        082   12   12       119   78   Σ+
009   11   11       046   44   SUM      083   42   STO      120   01   1
010   92   RTN      047   10   10       084   14   14       121   44   SUM
011   91   R/S      048   44   SUM      085   32   X ≷ T    122   10   10
012   76   LBL      049   11   11       086   42   STO      123   44   SUM
013   14   D        050   73   RC*      087   15   15       124   11   11
014   28   LOG      051   10   10       088   94   +/-      125   97   DSZ
015   72   ST*      052   42   STO      089   35   1/X      126   00   00
016   10   10       053   08   08       090   75   -        127   01   01
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017   01   1        054   32   X ≷ T    091   43   RCL      128   08   08
018   44   SUM      055   73   RC*      092   40   40       129   69   OP
019   10   10       056   11   11       093   95   =        130   12   12
020   69   OP       057   42   STO      094   42   STO      131   42   STO
021   27   27       058   09   09       095   16   16       132   19   19
022   91   R/S      059   53   (        096   91   R/S      133   91   R/S
023   76   LBL      060   53   (        097   76   LBL      134   76   LBL
024   15   E        061   43   RCL      098   11   A        135   12   B
025   72   ST*      062   08   08       099   43   RCL      136   32   X ≷ T
026   11   11       063   75   -        100   07   07       137   94   +/-
027   01   1        064   43   RCL      101   42   STO      138   91   R/S
028   44   SUM      065   20   20       102   00   00       139   69   OP
029   11   11       066   54   )        103   10   E'       140   13   13
030   91   R/S      067   55   ÷        104   36   PGM      141   91   R/S
031   76   LBL      068   53   (        105   01   01       142   00   0
032   13   C        069   43   RCL      106   71   SBR      143   42   STO
033   10   E'       070   09   09       107   25   CLR      144   07   07
034   43   RCL      071   75   -        108   53   (        145   61   GTO
035   07   07       072   43   RCL      109   73   RC*      146   10   E'
036   75   -        073   40   40       110   11   11
```