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Note

# A NUMERICAL PROCEDURE FOR EVALUATING THE CONSTANTS FOR THE FROST–KALKWARF EQUATION BY THE REFERENCE POINT METHOD

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Thermodynamic properties are frequently calculated by means of vapor pressure relationships. Therefore, a great deal of effort has been expended to establish vapor pressure correlations [1], and the Frost–Kalkwark equation is one of the most accurate of these [1,2]. This equation is written as

$$\log p = A + \frac{B}{T} + C \log T + \frac{Dp}{T^2} \tag{1}$$

where $A$, $B$, $C$, and $D$ are constants, $T$ is the temperature (K), and $p$ is the vapor pressure (Torr). The constant $D$ is related to the van der Waals **a** parameter by $D = \mathbf{a}/2.303R^2$ [2]. Fitting the vapor pressure data to this equation to determine the four constants requires a non-linear least-squares approach. However, Frost and Kalkwarf described a graphical procedure for determining $A$, $B$, and $C$ when $D$ is known from the van der Waals **a** parameter [2]. Since this equation has been of considerable use in recent work on vapor pressure relations [3], we have developed a numerical procedure to replace the graphical method previously described. We report here the procedure for performing this numerical analysis by means of a programmable calculator.

## METHOD

### *The procedure*

The procedure described by Frost and Kalkwarf involves choosing a reference point ($p_0$, $T_0$) which is presumed to be known exactly [2]. Frost and Kalkwarf chose the critical point as the reference point for hydrocarbons but chose the triple point for carbon dioxide and the boiling point for water. In this work, we have chosen the critical point as the reference point except for water. For this reference point, the equation can be written as

$$\log p_0 = A + \frac{B}{T_0} + C \log T_0 + \frac{Dp_0}{T_0^2} \tag{2}$$

while for other conditions we can write

$$\log p_t = A + \frac{B}{T_t} + C \log T_t + \frac{Dp_t}{T_t^2} \tag{3}$$

Subtracting eqn. (2) from eqn. (3) and rearranging yields

$$\log \frac{p_t}{p_0} = B\left(\frac{1}{T_t} - \frac{1}{T_0}\right) + C \log \frac{T_t}{T_0} + D\left(\frac{p_t}{T_t^2} - \frac{p_0}{T_0^2}\right) \tag{4}$$

Thus, by rearranging eqn. (4) and dividing by $[(1/T_t) - (1/T_0)]$ we can write

$$\frac{\log \frac{p_t}{p_0} - D\left(\frac{p_t}{T_t^2} - \frac{p_0}{T_0^2}\right)}{\frac{1}{T_t} - \frac{1}{T_0}} = \frac{C\left(\log \frac{T_t}{T_0}\right)}{\frac{1}{T_t} - \frac{1}{T_0}} + B \tag{5}$$

Now

$$D = \mathbf{a}/2.303R^2 \tag{6}$$

where **a** is the van der Waals constant. However, this constant can be expressed in terms of the critical temperature, $T_c$, and the critical pressure, $p_c$, as

$$\mathbf{a} = 27R^2T_c^2/64p_c \tag{7}$$

Consequently, we can write

$$D = 0.183218T_c^2/p_c \tag{8}$$

Therefore, if the critical temperature and critical pressure are known, $D$ can be evaluated. With $D$ being known, eqn. (5) can be considered as a linear equation having a slope of $C$ and an intercept of $B$ when the left-hand side of eqn. (5) is plotted vs. $\log(T_t/T_0)/[(1/T_t) - (1/T_0)]$. The constant $A$ can then be determined by substituting the values for $B$, $C$, and $D$ in eqn. (2). While the original procedure was carried out graphically, we have programmed the calculation for numerical analysis using a Texas Instruments TI-59 programmable calculator. In addition to using linear regression to determine the values of $B$ and $C$, the computation makes use of the $B$, $C$, and $D$ values to calculate the value of $A$ from every data pair rather than using only the reference point. An average value of $A$ is then computed from all these individual values.

## *The program*

The program described here is designed for the TI-59 programmable calculator, but it can easily be modified for use with other machines of similar capacity or with microcomputers. Initialization consists of executing a procedure to clear all memories (CMS) by pressing key C. Next, the value of $D$ is stored in register 17. Initial addresses for data storage registers are set by pressing key D. The ($p_i$, $t_i$) data are entered with the temperature in °C being converted to Kelvin. First, $p_i$ is entered by pressing key A then $t_i$ is entered and key B is pressed. The reference point ($p_0$, $T_0$) is entered first. The data points are counted as the data are entered so that loop counters are set automatically, and the number of data points ($N$) is stored. This is necessary because ($N - 1$) points are used in linear regression but all $N$ points are used in computing the average value of $A$. In the Frost and Kalkwarf procedure, only one point was used to calculate $A$, but the program computes a value for $A$ for each point and calculates the average value and the standard deviation. After the data are entered, computation is initiated by pressing key E. At the end of the computation, the display shows the average value calculated for $A$. Repeated pressing of R/S displays the standard deviation in $A$ values, $B$, $C$, $D$, and the correlation coefficient of the linear relationship of eqn. (5) to be displayed in that order. A complete listing of the program is given in the Appendix. As designed, the program can accomodate up to 20 data pairs without repartitioning of the memory.

## RESULTS AND DISCUSSION

The program was used with vapor pressure data for the same compounds as were studied in the original graphical method of Frost and Kalkwarf. The values for $D$ were computed from critical constants tabulated by Reid et al. [1] using eqn. (8). Vapor pressures for the normal hydrocarbons from methane to *n*-octane were obtained from the values tabulated by Thodos [4]. These tables include data from a few Torr up to the critical pressures. Vapor pressures for water were obtained from the compilation of Stull [5] and include the range 5–760 Torr. In each case, the values for $A$, $B$, and $C$ were computed using the procedure described here and the results were compared with those reported by Frost and Kalkwarf [2]. Table 1 shows this comparison. In the compilation by Reid et al. [1], values for the constants are based on the natural logarithm form of eqn. (1) and, therefore, the tabulated values for $A$, $B$, and $D$ must be divided by ln(10) to make them comparable. Such values are also shown in Table 1.

The data shown in Table 1 indicate that, in general, the simple numerical procedure described here gives accurate values for the constants of the Frost–Kalkwarf equation. Agreement with the published values of Frost and Kalkwarf [2] and Reid et al., [1] is generally good. However, certain cases exist for which the values obtained for the constants agree rather more closely with those tabulated by one or the other of the published sets of values. For example, the constants obtained for propane and hexane agree more closely with those published by Frost and Kalkwarf. On the other

TABLE 1

A comparison of constants for the Frost–Kalkwarf equation

| | | This work [a] | Frost and Kalkwarf [2] | Reid et al. [1] [b] |
|---|---|---|---|---|
| Methane | $A$ | 13.24506 | 13.44740 | 13.339 |
| | $-B$ | 562.4546 | 567.5868 | 564.85 |
| | $-C$ | 2.604730 | 2.681065 | 2.641 |
| | $D$ | 0.192905 | 0.191423 | 0.192 |
| Ethane | $A$ | 16.89420 | 16.74451 | 16.832 |
| | $-B$ | 1072.611 | 1068.273 | 1070.28 |
| | $-C$ | 3.622538 | 3.566685 | 3.601 |
| | $D$ | 0.466493 | 0.457881 | 0.4686 |
| Propane | $A$ | 19.77665 | 19.05446 | 18.888 |
| | $-B$ | 1455.786 | 1429.728 | 1418.81 |
| | $-C$ | 4.486090 | 4.227769 | 4.179 |
| | $D$ | 0.786816 | 0.736275 | 0.786 |
| *n*-Butane | $A$ | 20.95181 | 21.68560 | 20.991 |
| | $-B$ | 1764.335 | 1793.194 | 1765.65 |
| | $-C$ | 4.767115 | 5.024486 | 4.781 |
| | $D$ | 1.162277 | 1.22954 | 1.16 |
| *n*-Pentane | $A$ | 22.60655 | 22.92307 | 22.880 |
| | $-B$ | 2082.845 | 2098.332 | 2096.37 |
| | $-C$ | 5.221270 | 5.328139 | 5.313 |
| | $D$ | 1.596491 | 1.61495 | 1.60 |
| *n*-Hexane | $A$ | 26.04122 | 25.08480 | 24.87595 |
| | $-B$ | 2487.404 | 2436.187 | 2426.586 |
| | $-C$ | 6.272973 | 5.955353 | 5.885 |
| | $D$ | 2.118302 | 2.07240 | 2.075 |
| *n*-Heptane | $A$ | 26.23013 | 26.86378 | 26.612 |
| | $-B$ | 2715.337 | 2750.888 | 2737.74 |
| | $-C$ | 6.248694 | 6.458216 | 6.373 |
| | $D$ | 2.608447 | 2.66736 | 2.606 |
| *n*-Octane | $A$ | 27.83453 | 29.02343 | 28.941 |
| | $-B$ | 3015.918 | 3087.966 | 3083.79 |
| | $-C$ | 6.695886 | 7.080892 | 7.053 |
| | $D$ | 3.183520 | 3.17191 | 3.17 |
| Water | $A$ | 22.02383 | 22.75017 | 24.032 |
| | $-B$ | 2874.894 | 2908.894 | 2983.39 |
| | $-C$ | 4.449218 | 4.695517 | 5.115 |
| | $D$ | 0.464118 | 0.424676 | 0.456 |

[a] Values are tabulated to these numbers of digits to match the listing given by Frost and Kalkwarf [2].

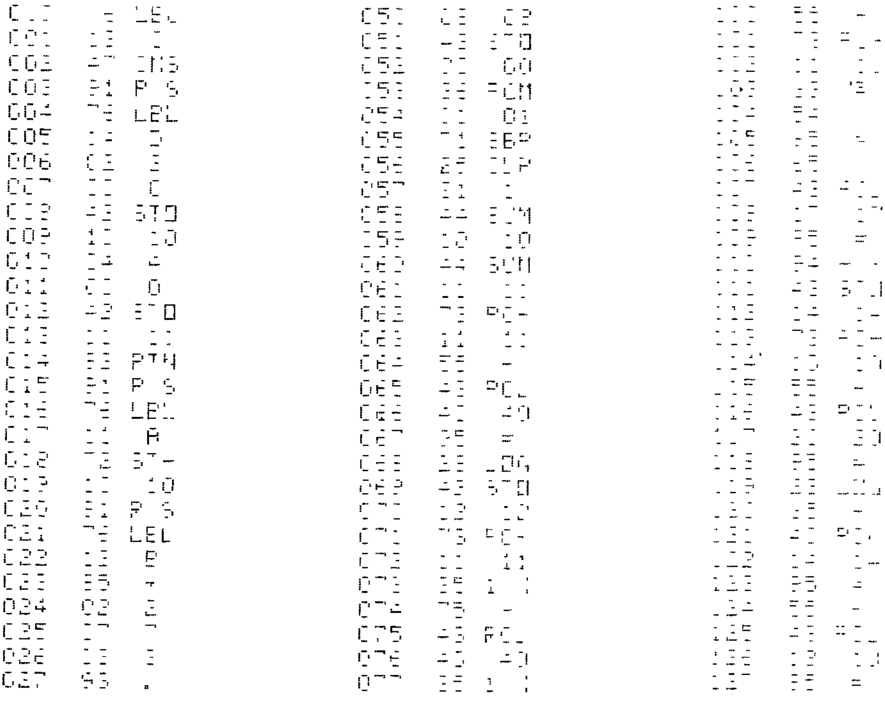
[b] Values for $C$ are those listed by Reid et al. [1]. Values for $A$, $B$, and $D$ are calculated from data given by Reid et al., with the number of digits retained to match those given in the original listings.

hand, the values for the constants for methane, butane, and heptane obtained in this work are in somewhat better agreement with those given by Reid et al., than with those given by Frost and Kalkwarf. In general, we obtain constants in better agreement with values published by Reid et al. Thus, constants obtained by the numerical method described here agree well with those obtained by computer methods.

Part of the apparent difference between the constants from different sources may lie in the fact that different ranges of vapor pressure are used in the calculations [2]. For example, we have used vapor pressure data in the range 5–760 Torr for the hydrocarbons [5] with the boiling point being taken as the reference point. In these cases, the computed constants are adequate, but the agreement with published values is generally worse than that illustrated by the data in Table 1. Therefore, the computed constants will not agree exactly unless the same vapor pressure ranges are used regardless of the computational technique employed. In any case, the constants obtained quickly and easily using the computational procedure given here are sufficiently accurate to reproduce the vapor pressures well enough for most purposes.

## APPENDIX

TI-59 program for calculating Frost-Kalkwarf constants.



```
028   01   1
029   05   5
030   95   =
031   72  ST*
032   11   11
033   01   1
034   44  SUM
035   10   10
036   44  SUM
037   11   11
038   69  OP
039   27   27
040   91  R/S
041   76  LBL
042   15   E
043   14   D
044   43  RCL
045   07   07
046   75   -
047   01   1
048   95   =
049   42  STO
150   07   07
151   42  STO
152   00   00
153   73  RC*
154   10   10
155   28  LOG
156   75   -
157   53   (
158   53   (
159   43  RCL
160   15   15
161   55   ÷
162   73  RC*
163   11   11
164   54   )
165   55   ÷
166   53   (
167   43  RCL
168   16   16
169   65   ×
170   73  RC*
171   11   11
172   28  LOG
173   54   )
174   85   +
175   53   (
176   43  RCL
177   17   17
178   65   ×
179   73  RC*
180   10   10
181   55   ÷
182   73  RC*
183   11   11
184   33  X²
185   54   )
```

```
078   95   =
079   42  STO
080   13   13
081   43  RCL
082   12   12
083   55   ÷
084   43  RCL
085   13   13
086   95   =
087   32  X:T
088   43  RCL
089   20   20
090   55   ÷
091   43  RCL
092   40   40
093   33  X²
094   95   =
095   94  +/-
096   55   ÷
097   53   (
098   73  RC*
099   10   10
186   54   )
187   95   =
188   78  Σ+
189   01   1
190   44  SUM
191   10   10
192   44  SUM
193   11   11
194   97  DSZ
195   00   00
196   01   01
197   53   53
198   79   x̄
199   42  STO
200   18   18
201   69  OP
202   11   11
203   42  STO
204   19   19
205   43  RCL
206   18   18
207   91  R/S
208   43  RCL
209   19   19
210   91  R/S
211   43  RCL
212   15   15
213   91  R/S
214   43  RCL
215   16   16
216   91  R/S
217   43  RCL
218   17   17
219   91  R/S
220   43  RCL
221   09   09
222   91  R/S
```

```
128   78  Σ+
129   97  DSZ
130   00   00
131   00   00
132   57   57
133   69  OP
134   12   12
135   42  STO
136   15   15
137   32  X:T
138   42  STO
139   16   16
140   69  OP
141   13   13
142   42  STO
143   09   09
144   36  PGM
145   01   01
146   71  SBR
147   25  CLR
148   14   D
149   43  RCL
```

## REFERENCES

1 R.C. Reid, J.M. Prausnitz and T.K. Sherwood, The Properties of Gases and Liquids, 3rd edn., McGraw-Hill, New York, 1977.
2 A.A. Frost and D.R. Kalkwarf, J. Chem. Phys., 21 (1953) 264.
3 J.E. House, Jr., unpublished results.
4 G. Thodos, Ind. Eng. Chem., 42 (1950) 1514.
5 D.R. Stull, Ind. Eng. Chem., 39 (1947) 517.