CORRELATION OF PURE COMPONENT VAPOR PRESSURES VIA A MODIFIED VAN DER WAALS EQUATION

Charles R. Koppany, PhD, Chem. Eng.

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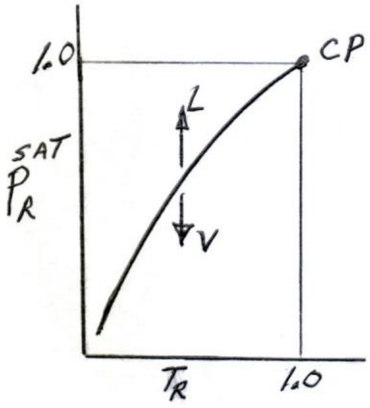

In a four part series of papers Koppany (3) modified the original van der Waals equation by making it a three parameter dependent (T_c, P_c, ω) equation of state where ω is the well known Pitzer acentric factor. This work was done in order to make the VDW equation better predict pure component vapor pressures and mixture vapor-liquid equilibria.

In this second paper of a two part series we show detailed graphical comparisons between reduced vapor pressures (P_R^{Sat} vs T_R) generated from the modified van der Waals equation and actual experimental data for a series of selected hydrocarbons and non hydrocarbon gases covering a range of acentric factors up to nearly 0.50. The modified VDW predictions are also graphically compared against the P_R^{Sat} versus T_R curves independently generated from the three-parameter Lee-Kesler (2) correlation for the same components considered above.

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CORRELATION OF PURE COMPONENT VAPOR PRESSURES VIA A MODIFIED VAN DER WAALS EQUATION

I. Introduction

Previous Paper In the previous paper (1) we developed "generalized" vapor pressure curves in reduced coordinate format (P_R^{Sat} as a function of T_R) using two classical cubic equations of state, namely the van der Waals and Redlich-Kwong equations, both converted to the reduced format i.e. $P_R = f(V_R, T_R)$. In turn, we compared the above predicted curves with the three-parameter corresponding states correlation (P_R^{Sat} as a function of T_R and ω) of Lee and Kesler (2). All of the above correlations were in turn compared against actual experimental vapor pressure data.

The three-parameter (T_c, P_c,ω) corresponding states correlation of Lee and Kesler provides an excellent representation of the vapor pressure of pure fluids displaying quite a range of acentric factors ω (extent of molecular complexity) and molecular polarity.
The two equations of state are simply two-parameter PVT correlations (T_c, P_c) and can only predict a single "generalized" reduced vapor pressure versus T_R curve because they are only capable of predicting a single value for the "effective" acentric factor as listed below:

EOS	$\omega_{effective}$
VDW	- 0.302
RK	0.062

The Redlich-Kwong (RK) equation provides an adequate representation of reduced vapor pressures if the molecular structure of the fluid of interest is close to being spherical i.e. for $0.0 \le \omega \le 0.10$. The van der Waals equation produces absurd results for the prediction of P_R^{Sat}. It predicts values that are excessively high and also an "effective" acentric factor that is negative.

In a four part series of papers Koppany (3) modified the original VDW equation in a similar fashion as did G. Soave (4) for the original RK equation to better predict pure component vapor pressures and mixture VLE. The proposed modification consisted of making the energy of interaction term (<u>a</u>) a general function of temperature as follows:

$$P = \frac{RT}{V-b} - \frac{a(T)}{V^2} \quad ; \quad a(T) = \alpha(T)\, a_c \qquad (1a,b)$$

Here V is the volume occupied by one mole of fluid.

$$\text{where} \qquad a_c = \frac{27 R^2 T_c^2}{64 P_c} \quad ; \quad b = \frac{R T_c}{8 P_c} \qquad (2a,b)$$

The alpha (α) function was in turn correlated against the reduced temperature T_R and the component acentric factor ω using pure component vapor pressures with the result being:

$$\alpha^{0.5} = 1 + m\left(1 - T_R^{0.5}\right) \tag{3}$$

with

$$m = 0.551088 + 1.452291\omega \tag{4}$$

In essence, this modification transformed the original VDW equation into a three-parameter equation of state i.e. it now becomes dependent not only upon T_c and P_c but on ω as well.

At this point we thought that it would be conceivable that this modified VDW equation could also be transformed to a three-parameter reduced coordinate format and then used with the equilibrium criterion:

$$\phi^L = \phi^V \tag{5}$$

to predict reduced vapor pressures P_R^{Sat} as a function of T_R with ω as parameter similar in scope to the Lee-Kesler correlation. However we found the mathematical analysis for this effort to be impossible. The fundamental problem here is that the equation of state constants $\underline{a}$ and $\underline{b}$ become absorbed with the reduced variables P_R, T_R and V_R, thus not permitting us to relate or incorporate the effect of the acentric factor itself.

This Study Because of our inability to work with a reduced form of the modified VDW equation, we simply proceeded to use Equations 1-4 directly in conjunction with the equilibrium criterion, Equation 5, to predict vapor pressures and the subsequent reduced vapor pressures for a series of selected pure components covering a rather broad range of acentric factors up to nearly 0.5. The modified VDW predictions were then graphically compared against the actual vapor pressure data and also against the curves generated from the three-parameter Lee-Kesler correlation for these same components.

II. Working Forms of the Modified VDW EOS and Fugacity Coefficient

Van der Waals Eqn. For programming purposes it is convenient to work with the compressibility factor form of the van der Waals equation. This is accomplished by substituting the following identities into Equation 1:

$$a = \frac{AR^2T^2}{P} \quad ; \quad b = \frac{BRT}{P} \quad ; \quad V = \frac{ZRT}{P} \tag{6a,b,c}$$

The final result after substitution and rearrangement becomes,

$$Z^3 - (B+1)Z^2 + AZ - AB = 0 \qquad (7)$$

In Equation 6a the term a is given by Equation 1b where the dimensionless, temperature dependent parameter α becomes unity at $T = T_c$.

Fugacity Coefficient For a single pure component phase (L or V), the general volume explicit form of the fugacity coefficient equation can be written as,

$$Ln\left(\frac{f}{P}\right) = Ln\phi = (Z-1) - Ln Z + \int_0^{1/V} (Z-1)V\, d\left(\frac{1}{V}\right) \qquad (8)$$

If we substitute Equation 1a and the identities given by Equations 6 a,b,c into Equation 8, then after rearrangement and simplification, we arrive at,

$$Ln\left(\frac{f}{P}\right) = Z - 1 - Ln(Z-B) - \frac{A}{Z} \qquad (9)$$

or its equivalent form,

$$Ln\left(\frac{f}{P}\right) = Ln\left(\frac{1}{Z-B}\right) + \frac{B}{Z-B} - 2\frac{A}{Z} \qquad (10)$$

III. Algorithm/Program for Computing Vapor Pressure

Z-Roots for EOS The compressibility factor form of the VDW equation can be expressed as a cubic polynomial in Z as shown by Equation 7. It can be solved rather conveniently for the desired root(s) by employing the rather robust Newton-Raphson numerical method. This procedure consists of an iterative (predictor/corrector) routine using Equation 11 below,

$$Z^{new} = Z^{old} - \frac{f\left(Z^{old}\right)}{f'\left(Z^{old}\right)} \qquad (11)$$

where f(Z) is given by Equation 7 and therefore,

$$f'(Z) = \frac{d\, f(Z)}{d\, Z} = 3Z^2 - 2(B+1)Z + A \qquad (12)$$

A subroutine (inner program loop) included in the program for computing vapor pressures will calculate two roots for Z, one for the saturated liquid and one for the saturated vapor. These roots consist of the lowest and highest ones respectively. Equation 11 generally requires a sound initial estimate for Z. For the liquid an initial trial value of $Z^L = 0.001$ and for the vapor an initial value of $Z^V = 1.00$ generally suffice.

Component Fugacities Once Z^L and Z^V are determined from the EOS based on a trial value of the vapor pressure for a specified temperature T, it is then necessary to see if Equation 5 is satisfied in the outer program loop. The value of P^{Sat} is adjusted if necessary until Equation 5 is satisfied within some specified error tolerance.

Equation 5 can be expressed in logarithmic form such that,

$$Ln\left(\frac{\phi^V}{\phi^L}\right) = 0 \quad or \quad Ln\,\phi^V - Ln\,\phi^L = 0$$

Now we can apply the Newton-Raphson procedure in the program's outer loop to converge on the correct value of P^{Sat}.

$$F\left(P\right) = Ln\, f^V - Ln\, f^L = 0 \quad at\ solution$$

$$d\,F\left(P\right) = d\,Ln\, f^V - d\,Ln\, f^L$$

Based on the fundamental definition of the fugacity, we can readily write,

$$d\,F = \frac{V^V}{RT}dP - \frac{V^L}{RT}dP \quad or \quad \frac{d\,F}{d\,P} = \frac{V^V - V^L}{RT}$$

The latter differentiation presumes that small variations in pressure have an insignificant effect on the vapor and liquid molar volumes. Therefore the Newton-Raphson iteration formula for the outer program loop iteration sequence can be expressed as follows:

$$P^{Sat(new)} = P^{Sat(old)} - \frac{F}{dF\,/\,dP^{Sat}}$$

$$or \qquad P^{Sat(new)} = P^{Sat(old)} - \frac{Ln\left(\dfrac{f^V}{f^L}\right)}{\dfrac{V^V - V^L}{RT}} \qquad (13)$$

Computational Algorithm The complete step-by-step algorithm for computing vapor pressures is summarized below:

1. For a specified $T < T_c$, estimate P^{Sat}.

2. Solve the compressibility factor form of the modified VDW Eqn. 7 for Z^L and Z^V using the Newton-Raphson numerical procedure (inner loop).

3. Then for the outer loop, calculate the liquid and vapor molar volumes:

$$V^L = \frac{Z^L\,RT}{P} \quad ; \quad V^V = \frac{Z^V\,RT}{P}$$

4. Calculate Ln ϕ^L, Ln ϕ^V and F = Ln ϕ^V - Ln ϕ^L using Equation 10.

5. Calculate

$$\frac{dF}{d\,P} = \frac{V^V - V^L}{RT} = F^{/}\left(P\right)$$

6. Calculate

$$P^{Sat(new)} = P^{Sat(old)} - \frac{F\left(P^{Sat(old)}\right)}{F^{/}\left(P^{Sat(old)}\right)}$$

7. Calculate the tolerance $\in$ = abs ($P^{Sat(new)}$ - $P^{Sat(old)}$).

8. If the value of $\in$ does not meet the required tolerance window, then replace the old value of the vapor pressure with the new one i.e. $P^{Sat(old)} = P^{Sat(new)}$.

9. Then return to Step 2 above.

10. If the tolerance window is met, then the outer loop is exited and the values of T, P^{Sat}, V^V and V^L (both in cuft/lb) are printed out.

Step 2 comprises the inner loop (subroutine) for the program. The balance of the steps outlined above represent the outer loop where the desired (converged) value of the vapor pressure is calculated.

BASIC Computer Program Table 1 is a listing of the BASIC program entitled VDWVP.BAS which performs the above computational algorithm using the modified VDW equation developed in Reference 3. Table 2 provides the output specifically for ethyl benzene over the temperature range 280 to 630 deg. F. In Line 30 of the program, the system temperature (deg. F) and an estimate of the vapor pressure (psia) are inputted. The required component equation of state parameters are calculated in Lines 45-70. The inner loop or subroutine (Line 760) is called upon at this point in order to calculate the liquid and vapor phase compressibility factors from Equation 7 of the text. Values of the liquid and vapor phase molar volumes calculated from these Z factors are subsequently fed to the outer loop (Lines 85-155) where the value of the vapor pressure is iterated upon using the fugacity coefficient expression given by Equation 10 applied to both phases. The inner loop is repeated as many times as necessary to obtain convergence. Upon convergence of the outer loop, the results are finally printed out in Line 160.

IV. Comparison of Predicted and Experimental Vapor Pressures

Modified VDW EOS Figures 1 and 2 show detailed graphical comparisons between reduced vapor pressure curves (P_R^{Sat} vs T_R) generated from the modified van der Waals equation and actual experimental data shown as individual plotted points. Figure 1 covers three paraffin hydrocarbons and four non hydrocarbons including the polar fluids NH_3 and H_2O. Figure 2 provides a similar comparison covering H_2S, butene-1, propyne and ethyl benzene. The majority of the data employed here were read from the vapor pressure charts published in the Data Book of the American Petroleum Institute (5). For water the data were extracted from the steam tables of Keenan and Keyes (6). And for CO_2, the tabulated data of Din (7) were utilized. Beside each component listed on these charts are given their respective acentric factors.

Figure 1 - Comparison of Reduced Vapor Pressure Curves Predicted from the Modified VDW Equation Against Actual Data

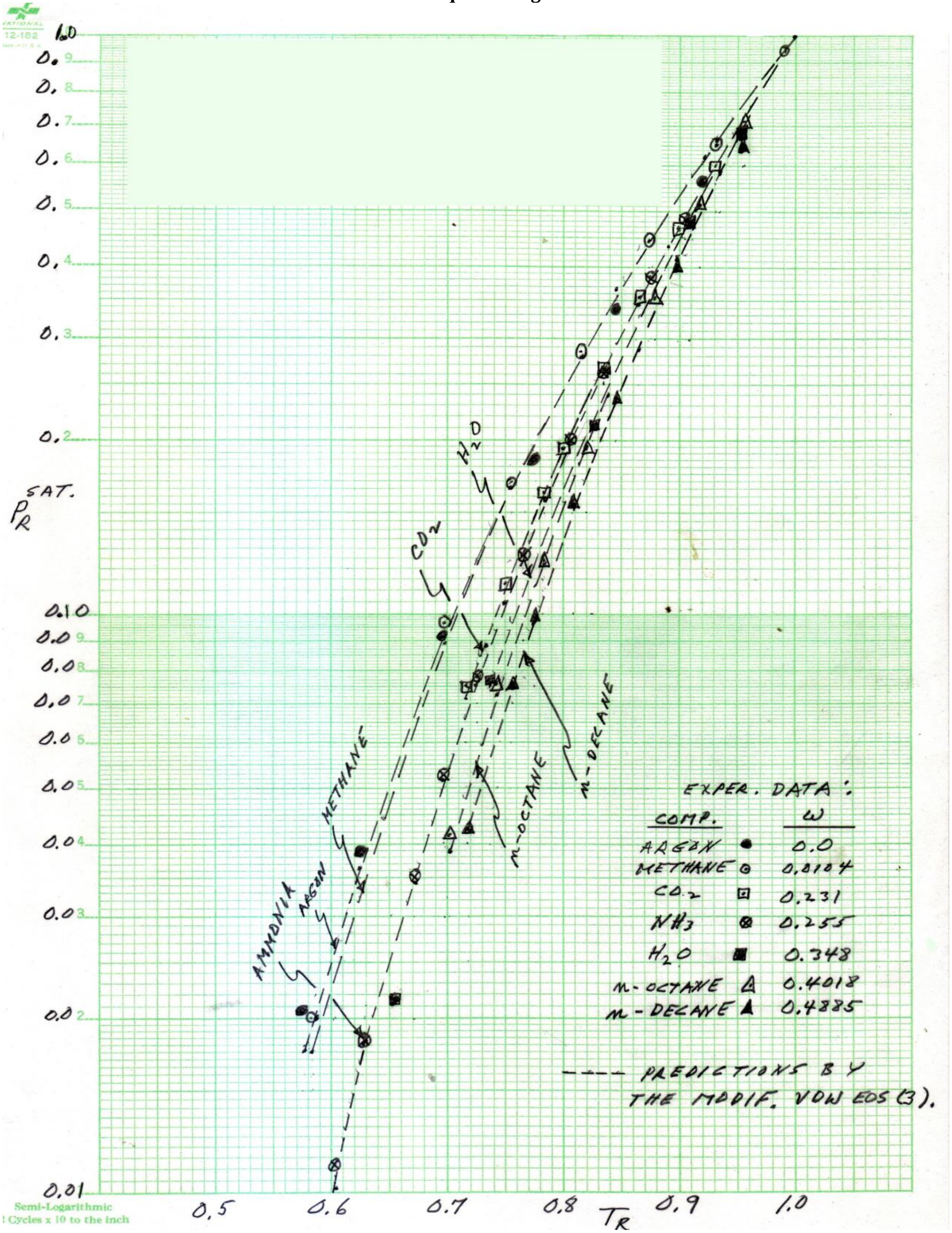
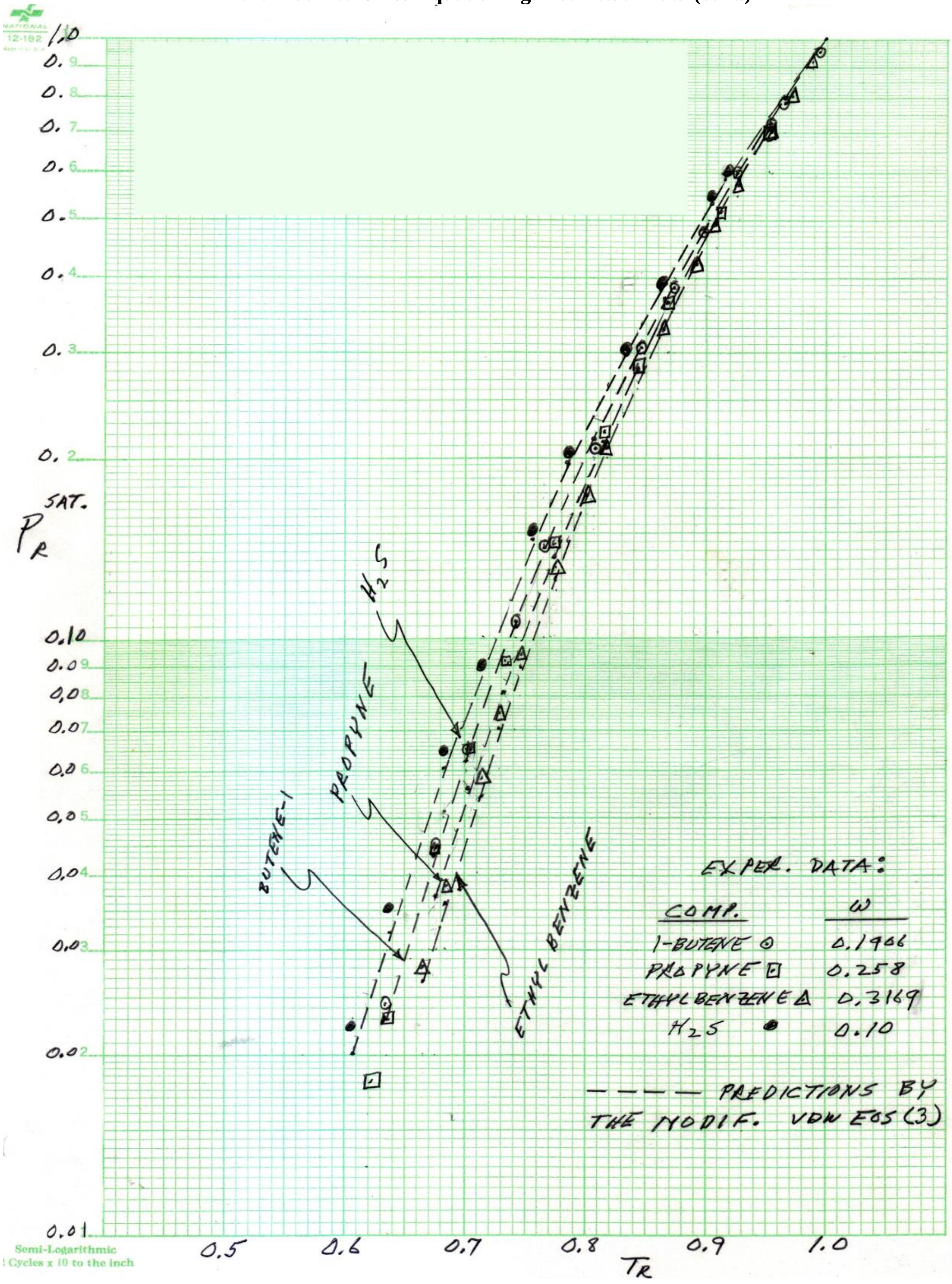


Figure 2 - Comparison of Reduced Vapor Pressure Curves Predicted from the Modified VDW Equation Against Actual Data (cont.)



In general the modified VDW curves provide an excellent match with the plotted data points. The only exception here would be for the component propyne in the lower temperature region. For instance, at T_R values around 0.70 and lower, the predicted curve lies about 16 to 20 percent lower than the plotted data.

Modified VDW vs Lee-Kesler Figure 3 shows a graphical comparison between the predicted reduced vapor pressure curves from the modified VDW equation (dashed) and the three-parameter CS Lee-Kesler correlation (solid lines) specifically for argon, ammonia and n-decane. Figure 4 provides a similar graphical comparison for H_2S, butene-1 and ethyl benzene. The Lee-Kesler correlation (2) was described in detail in our previous study (1). In either plot the curves from the two independent correlations are basically indistinguishable.

In Figure 5 we compare the two independent correlation curves for propyne against plotted experimental data points. The separate curves show excellent agreement. However, below T_R = 0.75, the data points lie significantly higher than the predicted curves. This result is consistent with the comparison shown in Figure 2 for propyne. It suggests that the measured VP data for propyne may be biased or exhibiting some degree of experimental error. Propyne is classified as a compound belonging to the acetylenic group. These materials can decompose explosively when temperature and partial pressure exceed certain limits. As a result, the measurement of any physical property such as vapor pressure must be conducted with extreme caution.

Concluding Remarks Both the three-parameter (P_c, T_c, ω) correlations of Lee-Kesler and the modified VDW equation provide an excellent representation of the vapor pressure of pure fluids displaying quite a range of acentric factors (extent of molecular complexity) and molecular polarity.

Any further effort to work with the modified VDW equation in direct reduced parameter form was dropped at this time. Any success in finally overcoming the obstacles of such an analysis would only amount to a purely academic triumph.

Figure 3 - Comparison of Predicted Reduced Vapor Pressures from the Lee-Kesler and Modified VDW Correlations

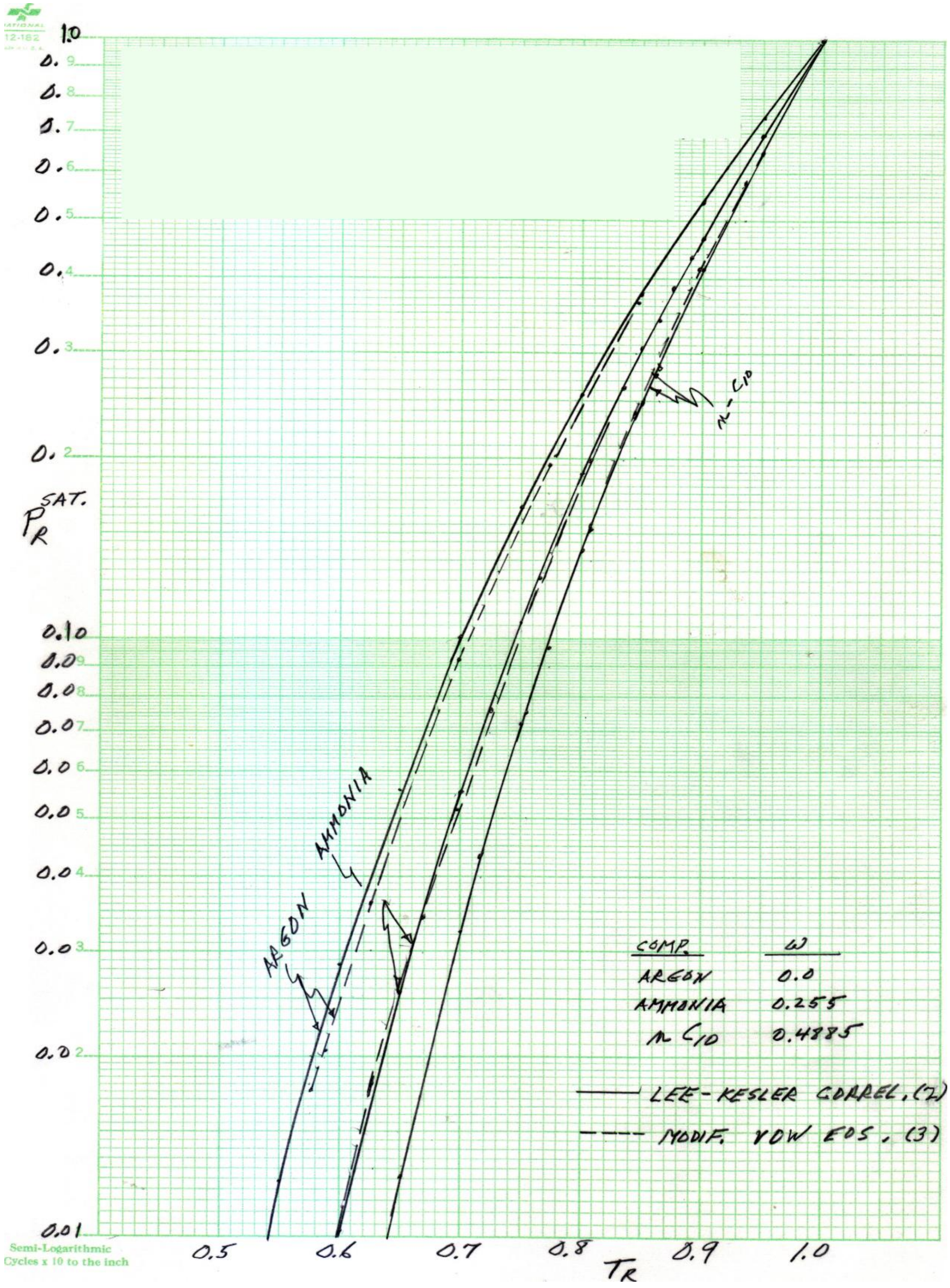


Figure 4 - Comparison of Predicted Reduced Vapor Pressures from the Lee-Kesler and Modified VDW Correlations (cont.)

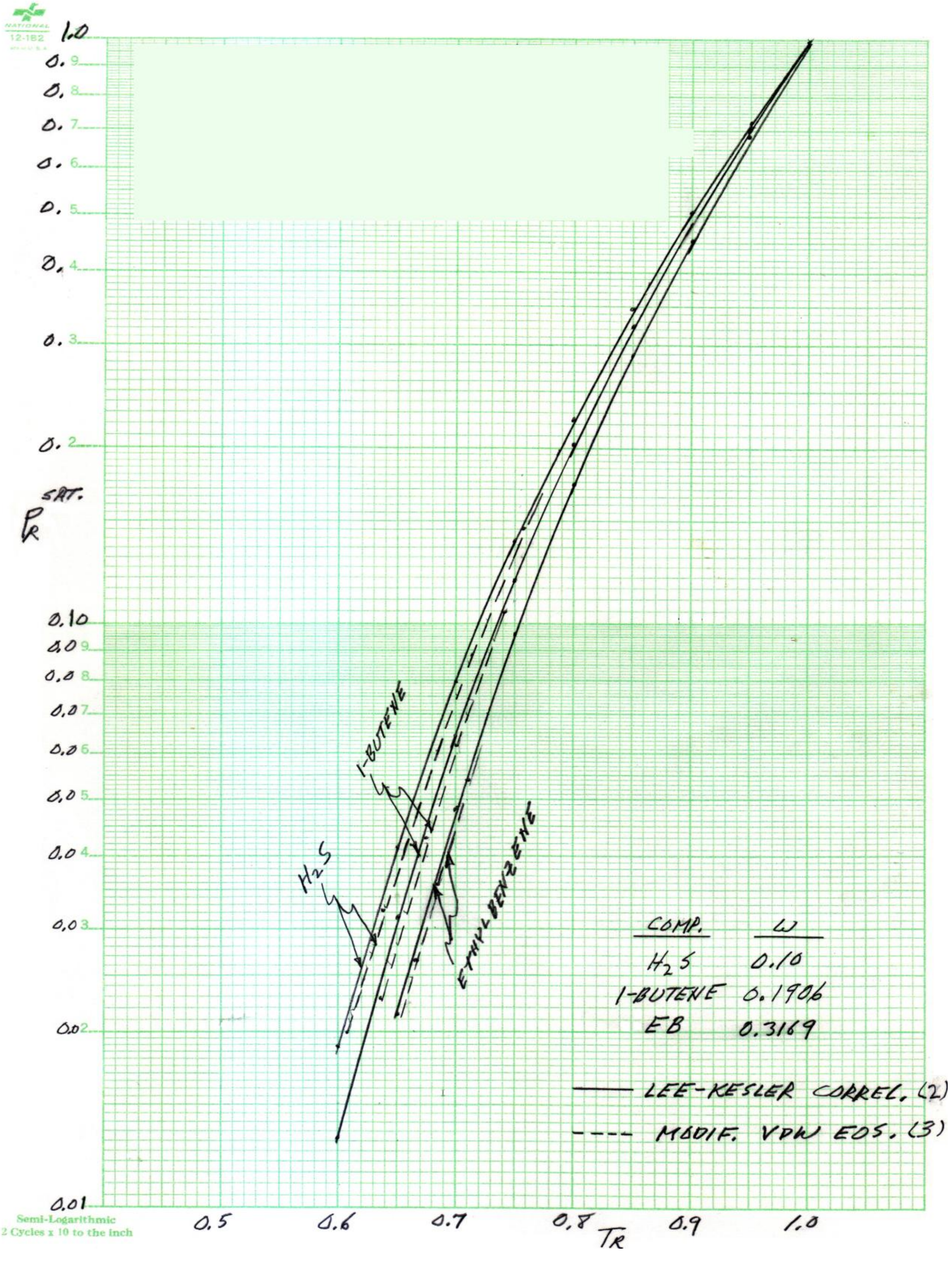
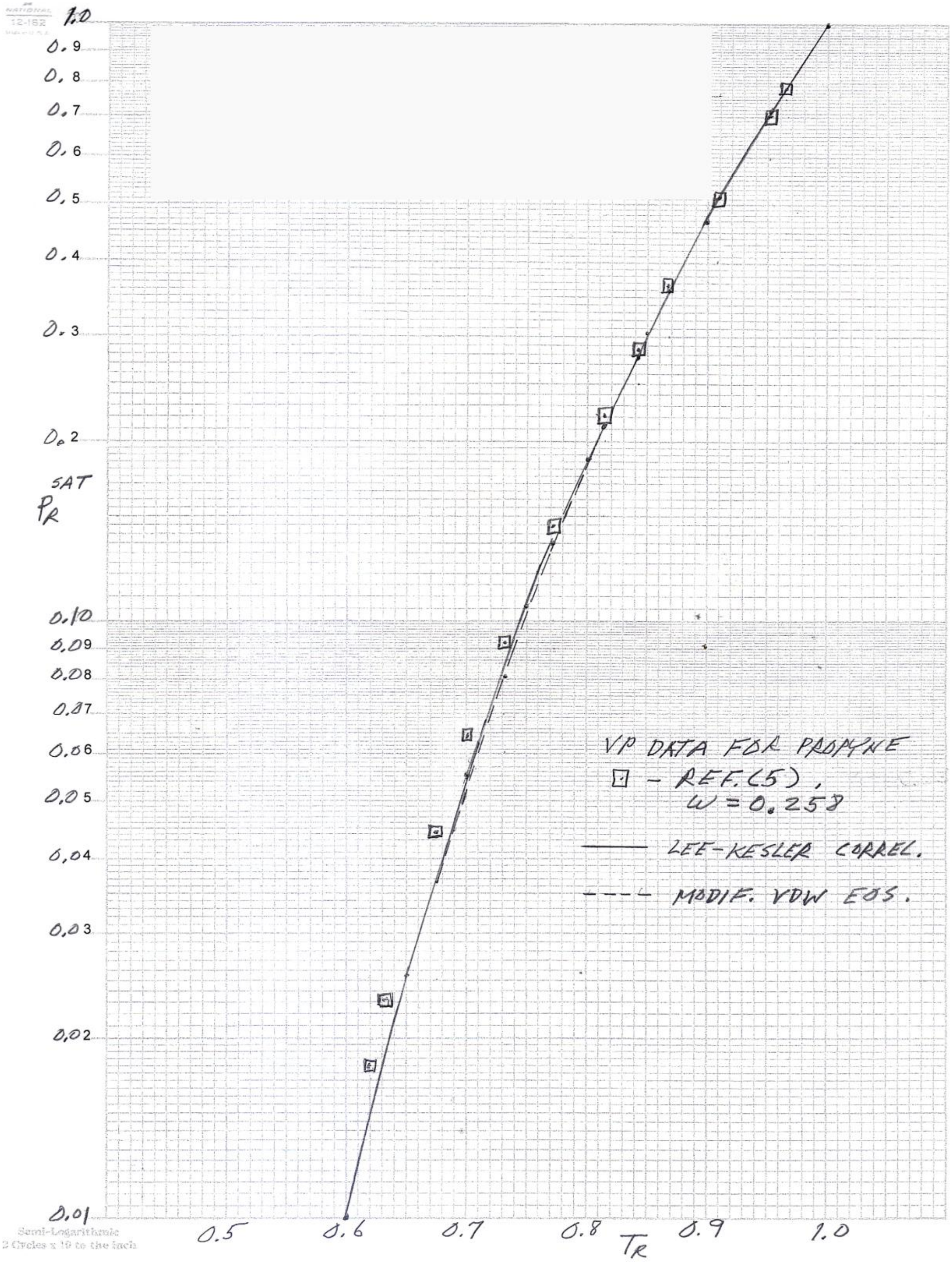


Figure 5 - Analysis and Comparison of Vapor Pressure Data of Propyne Based on the Lee-Kesler and Modified VDW Correlations



V. References

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3. Koppany C.R., "Improved Predictions of Liquid Specific Volumes and Thermodynamic Properties from Two Separate Modifications of the van der Waals Equation", Parts 1-4 (2010-2011). See the Website CRKTECH.COM

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7. Din, F., "Thermodynamic Properties of Gases", Vol. 1, NH_3, CO_2, CO, Butterworths, (1956).

Table 1 - Listing of BASIC Program VDWVP.BAS

```
2 OPEN "VDWVPOUT" FOR OUTPUT AS #1
5 READ A$, PC, TC, W, MW
6 PRINT #1, ""
10 PRINT #1, "COMPONENT IS ="; A$
15 PRINT #1, ""
17 PRINT #1, "T,F", "VP,PSIA", "VG", "VL"
19 PRINT #1, ""
20 TCR = TC + 459.7
25 R = 10.731
30 READ T, PEST
35 TR = T + 459.7
40 P = PEST
45 M = .551088 + 1.452291 * W
50 ALPHA = (1 + M * (1 - SQR(TR / TCR))) ^ 2
55 S1 = (27 / 64) * ALPHA * R * R * TCR * TCR / PC
60 S2 = (R / 8) * TCR / PC
65 A = (S1 * P) / (R * R * TR * TR)
70 B = (S2 * P) / (R * TR)
75 F = 1
80 GOSUB 760
85 VL = Z * R * TR / P
87 VLM = VL / MW
90 LNPHIL = LOG(1 / (Z - B)) + B / (Z - B) - 2 * A / Z
100 F = 2
105 GOSUB 760
110 VG = Z * R * TR / P
112 VGM = VG / MW
115 LNPHIG = LOG(1 / (Z - B)) + B / (Z - B) - 2 * A / Z
125 DERIV = (VG - VL) / (R * TR)
130 FU = LNPHIG - LNPHIL
135 P1 = P - FU / DERIV
140 E1 = ABS(P - P1)
142 PRINT #1, P, P1
145 IF E1 < .001 THEN 160
150 P = P1
155 GOTO 65
160 PRINT #1, T, P1, VGM, VLM
165 PRINT #1, ""
170 GOTO 30
760 REM SUBROUTINE FOR SOLVING THE VDW EOS FOR Z
765 IF F = 1 THEN 780
770 Z = 1
775 GOTO 785
780 Z = .001
785 Q10 = Z ^ 3 - (B + 1) * Z * Z + A * Z - A * B
790 Q20 = 3 * Z * Z - 2 * (B + 1) * Z + A
795 Z1 = Z - Q10 / Q20
800 E20 = ABS(Z - Z1)
805 IF E20 < .00001 THEN 820
810 Z = Z1
815 GOTO 785
820 RETURN
1000 DATA ETHYLBENZENE,532.5,651.24,0.3169,106.17
1010 DATA 280,12,300,15,330,25,350,35,370,45,400,65
1020 DATA 430,90,450,110,500,170,530,220,550,255
1030 DATA 570,300,600,375,620,425,630,455
2000 CLOSE #1
9999 END
```

Table 2 - Output for BASIC Program VDWVP.BAS

```
            COMPONENT IS =ETHYLBENZENE

T,F         VP,PSIA         VG            VL

 12         14.02892
 14.02892   14.21677
 14.21677   14.21812
 14.21812   14.21811
…
 280        14.21811        5.091666      3.169876E-02

 15         18.65255
 18.65255   19.15378
 19.15378   19.16102
 19.16102   19.16099
…
 300        19.16099        3.847982      3.207984E-02

 25         28.69662
 28.69662   29.00396
 29.00396   29.00579
 29.00579   29.00579
…
 330        29.00579         2.602288     3.27127E-02

 35         37.40328
 37.40328   37.49588
 37.49588   37.49603
…
 350        37.49603        2.039043      3.318191E-02

 45         47.69941
 47.69941   47.79193
 47.79193   47.792
…
 370        47.792          1.616548      3.369527E-02

 65         67.11529
 67.11529   67.15569
 67.15569   67.15573
…
 400        67.15573        1.162998      3.456307E-02

 90         91.75941
 91.75941   91.78062
 91.78062   91.78062
…
 430        91.78062        0.8551963     3.558541E-02

 110        111.6895
 111.6895   111.7061
 111.7061   111.7061
…
 450        111.7061        0.7021984     3.636641E-02

 170        175.4531
 175.4531   175.5821
 175.5821   175.5822
…
 500        175.5822        0.4389919     3.882092E-02
```

Table 2 - Output for BASIC Program VDWVP.BAS (Cont.)

```
             COMPONENT IS =ETHYLBENZENE

 220        224.8968
 224.8968   224.9878
 224.9878   224.9878
. . .
 530        224.9878         0.3343796       4.080124E-02

 255        262.9448
 262.9448   263.1723
 263.1723   263.1723
. . .
550          263.1723        0.2790941       4.245003E-02

 300        305.7143
 305.7143   305.8321
 305.8321   305.8322
. . .
 570        305.8322         0.2325889       4.449189E-02

 375        379.0131
 379.0131   379.0746
 379.0746   379.0746
. . .
 600        379.0746         0.1747412       4.876452E-02

 425        434.0778
 434.0778   434.4931
 434.4931   434.4941
 434.4941   434.4941
. . .
 620        434.4941         0.1415037       5.31996 E-02

 455        463.836
 463.836    464.3029
 464.3029   464.3044
 464.3044   464.3044
. . .
 630        464.3044         0.1255429       5.644658E-02
```