PREDICTION OF VAPOR PRESSURES AND MIXTURE VLE FROM A SECOND MODIFICATION OF THE VAN DER WAALS EQUATION

Part 3

Review In the first two papers (1,2) in this series, we developed and tested a 3-parameter modification to the van der Waals equation of state that greatly enhances its ability to accurately predict saturated liquid specific volumes for pure component hydrocarbons and several nonhydrocarbons, including water.

The principal feature of the proposed VDW modification is application of a temperature-dependent correction parameter Beta (β) for the b constant which in turn is related to the volume occupied by the molecules of the species in question. A successful correlation of the Beta parameter (Eqns. 17, 19 and 20 of the first paper) as a function of T_r (reduced temperature) and ω (acentric factor) was achieved. The exception would be for the components hydrogen sulfide, ammonia and water. For these nonhydrocarbons it is best to use the specific coefficients listed in Table 3 of the first paper for use in Equation 17.

Using experimental saturated liquid volumes as the standard we compared the predictions of the proposed modified VDW equation, Peng-Robinson EOS (3) and Rackett equation (4) for three different hydrocarbon types i.e. propylene, n-pentane and benzene. Overall, the predictions of the modified VDW equation were better than those of the PR equation. However, the overall predictions of the Rackett equation were superior to the two equations of state, especially as the critical temperature of the hydrocarbon was approached. In this region, both equations of state predict v_{SL} values that trended high with deviations as high as 20 percent being observed.

For compressed liquid n-pentane, predicted v_L values from the modified VDW equation were generally better than those predicted by the PR equation except near the critical temperature (385.7 deg. F). For the prediction of saturated vapor volumes for n-pentane, the PR EOS was clearly superior to the modified VDW equation.

Finally, in the second paper, we developed an "average" Rackett parameter Z_{RA} for water based on saturated liquid volumetric data taken from the steam tables (5) over a range of temperatures covering the normal boiling point up to the critical point. Saturated specific liquid volumes for water were then predicted by both the modified VDW equation and Rackett equation and compared with the corresponding values from the steam tables. Overall, there is a tradeoff in prediction accuracy by either correlation.

This Study Some preliminary but brief studies were conducted to see how well the proposed modified VDW from the first two papers predicted pure hydrocarbon vapor pressures and mixture vapor-liquid equilibria (VLE). For the latter calculations, mixing rules similar to the type used by Chueh and Prausnitz (6) were employed for the vapor and liquid phases. Specifically, we tested the correlation with n-pentane vapor pressures and VLE data for CO_2/n-pentane and also some H_2-light hydrocarbon binaries. The prediction accuracy was very poor and would be unacceptable for use in engineering process design work.

In his classic 1971 paper (7) Giorgio Soave proposed what is probably the most popular and extensively used cubic EOS. Basically he modified the Redlich-Kwong equation (8) by replacing the term $a/T^{0.5}$ with a more generalized temperature-dependent term a(T). By doing this, Soave achieved a more accurate EOS for predicting pure component vapor pressures and mixture VLE with the exception of systems containing CO_2, H_2S, H_2 and other polar compounds in general.

In this third paper of the series, we perform a very similar or parallel analysis using the simple van der Waals EOS as a starting basis. This exercise is probably considered by many to be academic in nature, but it was conducted just out of a matter of curiosity from this author's standpoint.

The Alpha Function The original van der Waals equation of state is commonly written as,

$$P = \frac{RT}{v-b} - \frac{a}{v^2} \qquad (1)$$

For a given component, the constants a and b in this equation are treated as true constants independent of temperature. Generalized type expressions for these constants are readily derived utilizing the criteria that, at the critical point, the first and second derivatives of pressure with respect to volume are both zero. When these criteria are applied to Equation 1, the following expressions result,

$$a = a_c = \frac{27 R^2 T_c^2}{64 P_c} \quad ; \quad b = b_c = \frac{R T_c}{8 P_c} \quad ; \quad Z_c = 0.375 \qquad (2\,a, b, c)$$

Equation 1 is readily converted to the compressibility form by direct substitution of the following identities,

$$a = \frac{AR^2T^2}{P} \quad ; \quad b = \frac{BRT}{P} \quad ; \quad v = \frac{ZRT}{P} \qquad (3a,b,c)$$

The final result after substitution and rearrangement becomes,

$$Z^3 - (B+1)Z^2 + AZ - AB = 0 \qquad (4)$$

Following the same original premise as Soave, at temperatures other than the critical for a pure component, we define a temperature-dependent alpha (α) function such that,

$$a(T) = a_c\,\alpha(T) \qquad (5)$$

where α(T) is a dimensionless parameter which becomes unity at T = T_c. The a term of Equation 1 is replaced by Equation 5.

For a single pure component phase, the general volume-explicit form of the fugacity coefficient equation can be written as,

$$Ln\frac{f}{P} = Z - 1 - Ln\,Z + \int_0^{1/v} (Z-1)\,v\,d\left(\frac{1}{v}\right) \qquad (6)$$

If we substitute Equation 1 and the identities given by Equations 3 a,b,c into Equation 6, after rearrangement and simplification, we arrive at,

$$Ln\frac{f}{P} = (Z-1) - Ln(Z-B) - \frac{A}{Z} \qquad (7)$$

For a pure component at a given temperature and at the saturation pressure (vapor pressure),

$$f^L = f^V \qquad (8)$$

If we impose an experimental value of the vapor pressure at a given temperature onto Equation 7 for both the liquid and vapor phases, then there is a unique value for a(T) or α(T) in which the equality of Equation 8 will be satisfied. Thus it is possible by trial and error to calculate from experimental vapor pressures a set of values of α(T) for a host of substances.

We performed such an exercise for 18 hydrocarbons and 5 nonhydrocarbons including hydrogen and water. Appendix I of the first paper (1) provides an extensive tabulation of these vapor pressure data. These data generally cover temperatures over the range of around the normal boiling point up to close to the critical point.

We employed the same functional relationship as did Soave for relating α to the reduced temperature T_r, namely,

$$\alpha^{0.5} = 1 + m\left(1 - T_r^{0.5}\right) \qquad (9)$$

This equation satisfied the requirement that for all pure components, the alpha function must become unity at the critical point,

$$\alpha \rightarrow 1 \quad as \quad T_r \rightarrow 1 \qquad (10)$$

Soave then proceeded to cross correlate the slope term m as a function of the Pitzer acentric factor, ω. He arrived at the relationship,

$$m = 0.480 + 1.574\,\omega - 0.176\,\omega^2 \qquad (11)$$

where $$\omega = -1 - Log_{10}\left(P_r^S\right)_{T_r = 0.7} \qquad (12)$$

We took a similar approach by first solving Equation 9 for m,

$$m = \frac{\alpha^{0.5} - 1}{1 - T_r^{0.5}} \qquad (13)$$

For each component listed in Appendix I of the first paper, we evaluated Equation 13 for each temperature-vapor pressure pair and then computed the arithmetic average. Values of m displayed very little variation over the temperature ranges covered. Table 1 provides a listing of these values by component, and Figure 1 is a plot of m versus acentric factor for ω values up to nearly 0.5. It appears that m can be expressed as simple linear function of ω (see the solid line). A least squares fit yielded the following correlation,

$$m = 0.551088 + 1.452291\,\omega \qquad (14)$$

The average trend in prediction accuracy of Equation 14 for 23 points correlated turned out to be + 0.25 percent. The dashed line lying just below the correlation line of Eqn. 14 was developed by Soave and represents Equation 11 above.

<u>Hydrogen</u> The configurational properties of low molecular weight gases such as hydrogen and helium are described by quantum rather than the classical statistical mechanics. As a result, the commonly used equations of state and corresponding states methods do not predict satisfactory values for the PVT properties of such gases. Chueh and Prausnitz (6) have developed temperature-dependent effective critical constants with which the properties of quantum gases can be made to match those for classical gases. These effective critical constants were found to depend on the molecular mass m and temperature T in a relatively simple manner. The effective critical temperature and effective critical pressure are given by,

$$T_c = \frac{T_c^o}{1 + \frac{c_1}{mT}} \quad ; \quad with\, T_c, T_c^o, T\ in\, \deg.K \qquad (15)$$

$$P_c = \frac{P_c^o}{1 + \frac{c_2}{mT}} \quad ; \quad with\, P_c\ and\ P_c^o\ in\, atm \qquad (16)$$

where c_1 = 21.8 deg. K ; c_2 = 44.2 deg. K

Here T_c^o and P_c^o are the classical critical temperature and pressure or the effective critical temperature and critical pressure in the limit of high temperature. For hydrogen, we have,

T_c^o = 43.6 deg. K ; P_c^o = 20.2 atm and m = 2.02

If we choose to employ units of deg. R and psia, then, for hydrogen, Equations 15 and 16 can be equivalently expressed by,

$$T_c, \deg.R = \frac{78.48}{1 + \frac{19.43}{T, {}^o R}} \qquad (17)$$

$$P_c, Psia = \frac{296.94}{1 + \frac{39.39}{T, {}^o R}} \qquad (18)$$

Equations 17 and 18 were employed in the development of the m parameter for hydrogen (see Equation 13). These effective critical constant expressions were also used for H_2 in the BASIC programs we employed to test the proposed modified VDW for the prediction of mixture VLE.

Vapor Pressure Check Table 2 provides a brief comparison of experimental vapor pressures with the predictions of the proposed modified VDW equation for six hydrocarbons and the nonhydrocarbons hydrogen sulfide and water. The comparisons are in general quite good. Hydrogen sulfide shows a negative (predictive) trend that exceeds 5 percent. Inspection of Figure 1 shows that the individual value of m for hydrogen sulfide lies somewhat below the correlation line of Eqn. 14. In fact, this point lies closer to the Soave correlation line (Eqn. 11).

Tables 3 and 4 compare the experimental and calculated liquid and vapor specific volumes for n-pentane and water. The predicted specific volumes resulted from the calculations above for the corresponding vapor pressures i.e.a trial and error routine which varied the value of the vapor pressure until the equality (fugacity) constraint of Eqn. 8 was satisfied. Appendix I lists the BASIC routine entitled VDWVP.BAS which was used in performing the specific volume/ vapor pressure calculations. The overall trends in the volume predictions are summarized below:

Comp.	No. of Pts.	% Trend in v^L	% Trend in v^G
n-pentane	5	+ 46.9	+ 5.5
water	4	+ 83.6	+ 9.9

As expected, the prediction of the liquid volume is very poor. The predictions of the vapor specific volumes are satisfactory. In the first paper (1) we modified the b term so as to significantly improve the prediction of v^L. And as I stated in the second paper (2) (Future Work), modification and recorrelation of both the attractive a and repulsive b terms simultaneously would no doubt require a monumental effort.

Mixture VLE Predictions For the correlation of mixture vapor-liquid equilibria an equation of state, such the VDW equation, can be employed to compute component fugacity coefficients for both the vapor and liquid phases. The vapor-liquid equilibrium ratio is calculated by the following expression:

$$K_i = \frac{f_i^L / x_i P}{f_i^V / y_i P} = \frac{\phi_i^L}{\phi_i^V} \qquad (19)$$

The same equation, such as the modified VDW equation in this case, is used to compute ϕ_i^L and ϕ_i^V as a function of the liquid or vapor composition, pressure, and temperature.

The rigorous thermodynamic expression for the fugacity coefficient of component i in a single phase mixture is given by Equation 20,

$$RT\,Ln\,\phi_i = \int_V^{\infty} \left[\left(\frac{\partial P}{\partial n_i} \right)_{T,V,n_{j\neq i}} - \frac{RT}{V} \right] dV - RT\,Ln\,Z \qquad (20)$$

where V denotes the <u>total</u> phase volume.

Before we can substitute the appropriate form of the van der Waals equation into Eqn. 20, we need to employ mixing rules for use in Equations 1-5, 9 and 14. The mixing rules chosen in this study were similar to those employed by Chueh and Prausnitz (6) when they applied the Redlich-Kwong equation for the treatment of saturated vapor phase mixtures. However, we also used them for the equilibrium liquid mixtures as well. These mixing rules are summarized below:

Let z_i represent the mole fraction of component i in either the single phase vapor (y_i) or liquid phase mixture (x_i).

$$a = \sum_{i=1}^{N} \sum_{j=1}^{N} z_i\, z_j\, a_{ij} = \sum_{i=1}^{N} \sum_{j=1}^{N} z_i\, z_j\, \alpha_{ij}\, a_{cij} \qquad (21)$$

$$a_{cij} = \left(\frac{27}{64} \right) \left(\frac{R^2\, T_{cij}^2}{P_{cij}} \right) \qquad (22)$$

$$\alpha_{ij}^{0.5} = 1 + m_{ij} \left(1 - T_{Rij}^{0.5} \right) \qquad (23)$$

where

$$T_{Rij} = T / T_{cij} \quad ; \quad T_{cij} = \sqrt{T_{ci}\, T_{cj}}\ (1 - k_{ij}) \qquad (24a,b)$$

$$m_{ij} = 0.551088 + 1.452291\,\omega_{ij} \qquad (25)$$

$$\omega_{ij} = \frac{\omega_i + \omega_j}{2} \quad ; \quad P_{cij} = \frac{P_{ci} + P_{cj}}{2} \qquad (26a,b)$$

$$b = \sum_{i=1}^{N} z_i\, b_i \qquad (27)$$

When Equation 1 and the mixing rules, Equations 21-27, are incorporated into Equation 20, the analytical expression for the fugacity coefficient of component i in either the single phase vapor or liquid mixture is readily derived. The result is,

$$Ln\phi_i = Ln\left(\frac{v}{v-b}\right) + \frac{b_i}{v-b} - \frac{2\sum_{j=1}^{N} z_j\,\alpha_{ij}\,a_{cij}}{vRT} - Ln\,Z \qquad (28)$$

To test the proposed Modified VDW equation for the prediction of mixture VLE, we developed a bubble-pressure routine employing the above mixing rules and Equation 28 for both phases. Figure 2 provides the schematic diagram for this routine, and Appendix II lists the BASIC program file entitled VDWBP1.BAS. The input consists of basically the critical constants and acentric factors for the pure components. If hydrogen is present, the critical constants are computed from the temperature-dependent correlations, Eqns. 17 and 18, taken from Chueh and Prausnitz (6). Then for each data point tested, we input the temperature (deg. F) and liquid phase mole fractions of each component. The output consists of the calculated bubble pressure and vapor composition in mole fraction. Additional output consists of the component equilibrium ratios and individual component fugacity coefficients.

Given: T, x_i (i=1 to N-1) Calculate: P, y_i (i=1 to N).

The comparison of predicted results against the experimental are discussed below system by system.

<u>P-X-Y Diagrams</u> Program VDWBP1.BAS was applied to several binary systems and the results compared with experimental data on P-X-Y diagrams. Figure 3 shows the results obtained for the binary methane-ethylene at - 50 deg. F. The experimental data were unpublished. The proposed modification of the VDW equation fits the measured V/L coexistence curves very well. Figure 4 shows a very similar type comparison for the binary nitrogen-methane at -180 and - 240 deg. F. Once again a very good match of the coexistence curves is obtained. The experimental data were taken from the work of Cines et. al. (9).

Figures 5 through 7 cover comparisons for some wider boiling mixtures, namely CO_2/nC_5H_{12} (10) at 100 deg. F, H_2/C_2H_6 (11) at -150 deg. F and H_2/nC_6H_{14} (12) at 400 deg. F. For the CO_2/nC_5H_{12} binary, the predicted vapor curve matches the data quite well, whereas, for the liquid, the predicted coexistence curve lies to the right of the data by about 7 mole percent on the average. For H_2/C_2H_6, the predictions match the data quite well for both liquid and vapor. For the binary H_2/nC_6H_{14}, the predicted liquid

curve basically straddles the data, and the predicted vapor curve is on the high side, especially at the higher pressure levels.

<u>α versus x diagrams</u> The remaining systems with which the modified VDW equation was tested consisted of close-boiling hydrocarbon pairs. The comparisons were performed on relative volatility (α) versus liquid composition (x) diagrams. The systems and figure numbers are summarized below:

System	Figure (α-x plot)	Data Ref.
Propane-Isobutane	8	Hipkin (13)
Ethylene-Ethane	9	Hanson (14) McCurdy & Katz (15)
Propylene-Propane	10	Howat & Swift (16)
Isobutane-n-Butane	11	Smooth Data of Connolly (17)

At 20, 80 and 150 deg. F, the predicted relative volatility lines for propane-isobutane lie somewhat above the plotted data points. At 200 deg. F the predicted curve and data points coincide nicely.

For all of the other close-boiling systems tested (see Figures 9-11) we make the general observation that the data straddle the predicted curves at each isotherm. In addition, the predicted curves are flatter and show less variation with changes in the liquid composition. In other words, the modified VDW is predicting that these systems are more ideal than the data would indicate.

For these binaries, the relative volatility is defined precisely by the expression,

$$\alpha = \frac{y(1-x)}{x(1-y)} \qquad (29)$$

where x and y are the mole fractions of the lighter component in the liquid and vapor phases respectively. This expression places quite a strain on the precision of the measurements of composition because the liquid and vapor compositions appear in both the numerator and denominator. This effect undoubtedly accounts for the scatter in the experimental data points plotted on Figures 8-11.

Interaction Constants For all of the bubble pressure calculations performed above, the interaction term k_{ij} of Eqn. 24b was set equal to zero i.e. $k_{ij} = 0$ for all binary pairs. As Soave pointed out, k_{ij} is an empirical correction (interaction) factor, to be determined from binary experimental data for each ij pair. For an N-component mixture, the number of binary pairs will be N(N-1)/2. In principle this binary parameter can be considered to be independent of system temperature, pressure and composition. The P-X-Y comparisons above suggest that it would be worth while to develop interaction parameters for systems involving mixtures of light hydrocarbons with CO_2 or H_2.

In a series of three papers (18, 19, 20) Graboski and Daubert presented a modified Soave (SRK) equation of state for phase equilibrium calculations. Specifically for binary mixtures containing hydrocarbons paired with other hydrocarbons or with either CO_2, H_2S, N_2 or CO, they proposed the following mixing rules:

$$a_m = \alpha\, a_c = \sum_{i=1}^{N}\sum_{j=1}^{N} z_i\, z_j\, \alpha_{ij}\, a_{cij} \qquad (20)$$

$$\alpha_{ij}\, a_{cij} = \left(1 - C_{ij}\right)\left(\alpha_i\, a_{ci}\, \alpha_j\, a_{cj}\right)^{0.5}$$

$$b_m = \sum_{i=1}^{N} z_i\, b_i \qquad (21)$$

For strictly hydrocarbon mixtures, the authors suggest that $C_{ij} = 0$. For binary mixtures of hydrocarbons with the nonhydrocarbon gases mentioned above, Graboski et. al. have done some very comprehensive work in developing interaction parameters C_{ij} by regressing binary VLE data. In turn, they successfully correlated these values against the absolute value of the difference in solubility parameter between the gas itself and the hydrocarbon it is interacting with. The bottom line here is that a similar approach could be attempted with the modified VDW equation proposed in this paper.

Original VDW Eqn. Before concluding this discussion we need to show what improvements, if any, are achieved by employing the proposed alpha-modification of the VDW equation as opposed to the original version.

On Figure 3 we have plotted the P-x-y coexistence curves predicted by the original VDW equation for methane-ethylene at - 50 deg. F. These curves were generated from the bubble pressure routine (Appendix II) by simply setting the alpha value of Equation 5 equal to unity.

The predicted coexistence curves, as well as the vapor pressure of ethylene, all plot in a region that is significantly higher than the plotted data points would indicate. And, as discussed earlier, the modified VDW does a very precise job of fitting the measured P-x-y data.

Figure 5 shows a similar comparison for the binary carbon dioxide - n-pentane at 100 deg. F. The comparisons of the VDW predictions with the measured coexistence curve display similar trends as for the methane-ethylene binary.

Finally, on Figure 10, we have plotted the 40 deg. F (relative volatility-composition) isotherm for propylene-propane as predicted by the original VDW equation. This predicted curve is too low and lies between the 100 and 160 deg. F isotherms shown for the plotted data points or predicted by the modified VDW equation.

This brief comparison clearly demonstrates the superiority of the proposed alpha-modification of the VDW equation over that of the original equation of state.

List of References

1. Koppany, C.R., "Prediction of Saturated Liquid Volumes from a Modified Van der Waals Equation", Part 1, (2010).

2. Koppany, C. R., "Prediction of Saturated Liquid Volumes from a Modified Van der Waals Equation", Part 2, (2010).

3. Peng, D.Y. and Robinson, D.B., "A New Two-Constant Equation of State", IEC Fund., Vol. 15, No. 1, (1976), Page 59.

4. Rackett, H.G., Jr. Chem. Engr. Data, Vol. 15, (1970) Page 514.

5. Keenan, Keyes, Hill and Moore, "Steam Tables", John Wiley & Sons (1969).

6. Prausnitz, J.M. and Chueh, P.L., "Computer Calculations for High-Pressure Vapor-Liquid Equilibria", Prentice-Hall, Inc., (1968).

7. Soave, G., Chem. Engr. Sci., Vol. 27, No. 6-A, (1972) Page 1197.

8. Redlich, O. and Kwong, J.N.S., Chemical Reviews, Vol. 44, (1949) Page 233.

9. Cines, M.R., Roach, J.T., Hogan, R.J. and Roland, C.H., CEP Symposium Series No. 6, Vol. 49, (?).

10. Besserer, G.J. and Robinson, D.B., Jr. of Chem. and Engr. Data, Vol. 18, No.4 (1973) Page 416.

11. Cohen, A.E., Hipkin, H.G. and Koppany, C.R., CEP Symposium Series, Vol. 63, No. 63 (1967) Page 10.

12. Nichols, W.B., Reamer, H.H. and Sage, B.H., AIChE Jr., Vol. 3, No. 2 (1957) Page 262.

13. Hipkin, H.G., AIChE Jr., Vol. 12, No. 3, (1966), Page 484.

14. Hanson, G.H., Hogan, R.J., Ruehlin, F.N. and Cines, M.R., Chem. Engr. Symp. Series, Vol. 49, No. 6 (1953) Page 37.

References Cont.-

15. McCurdy and Katz, Ind. Engr. Chem., Vol. 36, No. 7, (1944) Page 674.

16. Howat, C.S. and Swift, G.W., Ind. Engr. Chem. Process Des. Dev., Vol. 19 (1980), Pages 318-319.

17. Connolly, J.F., Jr. Phys. Chem., Vol. 66 (1962) Page 1082.

18. Graboski, M.S. and Daubert, T.E., Ind. Engr. Chem. Process Des. Dev. Vol. 17, No. 4 (1978) Page 443.

19. IBID Page 448.

20. IBID Vol. 18, No. 2 (1979) Page 300.

Table 1

Correlation of the m-function for the van der Waals equation
in terms of the acentric factor, w.

Comp.	acentric factor, w	Avg. m	Pred. m *	% Dev.
water	0.348	1.042	1.0565	1.39
methane	0.0104	0.5453	0.5662	3.83
ethane	0.0986	0.6836	0.6943	1.56
propane	0.1524	0.7836	0.7724	-1.43
isobutane	0.1848	0.8185	0.8195	0.12
n-pentane	0.2539	0.9442	0.9198	-2.58
n-hexane	0.3007	1.035	0.9878	-4.56
n-octane	0.4018	1.138	1.1346	-0.30
n-decane	0.4885	1.313	1.2605	-4.00
ethylene	0.0868	0.6616	0.6771	2.35
propylene	0.1405	0.7578	0.7551	-0.35
1-butene	0.1906	0.8241	0.8279	0.46
cyclopentane	0.1955	0.8472	0.8350	-1.44
cyclohexane	0.2133	0.8396	0.8609	2.53
acetylene	0.1803	0.8405	0.8129	-3.28
propyne	0.258	0.8521	0.9258	8.65
benzene	0.2125	0.8424	0.8597	2.05
toluene	0.2596	0.9924	0.9281	-6.48
ethylbenzene	0.3169	0.9306	1.0113	8.67
H_2S	0.1	0.6067	0.6963	14.77
CO_2	0.231	0.8817	0.8866	0.55
H_2	0	0.6676	0.5511	-17.45
NH_3	0.255	0.9134	0.9214	0.88
	Avg.	Trend, % =		0.26

* m(pred) = 0.551088 + 1.452291 w ; w = the acentric factor

Table 2

Comparison of Experimental Vapor Pressures with the Predictions
of the Proposed Modified VDW Equation

Comp.	Methane					n-Pentane					Propylene				
	Temp. deg. F	* Exper. VP, Psia	** Pred. VP, Psia	*** % Dev.	Abs. % Dev.	Temp. deg. F	* Exper. VP, Psia	** Pred. VP, Psia	*** % Dev.	Abs. % Dev.	Temp. deg. F	* Exper. VP, Psia	** Pred. VP, Psia	*** % Dev.	Abs. % Dev.
	-260	13.5	11.8	-12.59	12.59	100	15.69	14.58	-7.07	7.07	-50	16.2	15.0	-7.41	7.41
	-220	65	59.8	-8.00	8.00	160	42.48	40.98	-3.53	3.53	-30	25.9	24.3	-6.18	6.18
	-200	113	110.6	-2.12	2.12	220	94.91	93.92	-1.04	1.04	0	48	46.0	-4.17	4.17
	-180	190	187.1	-1.53	1.53	280	185.55	186.33	0.42	0.42	20	69.4	67.1	-3.31	3.31
	-160	300	295.4	-1.53	1.53	340	329.16	332.26	0.94	0.94	50	113.4	111.2	-1.94	1.94
	-140	440	441.5	0.34	0.34						70	151.9	150.6	-0.86	0.86
											100	227.6	227.7	0.04	0.04
	N = 6		Trend, %	-4.24		N = 5		Trend, %	-2.06		120	291.2	292.8	0.55	0.55
											140	367.1	370.2	0.84	0.84
		Abs. Avg.	Dev., %		4.35		Abs. Avg.	Dev., %		2.60	150	410.2	414.0	0.93	0.93
											160	457	461.3	0.94	0.94
											180	562.7	567.1	0.78	0.78
											N = 12		Trend, %	-1.65	
												Abs. Avg.	Dev., %		2.33

Table 2 (continued)

Comp.	Cyclohexane					Acetylene					Benzene				
	Temp. deg. F	* Exper. VP, Psia	** Pred. VP, Psia	*** % Dev.	Abs. % Dev.	Temp. deg. F	* Exper. VP, Psia	** Pred. VP, Psia	*** % Dev.	Abs. % Dev.	Temp. deg. F	* Exper. VP, Psia	** Pred. VP, Psia	*** % Dev.	Abs. % Dev.
	175	14	13.1	-6.43	6.43	-100	28	26.1	-6.79	6.79	180	15.5	14.5	-6.45	6.45
	190	18	16.8	-6.67	6.67	-80	46.5	45.0	-3.23	3.23	200	22	20.2	-8.18	8.18
	200	21.5	19.7	-8.37	8.37	-50	90	91.0	1.11	1.11	230	34	32.0	-5.88	5.88
	230	33.5	31.0	-7.46	7.46	-30	134	137.2	2.39	2.39	250	44.2	42.4	-4.07	4.07
	250	43.5	40.8	-6.21	6.21	0	230	235.8	2.52	2.52	300	81	79.9	-1.36	1.36
	270	56	53.0	-5.36	5.36	30	370	378.8	2.38	2.38	330	110	112.0	1.82	1.82
	300	78	76.1	-2.44	2.44	50	490	503.4	2.73	2.73	350	137	137.8	0.58	0.58
	320	96	95.2	-0.83	0.83	70	640	655.1	2.36	2.36	380	183	185.0	1.09	1.09
	350	130	130.0	0.00	0.00	80	722	742.0	2.77	2.77	400	220	222.5	1.14	1.14
	380	175	173.7	-0.74	0.74						430	289	288.7	-0.10	0.10
	400	209	208.2	-0.38	0.38						450	340	340.1	0.03	0.03
	430	270	269.1	-0.33	0.33						480	428	429.1	0.26	0.26
	450	318	316.2	-0.57	0.57						500	500	497.1	-0.58	0.58
	470	370	369.0	-0.27	0.27						520	570	572.4	0.42	0.42
	500	460	459.7	-0.07	0.07						540	658	655.6	-0.36	0.36
	N = 15		Trend, %	-3.07		N = 9		Trend, %	0.69		N = 15		Trend, %	-1.44	
		Abs. Avg.	Dev., %		3.07		Abs. Avg.	Dev., %		2.92		Abs. Avg.	Dev., %		2.16

Table 2 (continued)

Comp.	H2S					Water				
	Temp. deg. F	* Exper. VP, Psia	** Pred. VP, Psia	*** % Dev.	Abs. % Dev.	Temp. deg. F	* Exper. VP, Psia	** Pred. VP, Psia	*** % Dev.	Abs. % Dev.
	-80	12.8	11.7	-8.59	8.59	400	247.1	241.0	-2.47	2.47
	-50	29.5	26.2	-11.19	11.19	500	680	685.2	0.76	0.76
	-30	46.3	42.2	-8.86	8.86	600	1541	1570.1	1.89	1.89
	0	84	79.4	-5.48	5.48	650	2205	2240.2	1.60	1.60
	20	120	115.4	-3.83	3.83	670	2529	2559.5	1.21	1.21
	50	197	190.7	-3.20	3.20	690	2892	2910.7	0.65	0.65
	70	267	257.2	-3.67	3.67					
	100	400	387.5	-3.13	3.13					
	120	518	497.2	-4.02	4.02					
	150	725	700.9	-3.32	3.32					
	158	795	763.9	-3.91	3.91					
	N = 11		Trend, %	-5.38		N = 6		Trend, %	0.61	
		Abs. Avg.	Dev., %		5.38		Abs. Avg.	Dev., %		1.43

* The sources of experimental vapor pressure data for these components are found in references 1, 6, 7 and 8 of the first paper (1).

** Vapor pressures here are predicted from the proposed modified VDW equation of this third paper.

*** % Dev. = 100 x (VP-pred - VP-exp)/ VP-exp

Table 3

This spreadsheet compares predicted and measured vapor pressures
and saturated specific volumes for n-pentane

Predictions are by a modified van der Waals equation of state using
the alpha-function correlation modification.

The data source for n-pentane is: Sage and Lacey, IEC, Vol. 34, No. 6 (1942)

Temp. Deg. F	VP Psia Measured	VP Psia Pred.	% Dev. in VP	Meas. Sat. Liq. Spec. Vol. cuft/lb	Pred. Sat. Liq. Spec. Vol. cuft/lb	% Dev. in the sat. liq. Spec. vol.	Meas. Sat. Vap. Spec. Vol. cuft/lb	Pred. Sat. Vap. Spec. Vol. cuft/lb	% Dev. in the sat. vap. Spec. vol.
100	15.69	14.58	-7.07	0.02634	0.03888	47.6	5.079	5.511	8.51
160	42.48	40.98	-3.53	0.02812	0.040973	45.7	1.9727	2.0788	5.38
220	94.91	93.92	-1.04	0.03027	0.043984	45.3	0.8944	0.9270	3.64
280	185.55	186.33	0.42	0.03336	0.04876	46.2	0.4379	0.4545	3.79
340	329.16	332.26	0.94	0.03891	0.05823	49.7	0.2139	0.2267	5.98
		Trend, %	-2.06			46.9			5.46

Table 4

This spreadsheet compares predicted and measured vapor pressures and saturated specific volumes for water.

Predictions are by a modified van der Waals equation of state using the alpha-function correlation modification.

The data source is the Keenan and Keyes steam tables.

Temp. Deg. F	VP Psia Measured	VP Psia Pred.	% Dev. in VP	Meas. Sat. Liq. Spec. Vol. cuft/lb	Pred. Sat. Liq. Spec. Vol. cuft/lb	% Dev. in the sat. liq. Spec. vol.	Meas. Sat. Vap. Spec. Vol. cuft/lb	Pred. Sat. Vap. Spec. Vol. cuft/lb	% Dev. in the sat. vap. Spec. vol.
212	14.7	12.36	-15.92	0.01672	0.03085	84.5	26.80	32.15	19.96
400	247.1	241.0	-2.47	0.01864	0.03416	83.3	1.8661	1.9780	6.00
500	680	685.2	0.76	0.02043	0.03737	82.9	0.6761	0.7103	5.06
600	1541	1570.1	1.89	0.02363	0.043405	83.7	0.2677	0.2903	8.44
		Trend %	-3.93			83.6			9.86

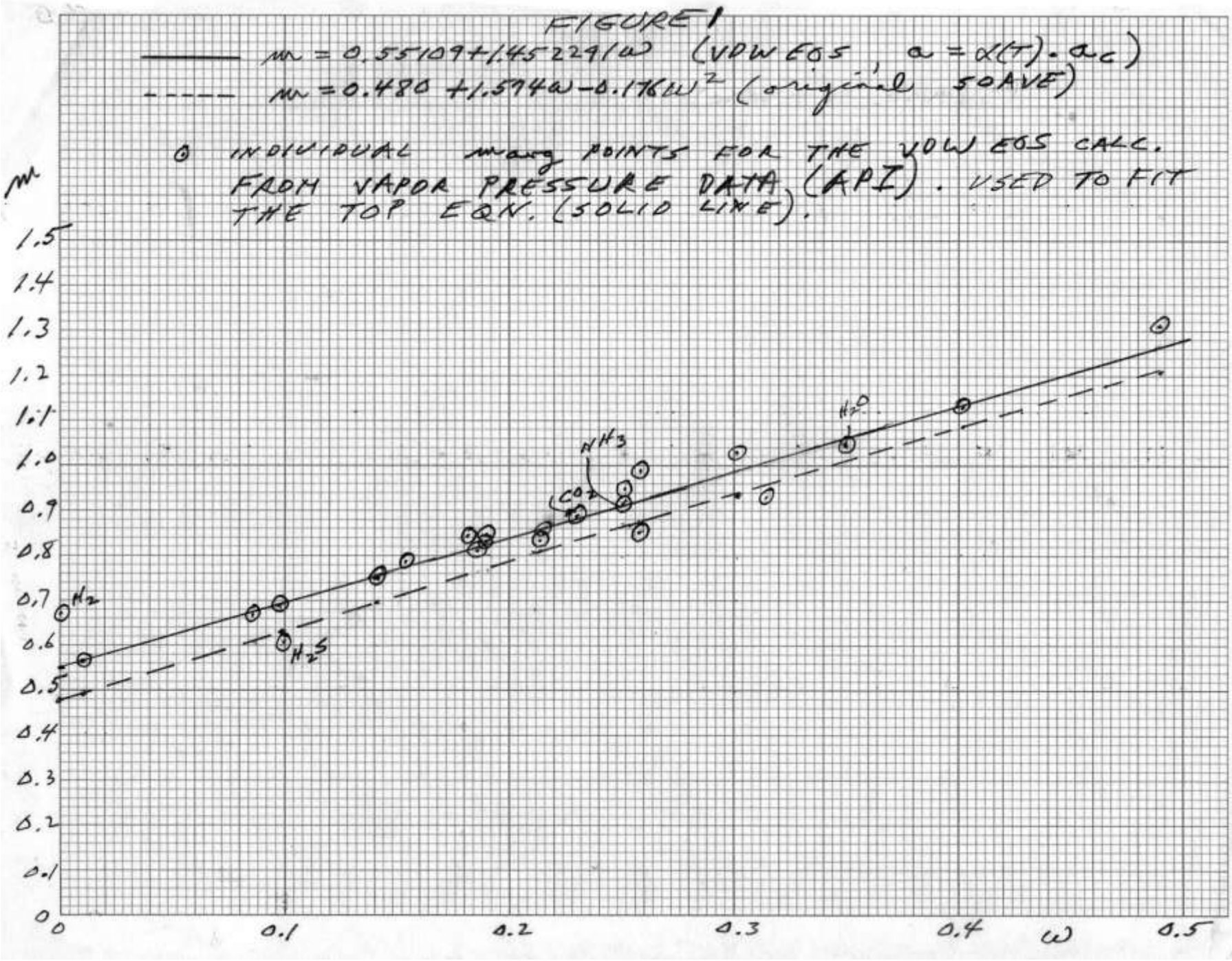
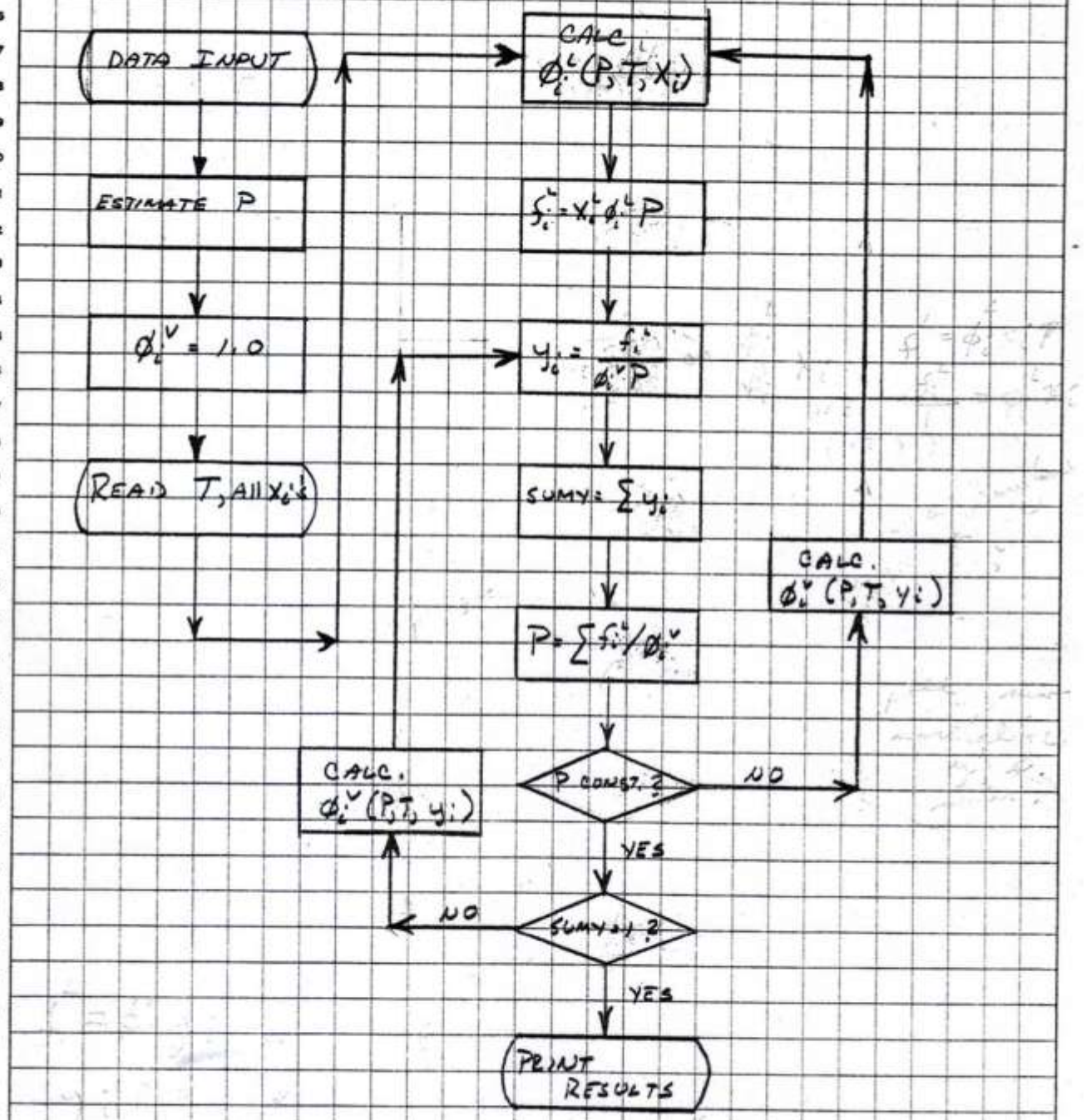


FIGURE 1
m = 0.55109+1.452291ω (VDW EOS, a = α(T)·a_c)
m = 0.480 +1.574ω−0.176ω² (original SOAVE)
INDIVIDUAL m avg POINTS FOR THE VDW EOS CALC. FROM VAPOR PRESSURE DATA (API). USED TO FIT THE TOP EQN. (SOLID LINE).
m
ω
H₂
H₂S
CO₂
NH₃
H₂O
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
1.1
1.2
1.3
1.4
1.5

FIGURE 2

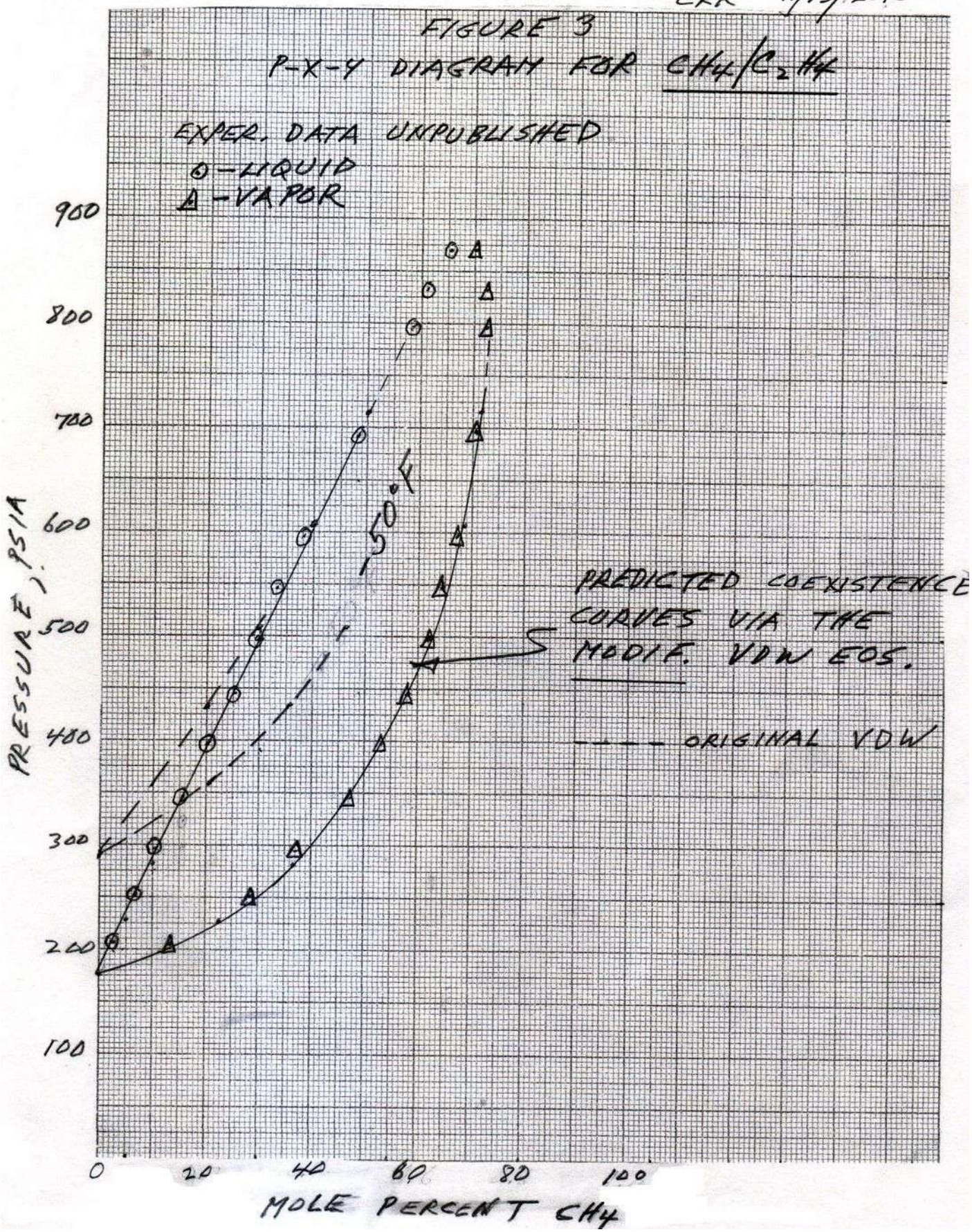
SCHEMATIC DIAGRAM FOR SOAVE BUBBLE-POINT PRESSURE ALGORITHM



CRK 11/13/2010

FIGURE 3

P-X-Y DIAGRAM FOR CH_4/C_2H_4



CRK 11/11/2010

FIGURE 4

P-X-Y DIAGRAMS FOR

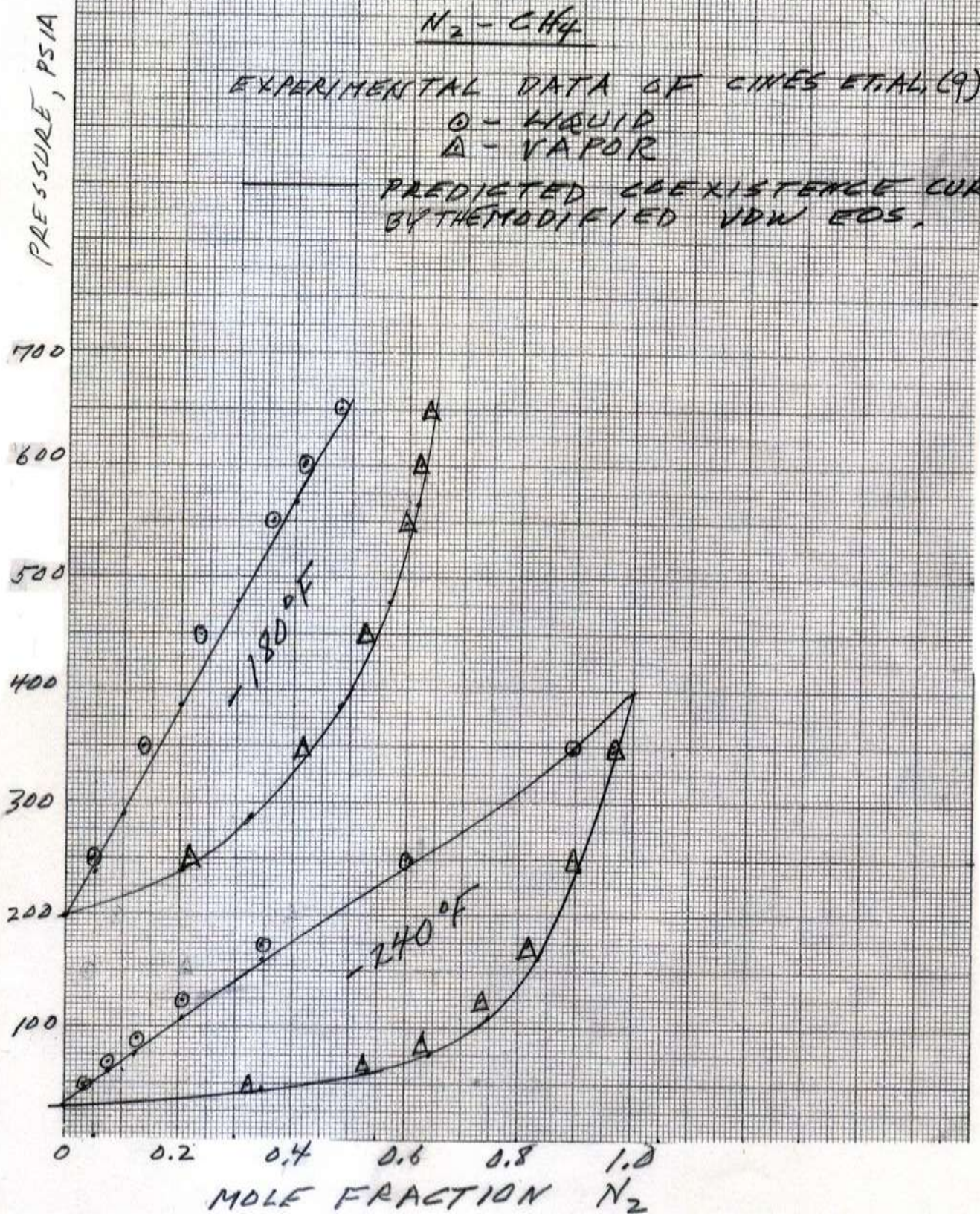
$N_2 - CH_4$

EXPERIMENTAL DATA OF CINES ET.AL. (9)

⊙ - LIQUID

Δ - VAPOR

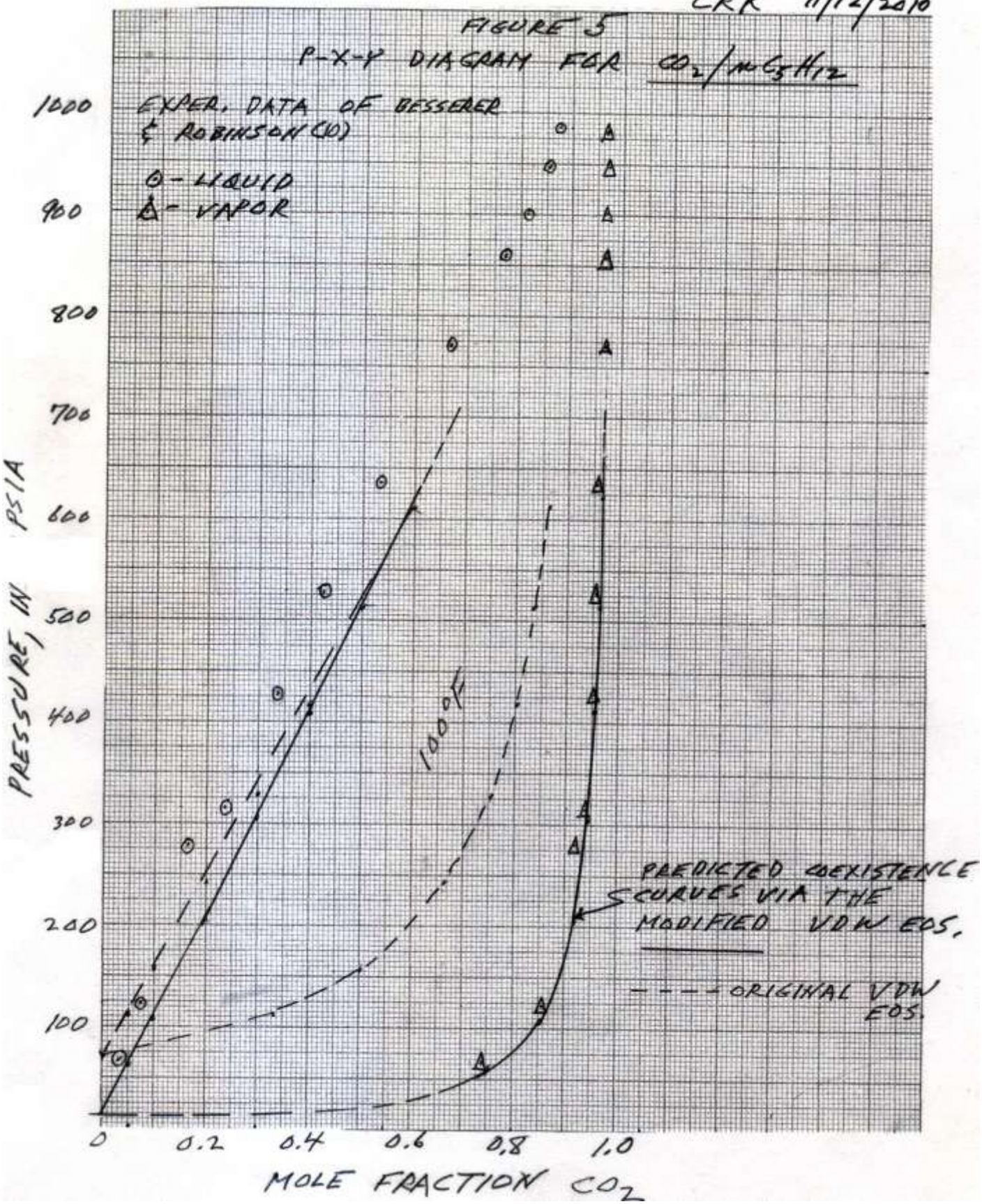
——— PREDICTED COEXISTENCE CURVES BY THE MODIFIED VDW EOS.



CRK 11/12/2010

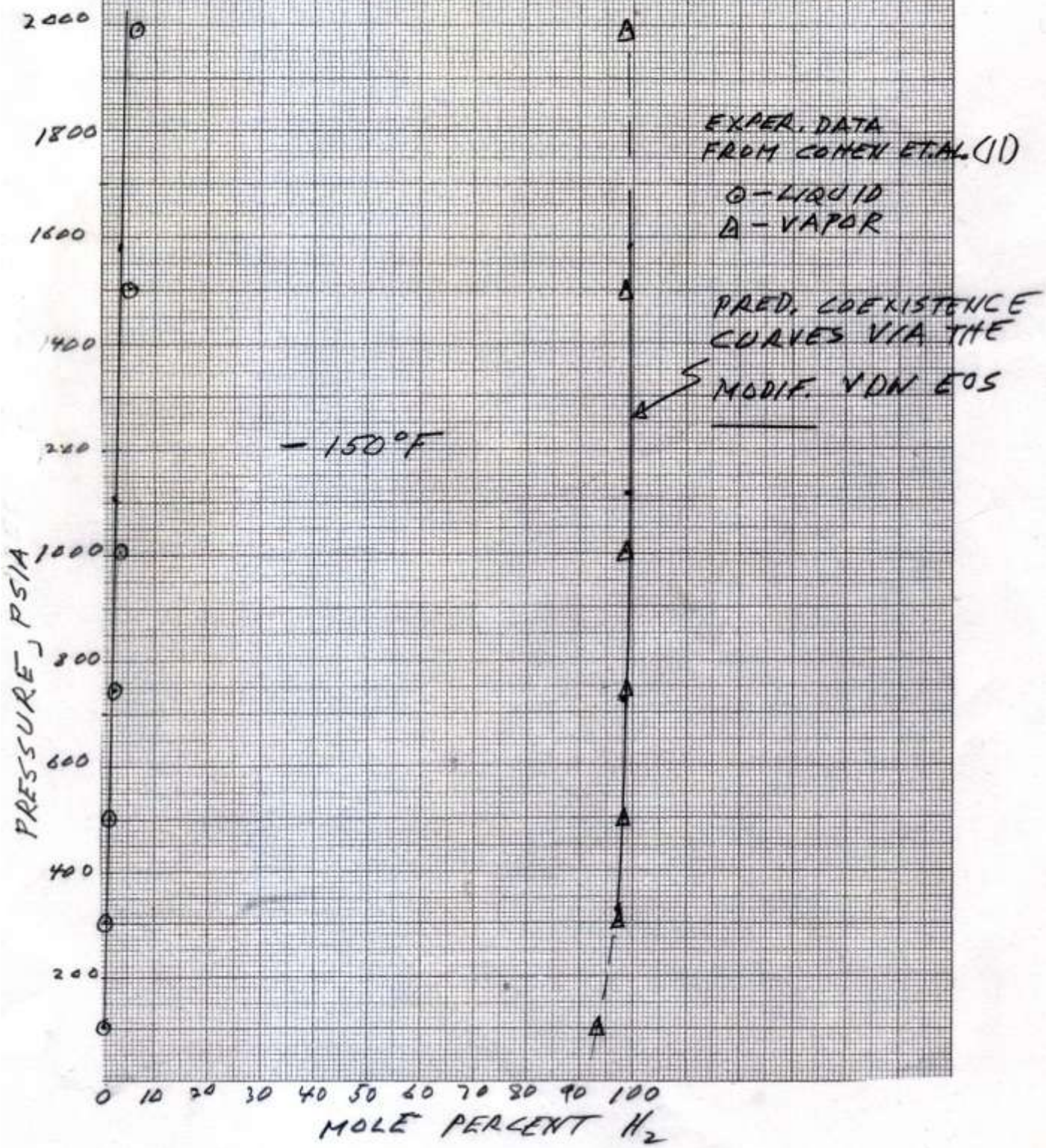
FIGURE 5

P-X-Y DIAGRAM FOR $CO_2/n\text{-}C_5H_{12}$



CRK 11/13/10.

FIGURE 6
P-X-Y DIAGRAM FOR H_2/C_2H_6



CRK 11/13/2010

FIGURE 7

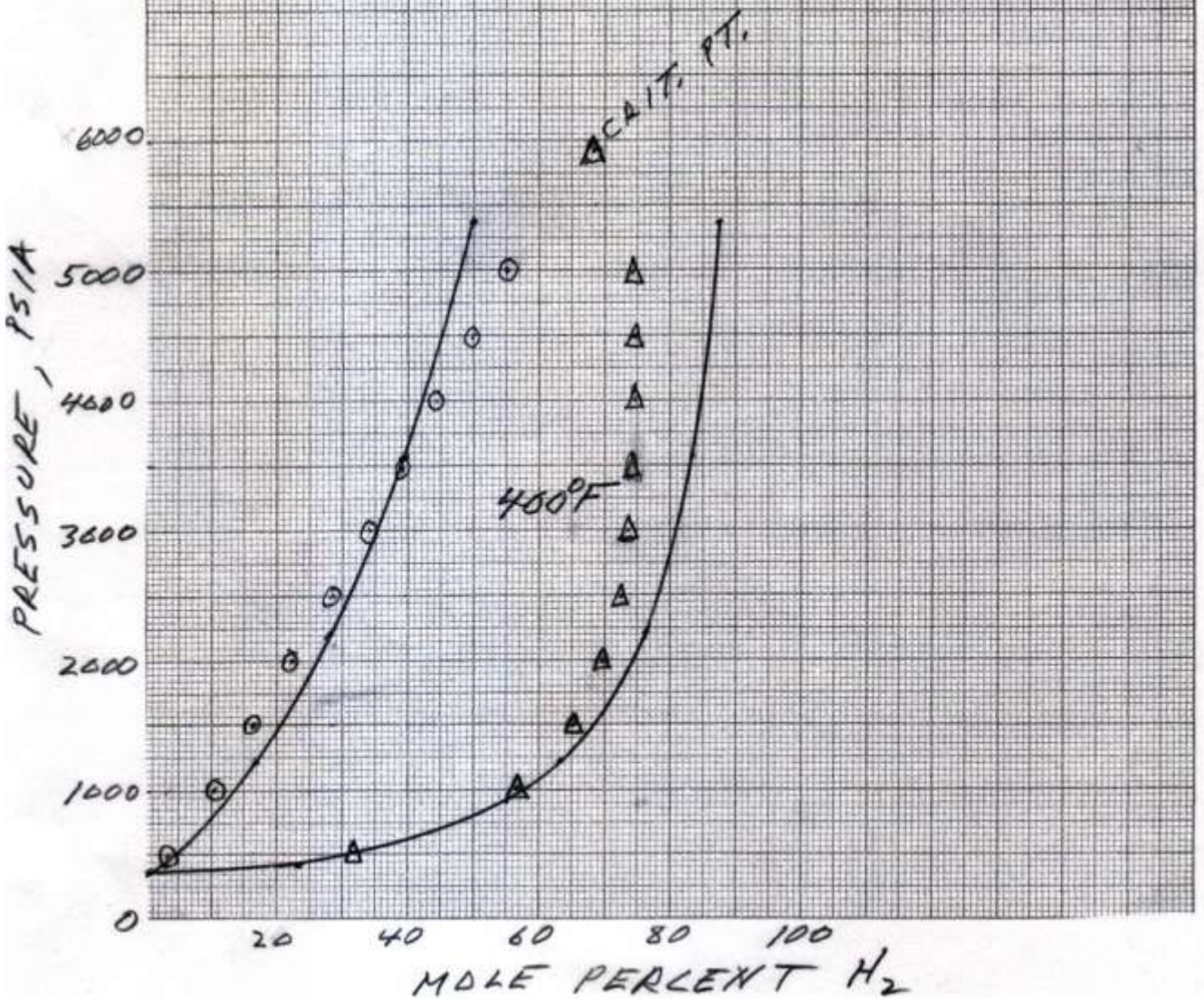
P-X-Y DIAGRAM FOR H_2 - n-C_6H_{14}

EXPERIMENTAL DATA OF NICHOLS ET.AL. (12)

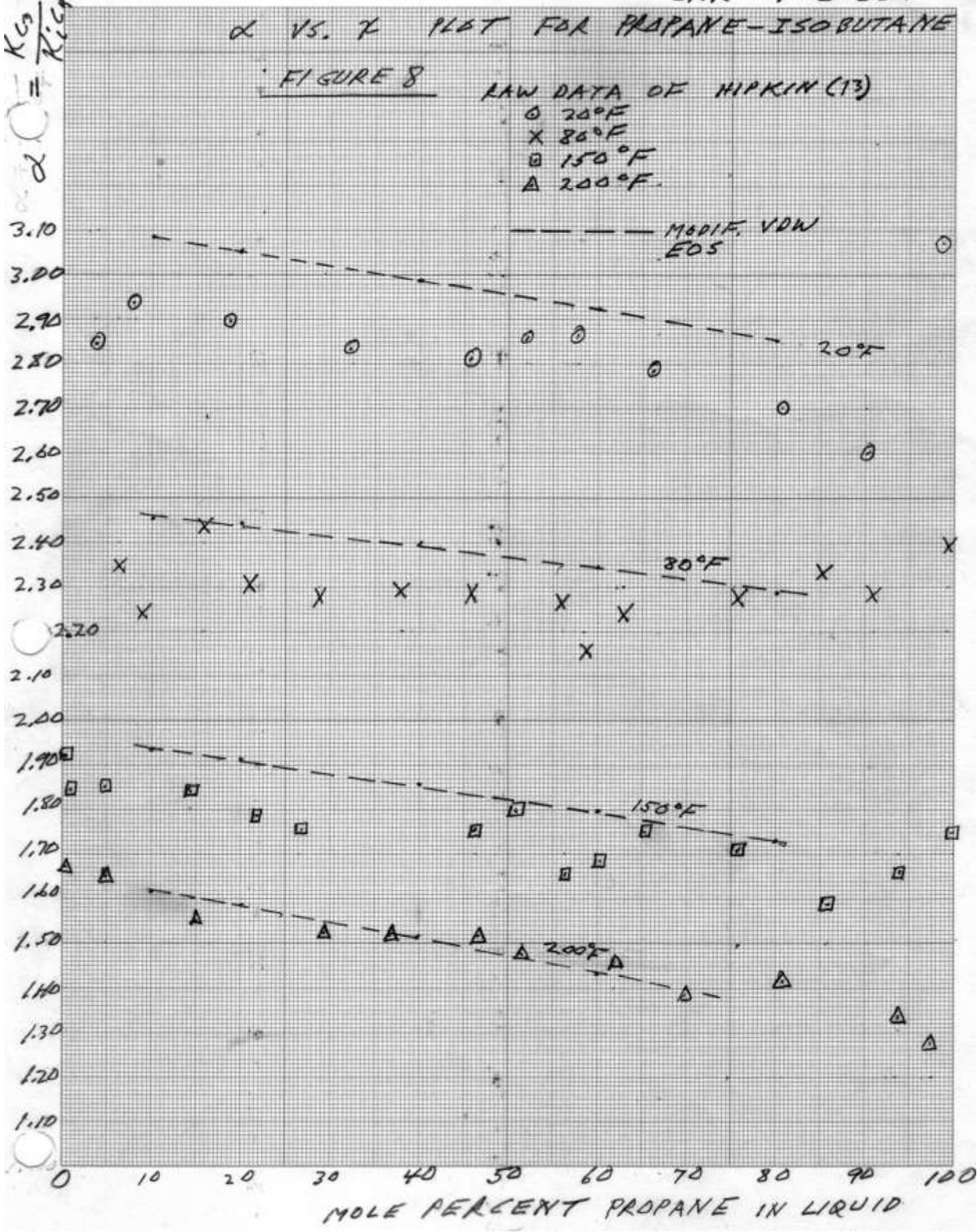
⊙ - LIQUID

Δ - VAPOR

PREDICTED COEXISTENCE CURVES VIA THE MODIF. VDW EOS



CRK 4-2-08.


α VS. x PLOT FOR PROPANE-ISOBUTANE
FIGURE 8
RAW DATA OF HIPKIN (13)
⊙ 20°F
X 80°F
⊡ 150°F
Δ 200°F.
MODIF. VDW EOS
20°F
80°F
150°F
200°F
α = K_C3 / K_iC4
3.10
3.00
2.90
2.80
2.70
2.60
2.50
2.40
2.30
2.20
2.10
2.00
1.90
1.80
1.70
1.60
1.50
1.40
1.30
1.20
1.10
0
10
20
30
40
50
60
70
80
90
100
MOLE PERCENT PROPANE IN LIQUID

CRK, 4-7-68,

FIGURE 9

α VS. x PLOT FOR ETHYLENE-ETHANE

DATA OF HANSON ET.AL.(14) AND McCURDY & KATZ (15)

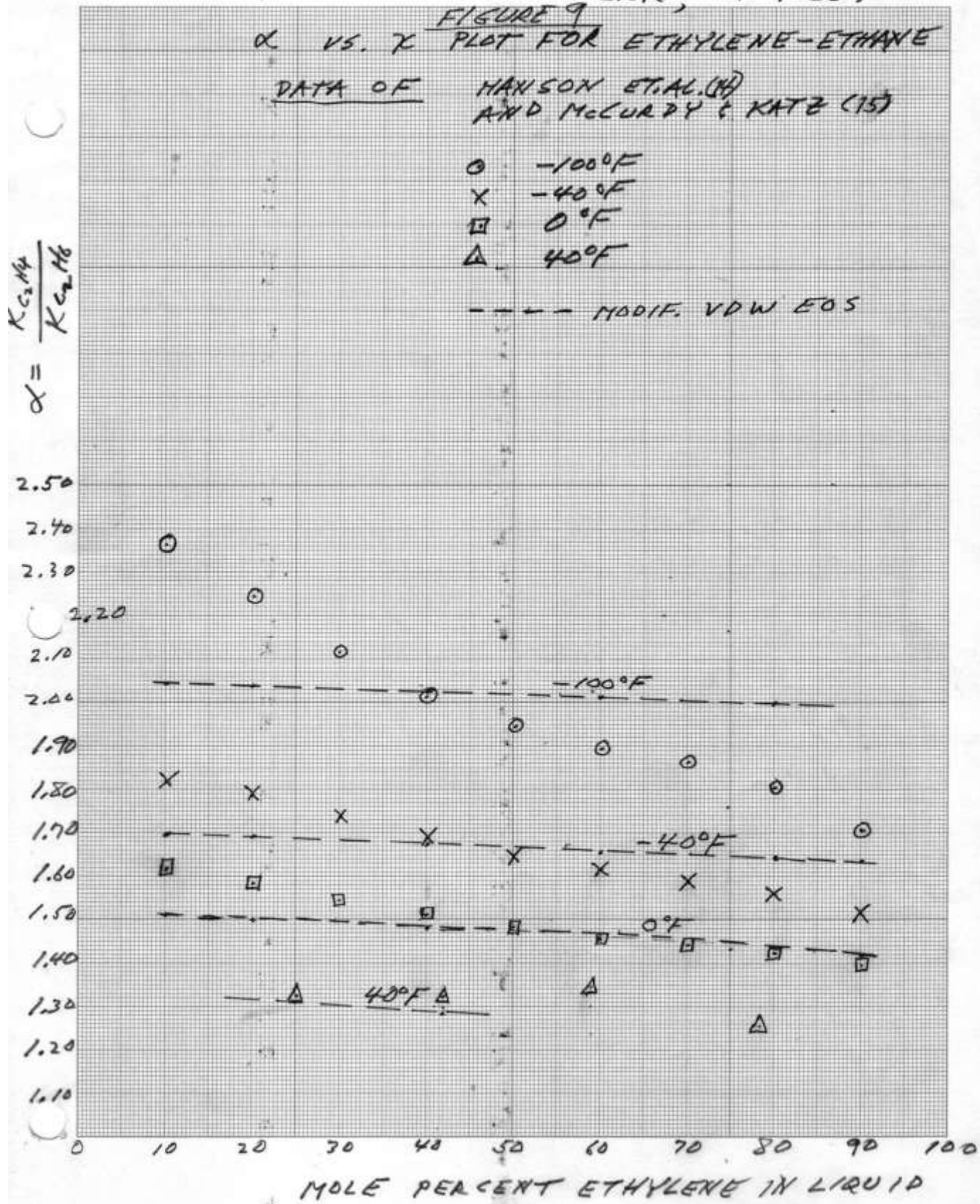
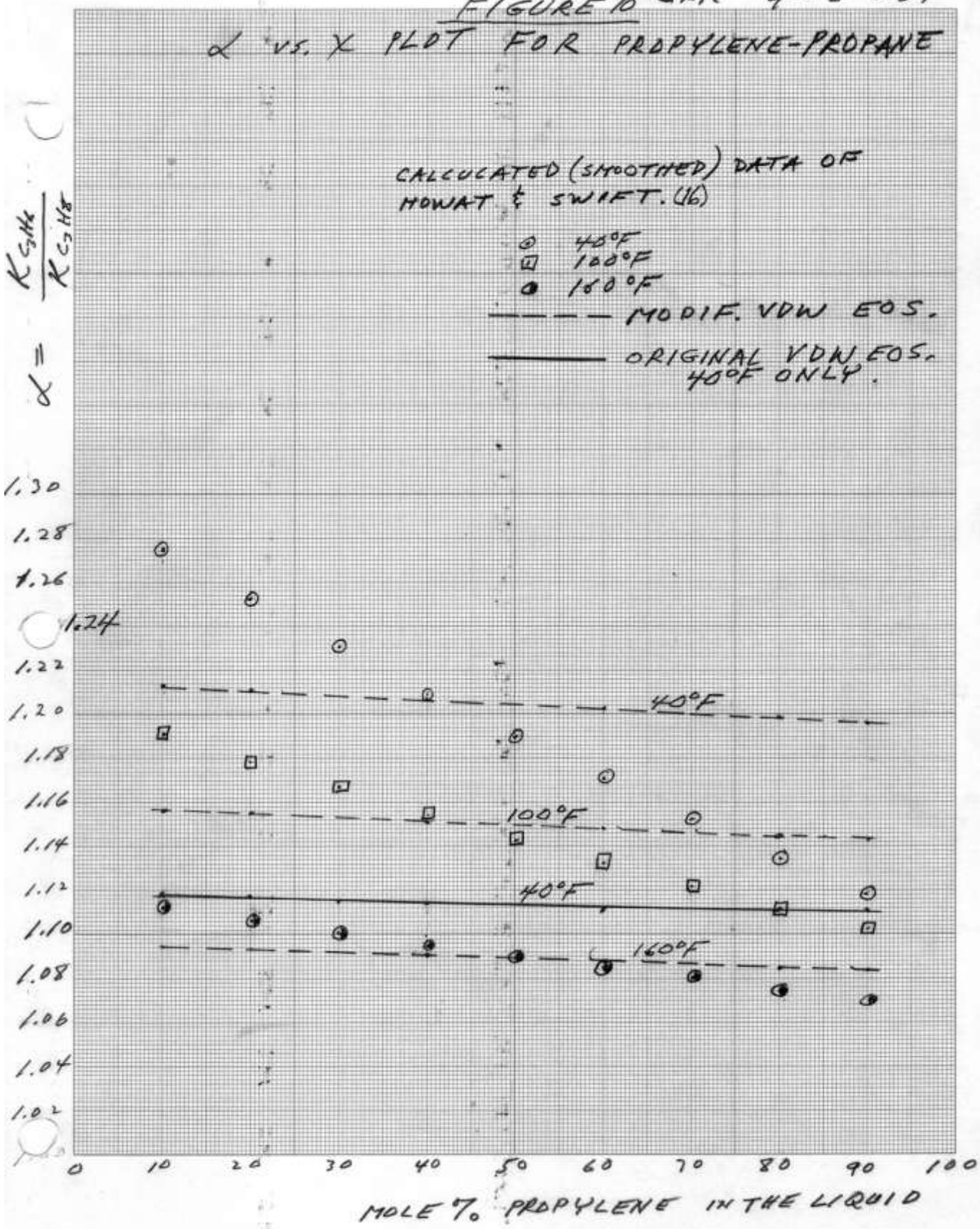


FIGURE 10 CAK 4-8-08.

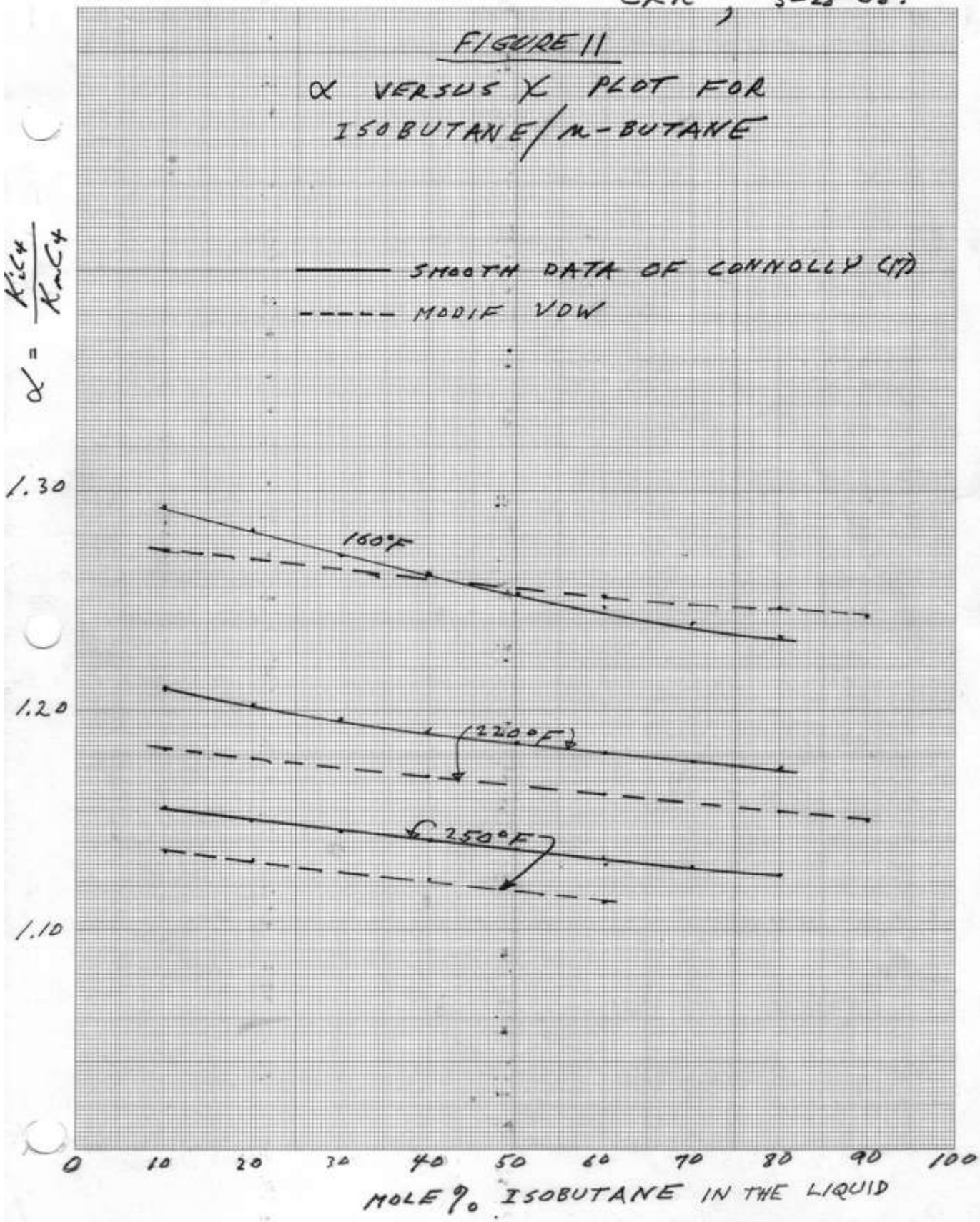
α VS. X PLOT FOR PROPYLENE-PROPANE



CRR, 3-28-08.

FIGURE 11

α VERSUS X PLOT FOR ISOBUTANE/n-BUTANE



APPENDIX I

```
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 WATER,3208,705.6,0.348,18.02
1010 DATA 400,245
2000 CLOSE #1
9999 END
```

SAMPLE OUTPUT

VDWVPOUT

COMPONENT IS =WATER

T,F	VP,PSIA	VG	VL
245	241.0033		
241.0033	241.038		
241.038	241.038		
400	241.038	1.978031	3.415947E-02

APPENDIX II

```
2 OPEN "VDWBP1OUT" FOR OUTPUT AS #1
5 REM BUBBLE PRESSURE BY A MODIF. VDW EQN.
7 REM MIXING RULES ARE MODIFIED CHUEH-PRAUSNITZ
9 REM ALPHA-FUNCTION IS USED TO ADJUST THE b-TERM
10 READ N, N0
15 FOR I = 1 TO N
20 READ A$(I)
25 NEXT I
30 REM READ IN CRITICAL PROPERTIES (PSIA, F)
35 REM AND ACENTRIC FACTORS FOR EACH COMPONENT
37 R = 10.731
40 IF N0 > 0 THEN 70
45 FOR I = 1 TO N
50 READ P(I), T(I)
55 T(I) = T(I) + 459.7
60 NEXT I
65 GOTO 90
70 FOR I = 2 TO N
75 READ P(I), T(I)
80 T(I) = T(I) + 459.7
85 NEXT I
90 FOR I = 1 TO N
95 READ W(I)
100 NEXT I
101 READ T1
102 T1 = T1 + 459.7
105 FOR I = 1 TO N
110 READ X(I)
115 NEXT I
135 P = 500
140 IF N0 = 0 THEN 155
145 P(1) = 296.94 / (1 + 39.39 / T1)
150 T(1) = 78.48 / (1 + 19.43 / T1)
155 FOR I = 1 TO N
170 A(4, I) = (R / 8) * T(I) / P(I)
180 B(8, I) = 1
185 NEXT I
190 S = 0
195 FOR I = 1 TO N
200 S(I) = 0
205 FOR J = 1 TO N
210 E(I, J) = (P(I) + P(J)) / 2
215 F(I, J) = (W(I) + W(J)) / 2
220 G(I, J) = .551088 + 1.452291 * F(I, J)
225 H(I, J) = SQR(T(I) * T(J))
230 Q(I, J) = 1 + G(I, J) * (1 - (T1 / H(I, J)) ^ .5)
235 C(I, J) = (27 / 64) * R * R * H(I, J) * H(I, J) / E(I, J)
240 S(I) = S(I) + X(J) * Q(I, J) * Q(I, J) * C(I, J)
245 S = S + X(I) * X(J) * Q(I, J) * Q(I, J) * C(I, J)
250 NEXT J
```

```
255 NEXT I
260 S1 = 0
265 FOR I = 1 TO N
270 S1 = S1 + X(I) * A(4, I)
275 NEXT I
280 A = (S * P) / (R * R * T1 * T1)
285 B = (S1 * P) / (R * T1)
290 REM F=1 LIQUID; F=2 VAPOR
295 F = 1
300 GOSUB 760
305 V = Z * R * T1 / P
310 FOR I = 1 TO N
315 B(1, I) = LOG(V / (V - S1)) + A(4, I) / (V - S1)
320 B(2, I) = 2 * S(I) / (V * R * T1) + LOG(Z)
330 B(4, I) = EXP(B(1, I) - B(2, I))
335 F(4, I) = X(I) * B(4, I) * P
340 NEXT I
345 S2 = 0
350 P1 = 0
355 FOR I = 1 TO N
360 Y(I) = F(4, I) / (B(8, I) * P)
365 S2 = S2 + Y(I)
370 P1 = P1 + F(4, I) / B(8, I)
375 NEXT I
377 PRINT #1, S2, P
380 E1 = ABS(P1 - P)
385 IF E1 < .1 THEN 530
390 P = P1
395 GOSUB 1100
400 GOTO 280
530 E2 = ABS(S2 - 1)
535 IF E2 < .001 THEN 600
540 GOSUB 1100
545 GOTO 345
600 PRINT #1, "COMP", "PC,PSIA", "TC,F", "W"
605 FOR I = 1 TO N
610 TF(I) = T(I) - 459.7
615 PRINT #1, A$(I), P(I), TF(I), W(I)
620 NEXT I
625 PRINT #1, ""
630 PRINT #1, "SYSTEM TEMP., F="; T1 - 459.7
635 PRINT #1, ""
640 PRINT #1, "CALCULATED BUBBLE-P,PSIA="; P1
645 PRINT #1, ""
647 PRINT #1, "COMP", "X", "Y", "K", "PHIL", "PHIV"
650 FOR I = 1 TO N
655 K(I) = Y(I) / X(I)
660 PRINT #1, A$(I), X(I), Y(I), K(I), B(4, I), B(8, I)
662 NEXT I
664 PRINT #1, ""
```

```
665 GOTO 675
666 PRINT #1, "COMP", "X", "ALPHA"
667 FOR I = 1 TO N
668 ALPHA(I) = K(I) / K(2)
670 PRINT #1, A$(I), X(I), ALPHA(I)
672 NEXT I
675 PRINT #1, ""
677 PRINT #1, ""
680 GOTO 101
760 REM SUBROUTINE FOR SOLVING THE VDW EOS FOR Z
765 IF F = 1 THEN 780
770 Z = 1
775 GOTO 785
780 Z = .005
785 Q10 = Z ^ 3 - Z * Z * (B + 1) + A * Z - A * B
790 Q20 = 3 * Z * Z - 2 * Z * (B + 1) + A
795 Z1 = Z - Q10 / Q20
800 E20 = ABS(Z - Z1)
805 IF E20 < .0001 THEN 820
810 Z = Z1
815 GOTO 785
820 RETURN
1100 REM SUBROUTINE FOR CALC. THE VAPOR FUG. COEFF.
1105 FOR I = 1 TO N
1110 Y1(I) = Y(I) / S2
1115 NEXT I
1120 S4 = 0
1125 FOR I = 1 TO N
1130 D(I) = 0
1135 FOR J = 1 TO N
1140 D(I) = D(I) + Y1(J) * Q(I, J) * Q(I, J) * C(I, J)
1145 S4 = S4 + Y1(I) * Y1(J) * Q(I, J) * Q(I, J) * C(I, J)
1150 NEXT J
1155 NEXT I
1160 S3 = 0
1165 FOR I = 1 TO N
1170 S3 = S3 + Y1(I) * A(4, I)
1175 NEXT I
1180 A = (S4 * P) / (R * R * T1 * T1)
1185 B = (S3 * P) / (R * T1)
1190 F = 2
1195 GOSUB 760
1200 V = Z * R * T1 / P
1205 FOR I = 1 TO N
1210 B(5, I) = LOG(V / (V - S3)) + A(4, I) / (V - S3)
1215 B(6, I) = 2 * D(I) / (V * R * T1) + LOG(Z)
1225 B(8, I) = EXP(B(5, I) - B(6, I))
1230 NEXT I
1235 RETURN
1500 DATA 2,0
```

```
1505 DATA CH4,C2H4
1510 DATA 667.8,-116.63,729.8,48.58
1520 DATA 0.0104,0.0868
1530 DATA -50,0.1,0.9
2000 CLOSE #1
9999 END
```

SAMPLE OUTPUT VDWBP1OU.T

```
 .5100298        500
 1.079578        255.0149
 1.020035        275.3085
 1.005435        280.8243
 1.001504        282.3505
 1.000418        282.7752
 1.000117        282.8936
COMP             PC,PSIA        TC,F          W
CH4               667.8         -116.63        .0104
C2H4              729.8          48.58002      .0868

SYSTEM TEMP., F=-50

CALCULATED BUBBLE-P,PSIA= 282.9266

COMP             X              Y              K              PHIL
PHIV
CH4               .1             .3653855       3.653855       3.507264

.9598805
C2H4              .9             .6347314       .7052571       .5487346

.7780632
```