PREDICTION OF PETROLEUM FRACTION ENTHALPIES FROM THE SECOND (ALPHA) MODIFICATION OF THE VAN DER WAALS EQUATION

Part 4

I. Review/Introduction

In the first two papers (1,2) of this series, we developed and tested a 3-parameter modification of the van der Waals equation of state that greatly enhances its ability to accurately predict saturated and compressed liquid specific volumes for pure component hydrocarbons and several nonhydrocarbons, including water. The principle feature of this modification is to make the b parameter temperature-dependent by introducing a new parameter β such that,

$$b = \beta(T) \bullet b_c$$

where b_c is the original VDW b parameter which accounts for the volume occupied by the molecules themselves. A successful correlation of the β parameter as a function of the reduced temperature T_r and the Pitzer acentric factor ω was achieved.

In the third paper (3) we proposed a second 3-parameter modification which provides an improvement for the prediction of pure component vapor pressures and VLE for mixtures. For this modification we followed a similar approach as did G. Soave (4) in his modification of the Redlich-Kwong equation. We proceeded to make the VDW a parameter a general function of temperature by incorporating a temperature-dependent function α such that,

$$a = \alpha(T) \bullet a_c$$

where a_c is the original VDW a parameter which accounts for the effect of intermolecular forces. Just as for the β parameter we achieved a successful correlation for the α parameter as a function of T_r and ω. For the VLE mixture calculations we employed mixing rules for the vapor and liquid phases that were quite similar to those used by Chueh and Prausnitz (5) when they applied the Redlich-Kwong equation for calculating fugacity coefficients for components present in saturated vapor mixtures.

In this fourth and final paper, we apply the alpha-modification of the VDW equation, developed in Part 3, to the prediction of petroleum fraction enthalpies. The prime objective here was to propose an alternative procedure to that published by Grayson-Johnson (6) and Lee-Kesler (7) for generating H-T diagrams for specified petroleum cuts.

Before developing this alternative method, we will first briefly discuss the following review and background topics:

    1. Conventional characterization parameters employed for petroleum fractions.

    2. Previous petroleum fraction enthalpy charts developed and published by Johnson-Grayson and Lee-Kesler for K_w (Watson characterization factors) values of 10.0, 11.0, 11.8 and 12.5.

    3. The advantage of using a cubic (in volume) equation of state for calculating isothermal enthalpy departures for petroleum fractions.

II. Petroleum Fraction Characterization

<u>Nature of Petroleum Fractions</u> In reality petroleum fraction cuts consist of a mixture of hydrocarbons having a specified boiling range, average boiling point and average molecular weight. The specific identity of the hydrocarbons that constitute a petroleum cut are generally unknown. As a result, it is difficult to rigorously define specific properties such as enthalpy for these complex mixtures. The petroleum industry has adopted the use of "pseudo" compounds to characterize petroleum fractions. If the boiling range of the petroleum fraction is not to large (say $\leq$ 100 deg. F), then the "pseudo" concept assumes that the mixture will, within limits, behave as a pure compound characterized by an average or mean boiling point, specific gravity (60F/60F), molecular weight, etc. Generally speaking, the specification of any two such properties sets the value of all the other properties.

<u>Characterization Parameters</u> The Watson (UOP) characterization factor, K_w, is a very satisfactory parameter for correlating the physical and thermodynamic properties of straight-run petroleum fractions. It is defined as the cube root of the absolute boiling point in deg. R divided by the liquid specific gravity at 60 deg. F/ 60 deg. F or:

$$K_w = \frac{\left(T_b, {}^o R\right)^{\frac{1}{3}}}{SG} \qquad (1)$$

Paraffinic and olefinic hydrocarbons typically have K_w values that average around 12.5 to 13 whereas aromatics assume values around 10 or greater. Naphthenes have K_w values that lie typically in the mid range such as 11.5. Here is a short list of Watson factors for several hydrocarbons that fall into the various classes described above:

Hydrocarbon	Type	K_w
n-pentane	paraffinic	13.04
n-octane	paraffinic	12.68
3,3 dimethyl hexane	paraffinic	12.40
1-butene	olefinic	13.03
1-pentene	olefinic	12.66
cyclopentane	naphthenic	11.12
n-propyl cyclo C_5	naphthenic	11.53
benzene	aromatic	9.73
toluene	aromatic	10.15
n-propyl benzene	aromatic	10.62

Five different boiling point definitions have proven useful as correlating parameters:

Volume Average Boiling Point, VABP:

$$VABP = \sum x_{vi} T_{bi} \qquad (2)$$

x_{vi} = volume fraction of species i

Molal Average Boiling Point, MABP:

$$MABP = \sum x_i T_{bi} \qquad (3)$$

x_i = mole fraction of species i

Weight Average Boiling Point, WABP:

$$WABP = \sum x_{wi} T_{bi} \qquad (4)$$

x_{wi} = weight fraction of species i

Cubic Average Boiling Point, CABP:

$$CABP = \left[\sum x_{vi} T_{bi}^{1/3} \right]^3 \qquad (5)$$

Mean Average Boiling Point, MeABP:

$$MeABP = \frac{(MABP + CABP)}{2} \qquad (6)$$

Either deg. F or deg. R units may be used for each individual boiling point in order to compute VABP, MABP or WABP. However, deg. R units must be used for CABP. To compute MeABP, the MABP and CABP must be expressed in the same units.

Petroleum fraction cuts are generally undefined mixtures, and the volume, mole and weight fractions are not known. However, ASTM D86 distillations for petroleum cuts are usually readily available or can easily be measured. The VABP is precisely defined as the weighted average of the ASTM D86 distillation temperatures after 10,30,50,70 and 90 percent by volume have been distilled, i.e.

$$VABP = \frac{t_{10} + t_{30} + t_{50} + t_{70} + t_{90}}{5} \qquad (7)$$

In the absence of the 90 percent temperature, an alternative expression can be used, namely,

$$VABP = \frac{t_{10} + 2t_{50} + t_{70}}{4} \qquad (8)$$

The American Petroleum Institute (API) has developed a graphical correlation that relates all of the average boiling points to the VABP via a parameter called the ASTM D86 10-90 slope, S, defined by,

$$S = \frac{t_{90} - t_{10}}{80} \quad or \quad \frac{t_{70} - t_{20}}{50} \qquad (9)$$

This correlation exists in graphical form and is not presented here. Knowing the value of S and the VABP, one can read off a correction factor Δt to be added to the VABP to give any one of the other boiling points for the petroleum fraction of interest.

The volumetric average boiling point (VABP) appears to be the logical candidate as an input characterization parameter for correlating thermodynamic properties of petroleum cuts. It lies approximately on the 50 vol. % distillation point of the ASTM D86 curve. For example, consider the following measured ASTM D86 distillation curve for an Alaska naphtha:

Vol. %	t, deg. F		Vol. %	t, deg. F
IBP	254		60	284
5	262		70	288
10	272		80	291
20	276		90	295
30	278		95	298
40	280		EP	308
50	282			

From Eqn. 7, we calculate,

$$VABP = \frac{272+278+282+288+295}{5} = 283 \text{ deg.} F$$

which is only 1 deg. F higher than the reported midpoint D86 temperature of 282 deg. F.

The final characterization parameter of great utility is the liquid specific gravity at 60 deg. F relative to water at 60 deg. F, namely SG 60/60. This is easily measured and is related to another gravity parameter commonly used in the petroleum industry called the API gravity via the expression,

$$API = \frac{141.5}{SG} - 131.5 \qquad (10)$$

or
$$SG = \frac{141.5}{API + 131.5} \qquad (11)$$

For example, if SG = 0.6882, then,

$$API \ gravity = \frac{141.5}{0.6882} - 131.5 = 74.1$$

It is quite apparent from these expressions that API decreases as the value of SG increases.

III. Enthalpy Charts - Previous Work

<u>Johnson and Grayson</u> In their 1961 publication (6) in the Petroleum Refiner, Johnson and Grayson improved upon the enthalpy chart published by Bauer and Middleton (8). The chart developed by the latter authors correlates the enthalpy of vapor and liquid petroleum fractions as a function of temperature, and density in degrees API. Separate graphs for Watson characterization factor and pressure corrections were provided on the same chart. Although this correlation provides reliable enthalpy values for most applications, the authors point out that the reliability decreases markedly in the region of the critical, which was not indicated on their chart. In their work, Johnson and Grayson used the same correlations as did Bauer and Middleton for the heats of vaporization and heat capacities of liquids and low pressure vapors. The major improvements introduced by Johnson and Grayson were in the following areas:

1. Introduction of saturation envelopes for more convenient estimation of latent heats and for visual display of phase conditions in relation to the pseudo-critical properties of the petroleum cut.

2. Development of four separate charts for different K_w values, namely 10, 11, 11.8 and 12.5.

3. Improved representation of pressure effects on enthalpy. Included on each chart are small run-around charts which provide corrections for the effect of pressure on vapor enthalpies as a function of total pressure, temperature, API gravity and the Watson factor K_w.

4. A change of basis, defining the zero enthalpy as that of the saturated liquid at - 200 deg. F rather than 0 deg. F.

<u>Kesler and Lee</u> Over 15 years later, Kesler and Lee (7) improved the accuracy of the Johnson-Grayson charts, particularly for high pressure conditions and near the critical region, by:

1. Using improved correlations of specific heats at zero pressure and for saturated liquids (9).

2. By improving the representation of the saturation envelopes.

3. By introducing new charts for more accurate representation of the effect
of pressure on vapor and liquid enthalpies.

Lee/Kesler performed steps 2 and 3 above using a generalized thermodynamic correlation (10) which they published in the previous year (1975). They used a modified Benedict-Webb-Rubin (BWR) equation of state to improve the three parameter corresponding states correlation of Pitzer for the prediction of volumetric and thermodynamic properties of vapor and liquid pure components and mixtures. The range of reduced parameters covered by this new correlation are $T_r = 0.3$ to 4 and $P_r = 0$ to 10. The isothermal effect of pressure on enthalpy is represented by Equation 12,

$$\frac{\left(H^o - H\right)}{RT_c} = \left[\frac{H^o - H}{RT_c}\right]^{(0)} + \omega\left[\frac{H^o - H}{RT_c}\right]^{(1)} \quad (12)$$

New values for the first and second order terms above were established by Lee and Kesler and published in both graphical and tabular form. The third parameter, ω, is the well-known Pitzer acentric factor defined precisely by,

$$\omega = -Log_{10}\left(\frac{P_{vp}}{P_c}\right)_{T_r = 0.7} - 1.00 \quad (13)$$

where P_{vp} is the vapor pressure at $T_r = 0.7$.

Use of Equation 12 requires values for the critical pressure P_c, critical temperature T_c, acentric factor ω and molecular weight M. These authors used correlations presented in the API Technical Data Book to estimate these parameters. In their paper (7) they graphically represent each parameter as a function of K_w and API gravity. In addition the authors present these correlations in analytical form as follows:

$$T_c, deg.R = 341.7 + 811\,SG + (0.4244 + 0.1174\,SG)T_b$$
$$+ (0.4669 - 3.2623SG)10^5 / T_b \quad (14)$$

$$Ln(P_c, psia) = 8.3634 - 0.0566/SG - (0.24244 + 2.2898/SG$$
$$+ 0.11857/SG^2)10^{-3}T_b + (1.4685 + 3.648/SG$$
$$+ 0.47227/SG^2)10^{-7}T_b^2$$
$$- (0.42019 + 1.6977/SG^2)10^{-10}T_b^3 \quad (15)$$

$$M = -12272.6 + 9486.4\, SG + (4.6523 - 3.3287\, SG)T_b$$
$$+ (1 - 0.77084\, SG - 0.0.02058\, SG^2)(1.3437 - 720.79/T_b)10^7/T_b$$
$$+ (1 - 0.80882\, SG + 0.02226\, SG^2)(1.8828 - 181.98/T_b)10^{12}/T_b^3 \quad (16)$$

Acentric factor for petroleum fractions is basically computed from the equation developed by W. C. Edmister (11),

$$\omega = \frac{3}{7}\left[\frac{Log_{10}\left(\dfrac{P_c}{14.7}\right)}{\left(\dfrac{T_c}{T_b}\right) - 1.0}\right] - 1.0 \quad (17)$$

In Equations 14 through 17, T_b is the normal boiling point in deg. R and SG is the liquid specific gravity at 60/60.

In their 1975 publication, Lee and Kesler (10) also presented a useful equation for estimating the vapor pressure of pure hydrocarbons and narrow-boiling petroleum fractions. If the critical properties and the acentric factor are known or can be estimated, the following equations in three-parameter format are recommended:

$$Ln\, P_r^{VP} = \left(Ln\, P_r^{VP}\right)^{(o)} + \omega\left(Ln\, P_r^{VP}\right)^{(1)} \quad (18)$$

where
$$\left(Ln\, P_r^{VP}\right)^{(o)} = 5.92714 - 6.09648/T_r - 1.28862\, Ln\, T_r$$
$$+ 0.169347\, T_r^6 \quad (19)$$

$$\left(Ln\, P_r^{VP}\right)^{(1)} = 15.2518 - 15.6875/T_r - 13.4721\, Ln\, T_r$$
$$+ 0.43577\, T_r^6 \quad (20)$$

Lee and Kesler point out that Eqns. 18 through 20 satisfy the following constraints:

1. The exact definition of the acentric factor as given by Eqn. 13.

2. The Riedel condition $d\,\alpha/d\,T_r = 0$ at $T_r = 1$; α = the Riedel parameter

3. The critical point requirement that $P_r^{VP} = 1.0$ at $T_r = 1.0$.

IV. Use of the Alpha-Modification of the van der Waals Equation

<u>Equation of State Review</u> Before applying it to the calculation of petroleum fraction enthalpies, we first review the gist of the alpha-modification of the van der Waals equation developed in Part 3 of this series (3).

The original form of the van der Waals equation of state is written as,

$$P = \frac{RT}{v-b} - \frac{a}{v^2} \quad ; \quad v = molar\,volume \qquad (21)$$

For a given component, the constants a and b are treated as true constants independent of temperature. So-called generalized expressions for these constants are readily derived using the criteria that, at the critical point, the first and second derivatives of the pressure with respect to the volume are both zero. When these criteria are applied to Equation 21, the following expressions result,

$$a = a_c = \frac{27\,R^2\,T_c^2}{64\,P_c} \quad ; \quad b = b_c = \frac{RT_c}{8\,P_c} \quad ; \quad Z_c = 0.375 \qquad (22\,a,b,c)$$

Equation 21 can readily be converted to the compressibility form by direct substitution of the following identities,

$$a = \frac{A\,R^2\,T^2}{P} \quad ; \quad b = \frac{B\,RT}{P} \quad ; \quad v = \frac{Z\,RT}{P} \qquad (23\,a,b,c)$$

The final result after substitution and rearrangement becomes,

$$Z^3 - (B+1)Z^2 + AZ - AB = 0 \qquad (24)$$

Following the same (original) premise as did Soave (4), at temperatures other than at the critical for a pure component, we define a temperature-dependent alpha (α) function such that,

$$a(T) = a_c\,\alpha(T) \qquad\qquad (25)$$

$\alpha(T)$ is a dimensionless parameter which becomes unity in the limit as $T \to T_c$. The original a term in Equation 21 is now replaced by Equation 25.

At this point we employed the same functional relationship as did Soave for relating α to the reduced temperature T_r, namely,

$$\alpha^{0.5} = 1 + m\left(1 - T_r^{0.5}\right) \qquad (26)$$

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

$$\alpha \rightarrow 1 \quad as \quad T_r \rightarrow 1 \qquad (27)$$

Using vapor pressure data for 18 hydrocarbons and 5 nonhydrocarbons, including water and hydrogen, we performed a regression analysis of the above expressions (Eqns. 21-26) and arrived at a generalized correlation for m as a function of the acentric factor. This turned out to be a simple linear function given by,

$$m = 0.551088 + 1.452291\omega \qquad (28)$$

<u>Pressure Effect on Enthalpy</u> The rigorous thermodynamic expression for the isothermal effect of pressure on enthalpy can be written as,

$$H - H^o = Pv - RT + \int_\infty^v \left[T\left(\frac{\partial P}{\partial T}\right)_v - P \right] dv \qquad (29)$$

The pressure derivative can be evaluated directly from the basic equation of state, Eqn. 21,

$$\left(\frac{\partial P}{\partial T}\right)_v = \frac{R}{v-b} - \frac{da/dT}{v^2}$$

This expression can now be substituted directly into Eqn. 29, and then the appropriate expression for the enthalpy departure derived,

$$H - H^o = Pv - RT + \int_\infty^v \left[\frac{RT}{v-b} - \frac{T\dfrac{da}{dT}}{v^2} - \frac{RT}{v-b} + \frac{a}{v^2} \right] dv$$

$$H - H^o = Pv - RT + \int_{\infty}^{v} \left[a - T \frac{d\,a}{d\,T} \right] \frac{d\,v}{v^2}$$

$$= Pv - RT - \left[a - T \frac{d\,a}{d\,T} \right] \left[\frac{1}{v} \right]_{\infty}^{v}$$

$$H - H^o = Pv - RT - \frac{a - T \frac{da}{dT}}{v} \qquad (30)$$

The derivative term (da/dT) in Eqn. 30 is readily derived from Eqns. 25 and 26 with the result being,

$$\frac{da}{dT} = a_c \frac{d\,\alpha}{d\,T} = -\frac{m \alpha^{0.5} a_c}{\sqrt{T T_c}} \qquad (31)$$

The total stream enthalpy can then be directly calculated from Eqn. 32,

$$H = H^o + (H - H^o) \qquad (32)$$

H^o is simply the ideal gas enthalpy evaluated at the same temperature as the actual liquid or vapor phase in question.

Ideal Gas Enthalpy/Datum For the enthalpy datum we define $H^o = 1000$ Btu/Lb for the ideal gas state at 0 deg. R.   The original datum used by Lee-Kesler was $H = 0$ for the saturated liquid at - 200 deg. F. For each K_w (chart) separate ideal curves resulted for each API gravity parameter.   For each K_w of interest we converted the Lee-Kesler ideal gas curves to the 1000 Btu/Lb ideal gas datum. When this process was completed, all of the ideal gas curves came together (coincided) regardless of the value for the API gravity. For each K_w (individual chart) we proceeded to fit the ideal gas curves to power series functions of temperature over the temperature range - 200 deg. F to 1200 deg. F. These curves can be represented by the following equations and are in quite a convenient format for programming purposes.

For $K_w = 10.0$

$$H^o = 1044.336 - 7.802478\left(\frac{T}{100}\right) + 3.406409\left(\frac{T}{100}\right)^2$$

$$- 4.867539x10^{-2}\left(\frac{T}{100}\right)^3 - 63.24663\left(\frac{100}{T}\right) \qquad (33)$$

For $K_w = 11.0$

$$H^o = 1066.963 - 9.93614\left(\frac{T}{100}\right) + 4.082524\left(\frac{T}{100}\right)^2$$

$$- 5.743644x10^{-2}\left(\frac{T}{100}\right)^3 - 71.30033\left(\frac{100}{T}\right) \qquad (34)$$

For $K_w = 11.8$

$$H^o = 1045.532 - 3.645153\left(\frac{T}{100}\right) + 3.890683\left(\frac{T}{100}\right)^2$$

$$- 4.858230x10^{-2}\left(\frac{T}{100}\right)^3 - 48.05258\left(\frac{100}{T}\right) \qquad (35)$$

For $K_w = 12.5$

$$H^o = 1200.242 - 47.1735\left(\frac{T}{100}\right) + 8.967712\left(\frac{T}{100}\right)^2$$

$$- 0.2259742\left(\frac{T}{100}\right)^3 - 230.1361\left(\frac{100}{T}\right) \qquad (36)$$

In these equations the units are T in degrees R and H^o in Btu/Lb. For intermediate values of K_w, H^o is determined by simple linear interpolation.

Vapor Pressure In order to generate the saturation V-L locus for a specified petroleum fraction, we need to have some reliable values for the vapor pressure. We could simply use the VP correlation of Lee-Kesler (Eqns. 18-20) shown on Page 8. However, it would be more appropriate and consistent if we use the modified VDW equation proposed here to calculate vapor pressures.

For a pure component single phase vapor or liquid, the general volume-explicit form of the fugacity coefficient equation is written as,

$$Ln\frac{f}{P} = Z - 1 - Ln\,Z + \int_{0}^{1/v} (Z-1)\,v\,d\left(\frac{1}{v}\right) \qquad (37)$$

If we next substitute Eqn. 21 and the identities Eqns. 23 a,b,c into Eqn. 37, and after rearrangement and simplification, we arrive at,

$$Ln\frac{f}{P} = (Z-1) - Ln(Z-B) - \frac{A}{Z} \qquad (38)$$

For a pure component at a specified temperature and at the vapor pressure, the fugacities in the vapor and liquid phases are equal, i.e.

$$f^{L} = f^{V} \qquad\qquad (39)$$

By trial and error the pressure is varied, and values of f are calculated via Eqn. 38 for both the liquid and vapor phases. When Eqn. 39 is finally satisfied, the selected pressure is the "true" vapor pressure.

Appendix I lists a BASIC program called MODVDWVP.BAS, which employs the alpha-modification of the van der Waals equation to calculate petroleum fraction vapor pressures. In Line 5, values for the normal boiling point (TBF) and API gravity are inputted. Then the specific gravity and Watson characterization factor are immediately calculated via Lines 15-20. Lines 30-125 are devoted to the calculation of molecular weight, critical pressure, critical temperature and acentric factor from the Lee-Kesler correlations, Eqns. 14-17. In Line 175, the temperature is inputted along with a sound estimate of the vapor pressure.

Characteristic EOS parameters are computed in Lines 190-215. Lines 220-240 are devoted to the calculation of the liquid compressibility factor and fugacity coefficient, and Lines 245-260 to the calculation of the same quantities for the vapor. A subroutine starting at Line 760 is used to calculate all of the compressibility factors.

Lines 270-310 employ a Newton-Raphson iterative procedure to calculate a (vapor) pressure such that the equality of Eqn. 39 is eventually satisfied. The final vapor pressure value at convergence is printed by Line 370. Line 375 directs the program back to L175 and allows it to input (read in) another set of values for T and P^{est}. A sample output is provided at the end of Appendix I for a petroleum fraction having a normal boiling point of 109.2 deg. F and API gravity of 70. The specified temperature is 50 deg. F whereby a vapor pressure of 3.644 psia is calculated and printed out.

A simple comparison was made between the vapor pressures predicted by Program MODVDWVP.BAS and the Lee-Kesler method (Eqns. 18-20) for the same petroleum cut defined above (TBP = 109.2 deg. F and API = 70). The results are summarized below:

Temp. F	Modif. VDW VP, Psia	LK VP, Psia
0	0.884	0.98
50	3.64	3.94
100	11.22	11.92
150	27.98	29.27
200	59.66	61.46
250	113.08	114.7
300	195.83	196.0
350	316.04	313.7
400	482.27	479.9

Enthalpy Program Appendix II features a BASIC program called MVDWPFH.BAS which computes single phase vapor or liquid enthalpies using our proposed alpha-modification of the VDW equation.

Lines 5-123 perform the same basic operations as the vapor pressure program (Appendix I). Here the API gravity and NBP are inputted, and S, K_w, molecular weight, critical constants and acentric factor are calculated and printed out. In Line 130 the operating temperature (deg. F), pressure (psia) and phase condition (F = 1 liquid; F = 2 vapor) are all specified. The ideal gas enthalpy is computed in Lines 150-245 using Eqns. 33-36 and a simple linear interpolation routine for intermediate values of K_w. Next the characteristic equation of state parameters are computed in Lines 250-295. In Line 280 subroutine 760 is called upon to calculate the phase compressibility factor. And finally, the enthalpy departure and total stream enthalpy are computed via Lines 300-315 and then printed from Line 325 along with the operating T and P.

The program is then directed back to L130 to read in another T, P and F if available from DATA lines 1200 and higher or is simply terminated indicating that the program is "OUT OF DATA".

Attached to the program listing in Appendix II is a sample output for a petroleum fraction with API gravity = 70 and NBP = 109.2 deg. F. The two points run here are for a saturated liquid and vapor at 50 deg. F with VP = 3.644 psia as computed and extracted from Program MODVDWVP.BAS (Appendix I).

Test of Prediction Accuracy In the early seventies, Lenoir and Hipkin (12,13) completed extensive measurements of both liquid and vapor enthalpies for a host of petroleum fractions. In their first publication (12), they reported enthalpy data for a single light naphtha. The second publication (13) covered eight separate petroleum cuts - 5 naphthas and 3 gas oils. All of the data were reported in the format of the enthalpy difference ΔH between the liquid state at 75 deg. F and some higher temperature (vapor or liquid state) all at fixed system pressure. The temperature range of the measurements was from 75 to 650 deg. F for pressures up to 1400 psia. These data are indeed rare. In fact, they are believed to be the only petroleum fraction enthalpy data currently available.

We selected two representative petroleum cuts from the Lenoir-Hipkin data bank in order to perform a brief accuracy check on the proposed alpha-modified VDW equation. These were an Alaska naphtha and a gas oil. The reported VABP and API gravity were inputted into Program MVDWPFH.BAS and enthalpies were calculated at the precise experimental pressures and temperatures reported by the authors. Table 1 provides a detailed comparison for the Alaska naphtha.   Table 2 gives a similar type comparison for the gas oil. The table below provides an overall summary of the comparisons:

Petrol. Cut	VABP,F	API Grav.	No. of Pts. Tested	Trend Btu/Lb	Abs Avg Dev Btu/Lb
Alaska Naphtha	283	50.5	71	-0.5	2.8
Gas Oil	539	35.3	70	-3.1	3.1

The trends and average deviations reported are quite acceptable. The accuracy of isobaric flow calorimeters generally ranges between ± 1-2 Btu/Lb.

Sample H-T Diagram We are now in a position to perform the necessary calculations for generating an H-T diagram for a specified petroleum fraction or cut. The illustration shown here will be for a petroleum cut for which:

$$Kw = 11.8 \text{ and API gravity} = 70$$

From Equations 1 and 11 we can readily calculate the liquid specific gravity and the value for the normal boiling point.

$$SG = \frac{141.5}{API + 131.5} = \frac{141.5}{70 + 131.5} = 0.7022$$

$$TBP = \left[(K_w)(SG) \right]^3 = \left[(11.8)(0.7022) \right]^3$$
$$= 568.9 \deg. R = 109.2 \deg. F$$

In order to generate the saturated V/L H-T locus, we need to first generate vapor pressures for a host of temperatures that are below the critical temperature. For the petroleum cut under consideration here, Eqn. 14 predicts a critical temperature of 419.2 deg. F. Next Program MODVDWVP.BAS was used to calculate vapor pressures over the temperature range of 0 to 400 deg. F. These data are basically listed in the middle of Page 14.

In the strictest sense, a petroleum cut, no matter how close boiling it may be, is comprised of a mixture of hydrocarbons. In actuality, we would get a separate bubble point and dew point temperature for a given pressure. However, these temperatures are generally very close to one another. As discussed previously, petroleum fractions are conventionally treated as hypothetical pure components with a single or unique value of the vapor pressure corresponding to each $T \leq T_c$.

The temperature/vapor pressure data generated above along with the TBP and API gravity were subsequently inputted into program MVDWPFH.BAS, and the corresponding liquid and vapor enthalpies calculated up to the critical temperature. In addition the ideal gas enthalpy data were also generated based on the datum of $H^o = 1000$ Btu/Lb at 0 deg. R.

All of the results were then plotted as an H-T diagram which is displayed here as Figure 1. Although some extrapolation for the liquid saturation curve was done, we show a complete temperature range of -200 to 500 deg. F.

Figure 5, Page 154, of the Lee-Kesler paper (7) gives the H-T diagram for the same petroleum cut as shown on Figure 1 (K_w = 11.8, API = 70). For the sake of comparison, we superimposed the H-T plot from our work here (modif. VDW eqn.) with that of Lee and Kesler. This comparison is shown graphically on Figure 2. The enthalpy datum for both sets of curves here is the same as employed by Lee and Kesler, namely H = 0 for the saturated liquid state at – 200 deg. F.

The ideal gas and saturated vapor curves agree quite well with one another. The saturated liquid curves intersect at around 300 deg. F. Below 300 deg. F the Lee-Kesler liquid curve is as much as 9 Btu/Lb higher than the modified VDW curve. Above 300 deg. F the Lee-Kesler liquid curve lies as much as 8 Btu/Lb below the corresponding liquid curve generated from the modified VDW equation.

In addition, we used program MVDWPFH.BAS to generate H-T charts for K_w = 11.8 at API liquid gravity values of 50 and 30 respectively. These charts appear as the attached Figures 3 and 4 and are based on the 1000 Btu/Lb ideal gas datum.

Original VDW Eqn. Before concluding this discussion, it is imperative that we show the improvement that is achieved by using the alpha-modif. of the VDW equation as opposed to using the original equation of state for the prediction of petroleum fraction enthalpies.

In Table 3 we show a brief comparison of both sets of predicted enthalpy traverses against the data of Lenoir and Hipkin (13) for the Alaska naphtha at a single pressure of 30 psia. The overall average trends and absolute average deviations are summarized below for a total of 18 points tested:

Equation	Overall Trend, %	Overall Abs. Avg. Dev., %
Alpha-Modif. VDW EOS	-1.5	1.7
Original VDW EOS	- 83.6	83.6

For this brief comparison, the improvement in prediction accuracy is rather obvious. Similar results would be expected for any of the other petroleum fraction cuts.

Assessment of Critical Constants In the BASIC programs (Appendices I and II) used to calculate petroleum fraction vapor pressures and enthalpies we used the Lee-Kesler (7) correlations (Eqns. 14-17) for calculating the required critical constants, molecular weight and acentric factor. Lenoir and Hipkin (13) report critical properties and molecular weights for five naphthas and three gas oils. The critical properties of the Alaska naphtha were measured by Prof. W. B. Kay at the Ohio State University. The critical constants for the jet naphtha and low-boiling naphtha were established from the enthalpy measurements. The other tabulated critical properties represented estimates by using the procedures in the Data Book of the American Petroleum Institute (API).

For the sake of completeness of our study here, we compared critical properties and molecular weights predicted by the Lee-Kesler correlations against the corresponding values reported by Lenoir and Hipkin for the eight hydrocarbon fractions. The results of this comparison are shown in Table 4. The overall trends in the predictions are briefly summarized below:

	Mol. Wt.	Crit. Temp.	Crit. Press.
No. of Pts.	9	8	8
Overall Trend, %	-2.1	-0.9	-9.7

Although the prediction accuracy for the critical pressure is rather marginal, the impact on the prediction accuracy for the vapor pressure and liquid/vapor enthalpies did not appear to be significant.

In Conclusion The principle advantage of using an equation of state such as our proposed alpha-modif. VDW equation is that it can be conveniently used to generate an H-T plot for any petroleum fraction characterized by a given K_w and API gravity (or NBP) with accuracy that is reasonably commensurate with the Lee-Kesler charts.

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 (2020).

3. Koppany, C.R., "Prediction of Vapor Pressures and Mixture VLE from a Modification of the van der Waals Equation", Part 3 (2010-2011).

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

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

6. Johnson, R.L. and Grayson, H.G., "Petroleum Refiner", Vol. 40, No. 2, (Feb. 1961) Page 123.

7. Kesler, M.G. and Lee, B.I., "Hydrocarbon Processing", Vol. 55, No. 3, (March 1976) Page 153.

8. Bauer, C.R. and Middleton, J.F., "Petroleum Refiner", Vol. 32, No. 1, (1953) Page 111.

9. Watson, K.M. and Nelson, E.F., "Ind. Engr. Chem." . Vol. 25 (1933), Page 880.

10. Kesler. M.G. and Lee, B.I., "AIChE Journ.", Vol. 21, No. 3, (May, 1975), Page 510.

11. Edmister, W.C., "Applied Hydrocarbon Thermo., Petrol. Refiner", Vol. 37 No. 4 (April, 1958).

12. Lenoir, J.M. and Hipkin, H.G., "Hydrocarbon Processing" (May, 1971) Page 95.

13. Lenoir, J.M. and Hipkin, H.G., "Journal of Chem. and Engr. Data", Vol. 18 No. 2 (1973) Page 195.

TABLE 1

This spreadsheet compares experimental petroleum fraction enthalpy traverses against the corresponding predictions from the alpha-modification of the van der Waals EOS

***

Petroleum Cut	Temp. F	Press. Psia	Phase	Exper. Delta-H* Btu/Lb	Modif. VDW Delta-H* Btu/Lb	Dev** Btu/Lb	Abs. Dev Btu/Lb
Alaska	280	30	L	108.5	106.6	-1.9	1.9
Naphtha	300	30	L	120.9	118.4	-2.5	2.5
	320	30	L	133.2	130.4	-2.8	2.8
VABP	330.6 BP	30	L	140.0	137.0	-3.0	3.0
283 F	342.3 DP	30	V	264.6	265.2	0.6	0.6
	360	30	V	273.7	274.2	0.5	0.5
50.5	380	30	V	284.2	284.5	0.3	0.3
Deg API	400	30	V	295.1	294.9	-0.2	0.2
	420	30	V	306.4	305.6	-0.8	0.8
	440	30	V	317.5	316.4	-1.1	1.1
	460	30	V	328.7	327.5	-1.2	1.2
	480	30	V	340.0	338.7	-1.3	1.3
	500	30	V	351.2	350.1	-1.1	1.1
	520	30	V	363.1	361.7	-1.4	1.4
	540	30	V	375.3	373.5	-1.8	1.8
	560	30	V	388.1	385.5	-2.6	2.6
	580	30	V	401.0	397.7	-3.3	3.3
	600	30	V	413.9	410.0	-3.9	3.9
	400	100	L	184.3	181.3	-3.0	3.0
	420	100	L	197.3	194.9	-2.4	2.4
	440	100	L	210.7	208.9	-1.8	1.8
	442 BP	100	L	212.0	210.3	-1.7	1.7
	451.6 DP	100	V	315.9	316.7	0.8	0.8
	460	100	V	320.7	321.5	0.8	0.8
	480	100	V	332.6	333.0	0.4	0.4
	500	100	V	344.6	344.7	0.1	0.1
	520	100	V	356.7	356.6	-0.1	0.1
	540	100	V	368.8	368.7	-0.1	0.1
	560	100	V	381.7	380.9	-0.8	0.8
	580	100	V	394.6	393.2	-1.4	1.4
	600	100	V	407.4	405.8	-1.6	1.6
	610	100	V	413.7	412.1	-1.6	1.6
	620	100	V	419.9	418.5	-1.4	1.4
	580	400	L	314.0	316.2	2.2	2.2
	600	400	L	330.3	337.0	6.7	6.7
	610	400	L	339.3	351.7	12.4	12.4
	615.1 BP	400	L	344.6	381.4	36.8	36.8
	620 DP	400	V	382.9	387.2	4.3	4.3
	624	400	V	386.9	391.3	4.4	4.4
	626	400	V	388.1	393.2	5.1	5.1

			TABLE 1 (continued)			
500	800	L	250.4	247.4	-3.0	3.0
520	800	L	264.5	262.0	-2.5	2.5
540	800	L	279.1	276.9	-2.2	2.2
560	800	L	293.8	292.2	-1.6	1.6
580	800	L	308.8	307.9	-0.9	0.9
600	800	L	324.0	324.0	0.0	0.0
610	800	L	331.7	332.2	0.5	0.5
620	800	L	339.4	340.6	1.2	1.2
624	800	L	342.6	343.9	1.3	1.3
626	800	L	343.9	345.7	1.8	1.8
280	1400	L	107.3	105.2	-2.1	2.1
300	1400	L	119.3	116.7	-2.6	2.6
320	1400	L	131.4	128.4	-3.0	3.0
340	1400	L	143.7	140.4	-3.3	3.3
360	1400	L	156.1	152.6	-3.5	3.5
380	1400	L	168.5	165.1	-3.4	3.4
400	1400	L	181.3	177.7	-3.6	3.6
420	1400	L	194.0	190.6	-3.4	3.4
440	1400	L	207.2	203.8	-3.4	3.4
460	1400	L	220.5	217.1	-3.4	3.4
480	1400	L	234.3	230.8	-3.5	3.5
500	1400	L	248.1	244.6	-3.5	3.5
520	1400	L	262.2	258.7	-3.5	3.5
540	1400	L	276.3	273.1	-3.2	3.2
560	1400	L	290.8	287.7	-3.1	3.1
580	1400	L	305.3	302.5	-2.8	2.8
600	1400	L	319.8	317.6	-2.2	2.2
610	1400	L	327.2	325.2	-2.0	2.0
620	1400	L	334.4	332.9	-1.5	1.5
624	1400	L	338.1	336.0	-2.1	2.1
626	1400	L	338.8	337.6	-1.2	1.2

N = 71   Overall   Trend =   -0.5

Abs. Avg.   Dev. =   2.8

* Delta-H from 75 F (liquid) to specified temperature T, all at fixed system pressure, Btu/Lb.

** Dev. = Delta-H (Modif. VDW) - Delta-H Exper. In Btu/Lb.

*** Experimental data from Lenoir and Hipkin, Jr. Chem. Engr. Data,

TABLE 2

This spreadsheet compares experimental petroleum fraction enthalpy traverses against the corrersponding predictions from the alpha-modification of the van der Waals EOS

***

Petroleum Cut	Temp. F	Press. Psia	Phase	Exper. Delta-H* Btu/Lb	Modif. VDW Delta-H* Btu/Lb	Dev** Btu/Lb	Abs. Dev Btu/Lb
Gas Oil	140	40	L	30.2	30.5	0.3	0.3
	160	40	L	40.2	40.3	0.1	0.1
VABP	180	40	L	50.4	50.3	-0.1	0.1
539 F	200	40	L	61.0	60.6	-0.4	0.4
	220	40	L	71.6	71.0	-0.6	0.6
35.3	240	40	L	82.3	81.7	-0.6	0.6
Deg API	260	40	L	93.8	92.6	-1.2	1.2
	280	40	L	105.4	103.7	-1.7	1.7
	300	40	L	117.1	115.0	-2.1	2.1
	320	40	L	129.1	126.5	-2.6	2.6
	340	40	L	141.2	138.2	-3.0	3.0
	360	40	L	153.6	150.2	-3.4	3.4
	380	40	L	166.0	162.3	-3.7	3.7
	400	40	L	178.7	174.7	-4.0	4.0
	420	40	L	191.6	187.3	-4.3	4.3
	440	40	L	204.8	200.2	-4.6	4.6
	460	40	L	217.9	213.2	-4.7	4.7
	480	40	L	231.1	226.5	-4.6	4.6
	500	40	L	244.3	239.9	-4.4	4.4
	520	40	L	257.9	253.7	-4.2	4.2
	540	40	L	272.2	267.6	-4.6	4.6
	560	40	L	287.1	281.8	-5.3	5.3
	580	40	L	302.8	296.2	-6.6	6.6
	140	700	L	30.2	30.4	0.2	0.2
	160	700	L	40.3	40.2	-0.1	0.1
	180	700	L	50.5	50.2	-0.3	0.3
	200	700	L	61.3	60.4	-0.9	0.9
	220	700	L	71.9	70.8	-1.1	1.1
	240	700	L	82.9	81.5	-1.4	1.4
	260	700	L	94.3	92.3	-2.0	2.0
	280	700	L	105.6	103.4	-2.2	2.2
	300	700	L	117.1	114.6	-2.5	2.5
	320	700	L	129.1	126.1	-3.0	3.0
	340	700	L	141.3	137.8	-3.5	3.5
	360	700	L	153.6	149.7	-3.9	3.9
	380	700	L	166.0	161.7	-4.3	4.3
	400	700	L	178.7	174.1	-4.6	4.6
	420	700	L	191.6	186.6	-5.0	5.0
	440	700	L	204.5	199.3	-5.2	5.2
	460	700	L	217.4	212.2	-5.2	5.2
	480	700	L	230.7	225.4	-5.3	5.3
	500	700	L	243.9	238.7	-5.2	5.2
	520	700	L	257.2	252.3	-4.9	4.9
	540	700	L	270.7	266.0	-4.7	4.7
	560	700	L	284.9	280.0	-4.9	4.9
	580	700	L	299.5	294.1	-5.4	5.4

TABLE 2 (continued)

140	1400	L	30.0	30.3	0.3	0.3
160	1400	L	40.0	40.1	0.1	0.1
180	1400	L	50.2	50.1	-0.1	0.1
200	1400	L	60.9	60.3	-0.6	0.6
220	1400	L	71.7	70.7	-1.0	1.0
240	1400	L	82.9	81.3	-1.6	1.6
260	1400	L	94.1	92.1	-2.0	2.0
280	1400	L	105.5	103.1	-2.4	2.4
300	1400	L	117.2	114.3	-2.9	2.9
320	1400	L	129.0	125.8	-3.2	3.2
340	1400	L	141.0	137.4	-3.6	3.6
360	1400	L	153.1	149.2	-3.9	3.9
380	1400	L	165.1	161.3	-3.8	3.8
400	1400	L	177.1	173.5	-3.6	3.6
420	1400	L	190.1	186.0	-4.1	4.1
440	1400	L	203.0	198.6	-4.4	4.4
460	1400	L	216.2	211.5	-4.7	4.7
480	1400	L	229.5	224.5	-5.0	5.0
500	1400	L	243.0	237.8	-5.2	5.2
520	1400	L	256.1	251.2	-4.9	4.9
540	1400	L	269.2	264.8	-4.4	4.4
560	1400	L	282.9	278.7	-4.2	4.2
580	1400	L	297.1	292.7	-4.4	4.4
600	1400	L	312.0	306.9	-5.1	5.1

N = 70   Overall   Trend =   -3.1
                 Abs. Avg.   Dev. =   3.1

*Delta-H from 75 F (liquid) to the specified temperature T, all at fixed system pressure, Btu/Lb.

** Dev. = Delta-H (Modif. VDW) - Delta-H Exper., Btu/Lb.

*** Experimental data from Lenoir and Hipkin, Jr. Chem. Engr. Data,
        Vol. 18, No. 2, 1973 (Page 195)

TABLE 3

This spreadsheet compares experimental petroleum fraction enthalpy traverses against the
corresrponding predictions from the alpha-modification of the van der Waals EOS

Sheet 1(3)   File: MODVWPFH.XLS
                                          ***

Petroleum Cut	Temp. F	Press. Psia	Phase	Exper. Delta-H* Btu/Lb	Modif. VDW Delta-H* Btu/Lb	Dev** Btu/Lb	Abs. Dev Btu/Lb	Orig, VDW Delta-H* Btu/Lb	Dev Btu/Lb	Abs. Dev Btu/Lb
Alaska	280	30	L	108.5	106.6	-1.9	1.9	85.5	-23.0	23.0
Naphtha	300	30	L	120.9	118.4	-2.5	2.5	95.2	-25.7	25.7
	320	30	L	133.2	130.4	-2.8	2.8	105.2	-28.0	28.0
VABP	330.6 BP	30	L	140.0	137.0	-3.0	3.0	110.6	-29.4	29.4
283 F	342.3 DP	30	V	264.6	265.2	0.6	0.6	167.1	-97.5	97.5
	360	30	V	273.7	274.2	0.5	0.5	175.9	-97.8	97.8
50.5	380	30	V	284.2	284.5	0.3	0.3	186.1	-98.1	98.1
Deg API	400	30	V	295.1	294.9	-0.2	0.2	196.5	-98.6	98.6
	420	30	V	306.4	305.6	-0.8	0.8	207.1	-99.3	99.3
	440	30	V	317.5	316.4	-1.1	1.1	217.8	-99.7	99.7
	460	30	V	328.7	327.5	-1.2	1.2	228.8	-99.9	99.9
	480	30	V	340.0	338.7	-1.3	1.3	240.0	-100.0	100.0
	500	30	V	351.2	350.1	-1.1	1.1	251.4	-99.8	99.8
	520	30	V	363.1	361.7	-1.4	1.4	262.9	-100.2	100.2
	540	30	V	375.3	373.5	-1.8	1.8	274.7	-100.6	100.6
	560	30	V	388.1	385.5	-2.6	2.6	286.6	-101.5	101.5
	580	30	V	401.0	397.7	-3.3	3.3	298.8	-102.2	102.2
	600	30	V	413.9	410.0	-3.9	3.9	311.1	-102.8	102.8

| | N=18 | | | Overall | Trend, % | -1.5 | | | -83.6 | |
| | | | | Abs Avg | Dev, % | | 1.7 | | | 83.6 |

* Delta-H from 75 F (liquid) to specified temperature T, all at fixed system pressure, Btu/Lb.
** Dev. = Delta-H (Modif. VDW) - Delta-H Exper. In Btu/Lb.
*** Experimental data from Lenoir and Hipkin, Jr. Chem. Engr. Data, Vol. 18, No. 2, 1973 (Page 195)

TABLE 4

Comparison of Molecular Weights and Critical Properties Predicted from the
Lee-Kesler Correlations Against the Data of Lenoir and Hipkin (12,13)

Ref: Two publications by J. M. Lenoir and H. G. Hipkin,   "Light Naphtha Enthalpy Measured", Hydrocarbon Processing, May 1971, Page 95;
"Measured Enthalpies Of Eight Hydrocarbon Fractions"; Journal of Chemical and Engineering Data, Vol. 18, No. 2, 1973, Page 195.

Petroleum Fraction Description	VABP Deg F	API Gravity	Watson Factor	Molecular Meas.	Weight * Pred.	% Dev	Critical Meas.	Temp. F * Pred.	% Dev	Critical Meas.	Press, Psia * Pred.	% Dev
Light Naphtha	196	60.6	11.80	102.4	97.9	-4.39	-	-	-	-	-	-
Alaska Naphtha	283	50.5	11.63	131	124.5	-4.96	626.5	616.9	-1.53	414.7	414.9	0.05
Jet Naphtha	322	44.4	11.48	144	135.9	-5.63	665	664.0	-0.15	440	403.9	-8.20
Aromatic Naphtha	255	34.5	10.50	126	106.1	-15.79	626	624.4	-0.26	709	551.9	-22.16
Low-boiling Naphtha	267	59.9	12.10	120	123	2.50	605	585.4	-3.24	463	384.0	-17.06
High-boiling Naphtha	318	54.2	12.10	142.4	139.5	-2.04	646	640.0	-0.93	371	356.0	-4.04
Kerosine	407	43.5	11.80	162.3	169.9	4.68	739	737.4	-0.22	361	323.4	-10.42
Fuel Oil	547	33.0	11.68	227.5	229.5	0.88	879	876.1	-0.33	290	264.7	-8.72
Gas Oil	539	35.3	11.80	214	227.3	6.21	868	862.9	-0.59	280	259.4	-7.36

Trend=   -2.06   -0.91   -9.74
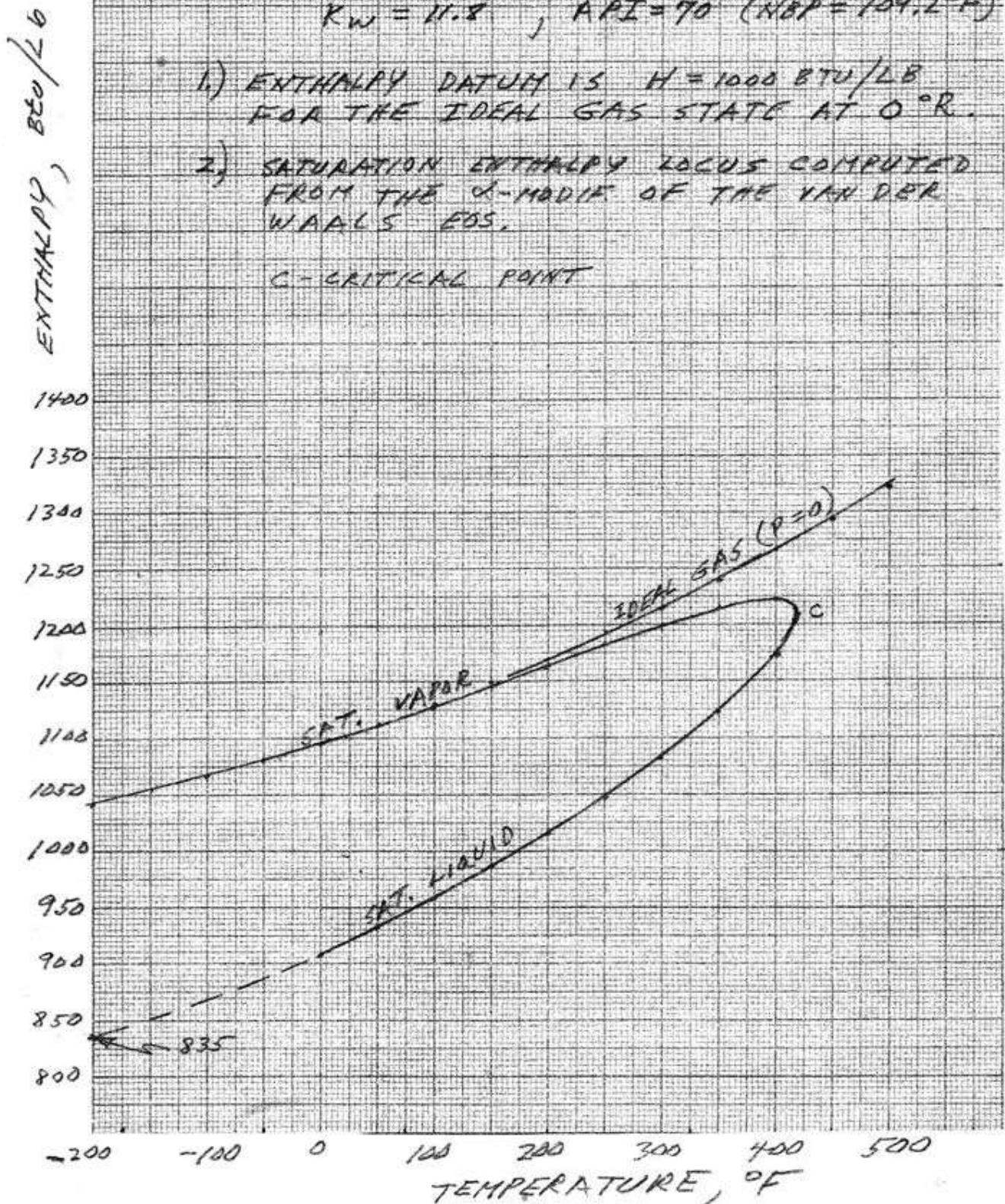
* Predicted molecular weight and critical properties from the correlations of Lee and Kesler (7).
See Equations 14-16 of the text (Pages 7-8).

FIGURE 1
H-T DIAGRAM FOR A PETROLEUM
FRACTION CUT WITH
$K_W = 11.8$, API = 70 (NBP = 109.2°F)

1.) ENTHALPY DATUM IS H = 1000 BTU/LB
FOR THE IDEAL GAS STATE AT 0 °R.

2.) SATURATION ENTHALPY LOCUS COMPUTED
FROM THE α-MODIF OF THE VAN DER
WAALS EOS.

C - CRITICAL POINT

ENTHALPY, BTU/LB

1400
1350
1300
1250
1200
1150
1100
1050
1000
950
900
850
800

IDEAL GAS (P=0)

C

SAT. VAPOR

SAT. LIQUID

835

-200   -100   0   100   200   300   400   500

TEMPERATURE, °F

CRK, 4/14/2011.

FIGURE 2

COMPARISON OF H-T DIAGRAMS
FOR A PETROLEUM CUT WITH
$K_W = 11.8$, $API = 70$ ($NBP = 109.2°F$)

——— α-MODIF. OF THE VAN DER WAALS EOS.

- - - LEE-KESLER (FROM FIG. 5, HYDRO.
PROC., MARCH, 1976, PAGE 154).

ENTHALPY DATUM: H=0 FOR THE SAT.
LIQ. AT -200°F.
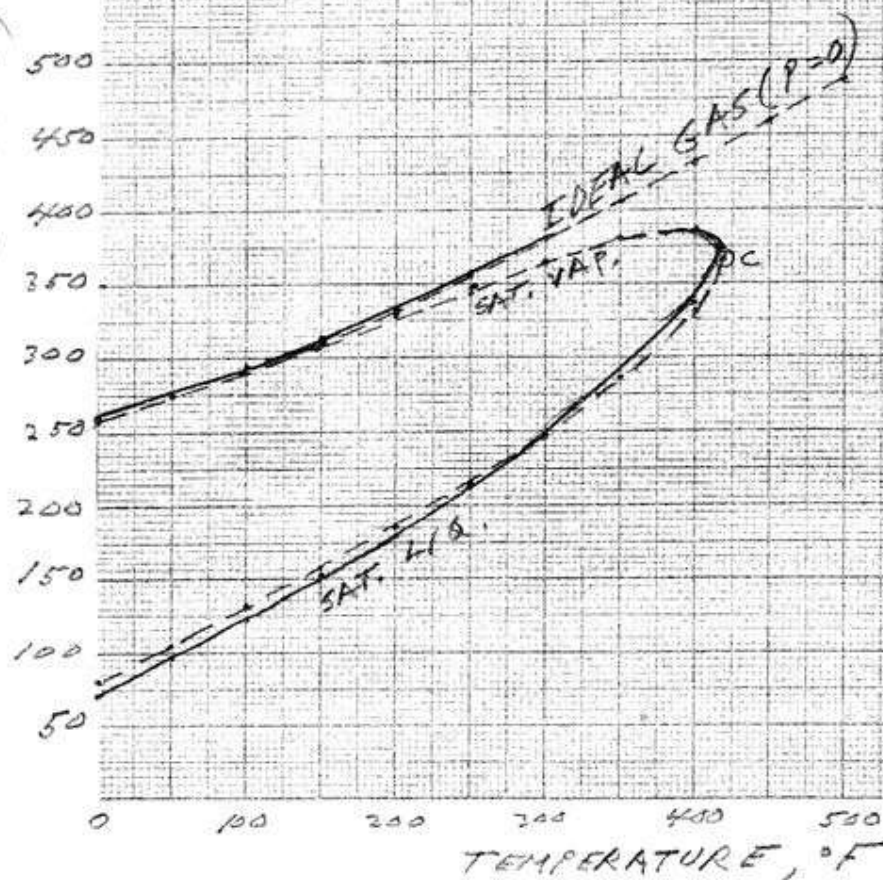
CRK. 4/25/11.

FIGURE 3

H-T DIAGRAM FOR A PETROLEUM
FRACTION CUT WITH

$K_W = 11.8$, $API = 50$ (NBP = 318.8°F)

1) ENTHALPY DATUM IS $H = 1000$ BTU/LB
FOR THE IDEAL GAS STATE AT 0°R.

2) SATURATION ENTHALPY LOCUS COMPUTED
FROM THE α-MODIF. OF THE
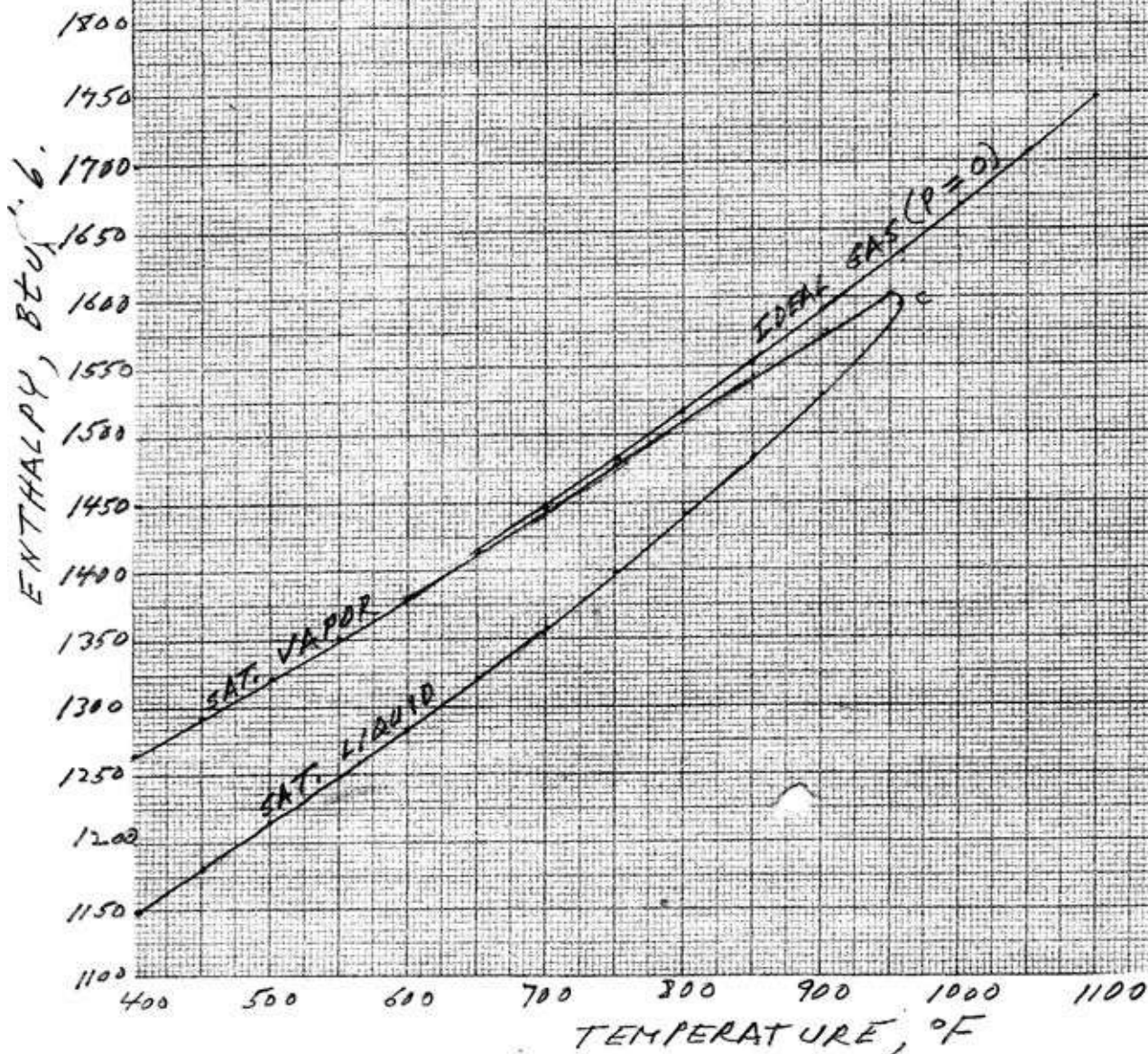VAN DER WAALS EOS.
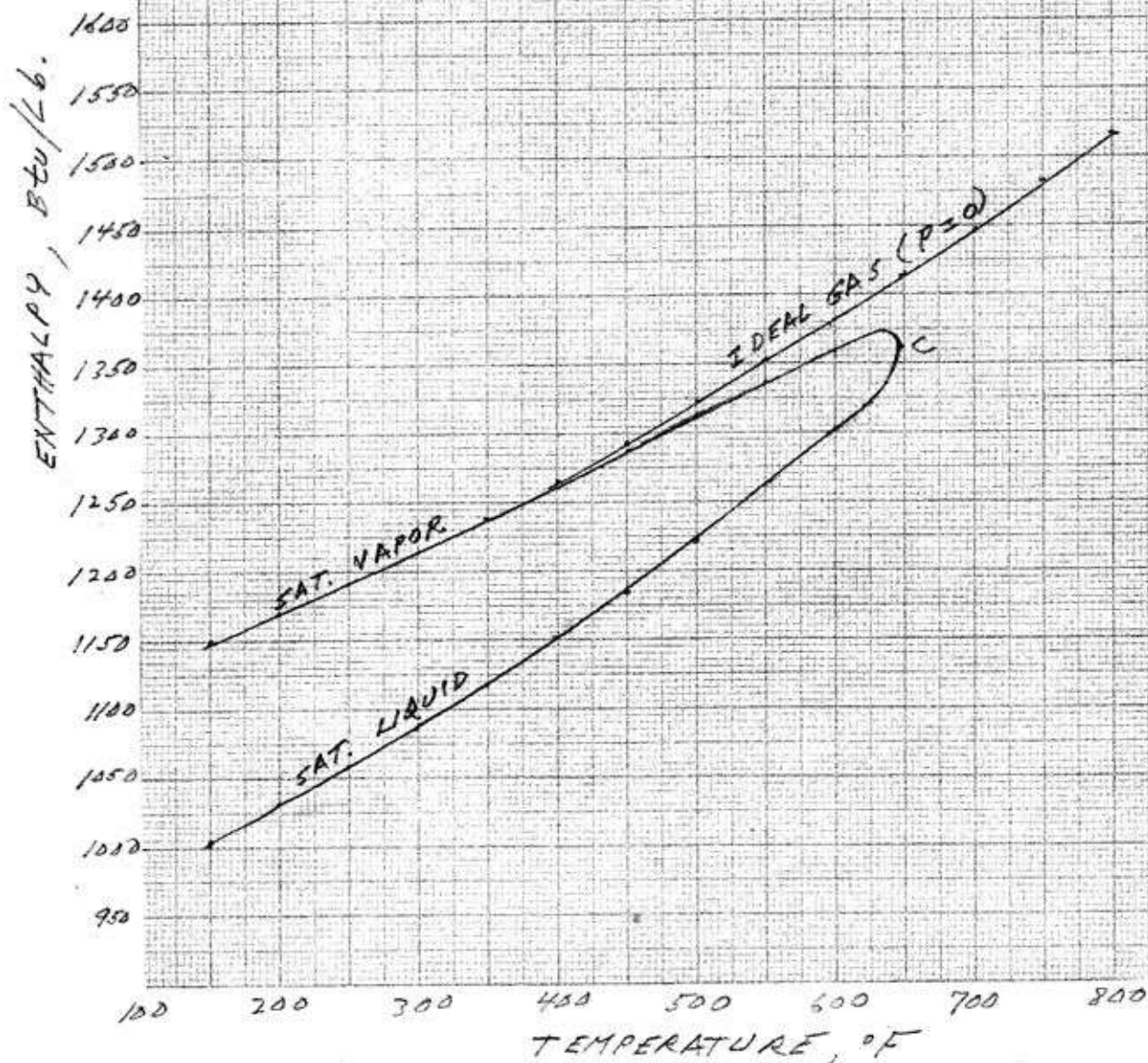
C — CRITICAL POINT

CRK 4/25/11.

FIGURE 4

H-T DIAGRAM FOR A PETROLEUM
FRACTION CUT WITH
$K_W = 11.8$, $API = 30$ $(NBP = 645.4°F)$

1) ENTHALPY DATUM IS $H = 1000$ BTU/LB
FOR THE IDEAL GAS STATE AT 0°R.

2) SATURATION ENTHALPY LOCUS
COMPUTED FROM THE α-MODIF.
OF THE VAN DER WAALS EOS.

C - CRITICAL POINT

APPENDIX I

```
2 OPEN "MODVDWVP.OUT" FOR OUTPUT AS #1
5 READ TBF, API
7 PRINT #1, "TBF,F="; TBF
8 PRINT #1, ""
10 PRINT #1, "API="; API
12 PRINT #1, ""
15 S = 141.5 / (API + 131.5)
17 TBR = TBF + 459.7
20 KW = (TBR ^ (1 / 3)) / S
22 PRINT #1, "KW="; KW
25 PRINT #1, ""
30 M1 = -12272.6 + 9486.4 * S + (4.6523 - 3.3287 * S) * TBR
35 M2 = (1 - .77084 * S - .02058 * S * S) * (1.3437 - 720.79 / TBR) *
(1E+07) / TBR
40 M3 = (1 - .80882 * S + .02226 * S * S) * (1.8828 - 181.98 / TBR) *
(1E+12) / (TBR ^ 3)
45 MW = M1 + M2 + M3
50 P1 = 8.3634 - .0566 / S
55 P2 = (.24244 + 2.2898 / S + .11857 / (S * S)) * (.001) * TBR
60 P3 = (1.4685 + 3.648 / S + .47227 / (S * S)) * (.0000001) * (TBR *
TBR)
65 P4 = (.42019 + 1.6977 / (S * S)) * (1E-10) * (TBR ^ 3)
70 PC = EXP(P1 - P2 + P3 - P4)
75 T1 = 341.7 + 811 * S + (.4244 + .1174 * S) * (TBR)
80 T2 = (.4669 - 3.2623 * S) * (100000!) / TBR
85 TCR = T1 + T2
90 TCF = TCR - 459.7
95 CH1 = 5.316 + 5478 / TBF + .554 * (TBF / 100)
100 CH2 = .8 * S * S - S
105 CH3 = (17598.1 / TBF) + 2.03 * (TBF / 100)
110 CH = CH1 + CH2 * CH3
115 R1 = (LOG(PC / 14.7)) / 2.303
120 R2 = (TCR / TBR) - 1
125 W = (3 / 7) * (R1 / R2) - 1
127 CF = 1.987 * TCR / MW
130 PRINT #1, ""
135 PRINT #1, "API", "MW", "PC,PSIA", "TC,F"
140 PRINT #1, API, MW, PC, TCF
145 PRINT #1, "API", "BP,F", "W", "C/H"
150 PRINT #1, API, TBF, W, CH
155 PRINT #1, "API", "SG)60/60)", "RTC/MW"
160 PRINT #1, API, S, CF
162 PRINT #1, ""
164 PRINT #1, "VP BY THE MODVDW EOS"
165 PRINT #1, ""
168 PRINT #1, "TEMP,F", "VP,PSIA"
172 R = 10.731
175 READ T, PEST
180 TR = T + 459.7
185 P = PEST
```

```
190 M = .551088 + 1.452291 * W
195 ALPHA = (1 + M * (1 - SQR(TR / TCR))) ^ 2
200 S1 = (27 / 64) * ALPHA * R * R * TCR * TCR / PC
205 S2 = .125 * R * TCR / PC
210 A = (S1 * P) / (R * R * TR * TR)
215 B = (S2 * P) / (R * TR)
220 F = 1
230 GOSUB 760
235 VL = Z * R * TR / P
240 PHIL = Z - 1 - LOG(Z - B) - A / Z
245 F = 2
250 GOSUB 760
255 VG = Z * R * TR / P
260 PHIG = Z - 1 - LOG(Z - B) - A / Z
270 DERIV = (VG - VL) / (R * TR)
275 FU = PHIG - PHIL
280 P1 = P - FU / DERIV
285 E1 = ABS(P - P1)
290 IF E1 < .001 THEN 370
300 P = P1
310 GOTO 210
370 PRINT #1, T, P1
375 GOTO 175
760 REM SUBROUTINE FOR SOLVING THE SOAVE RK 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
796 GOTO 800
797 PRINT #1, Z, Z1
800 E20 = ABS(Z - Z1)
805 IF E20 < .00001 THEN 820
810 Z = Z1
815 GOTO 785
820 RETURN
1000 DATA 109.2,70
1010 DATA 50,3.5
1200 CLOSE #1
9999 END
```

APPENDIX I
(continued)

TBF,F= 109.2

API= 70

KW= 11.79951

API	MW	PC,PSIA	TC,F
70	71.12146	560.3616	419.2358
API	BP,F	W	C/H
70	109.2	.2432042	5.811809
API	SG)60/60)	RTC/MW	
70	.7022333	24.55581	

VP BY THE MODVDW EOS

TEMP,F	VP,PSIA
50	3.644408

APPENDIX II

```
2 OPEN "MVDWPFH.OUT" FOR OUTPUT AS #1
5 READ A1, B1
6 PRINT #1, "API="; A1
7 PRINT #1, ""
8 PRINT #1, "TB,F="; B1
9 PRINT #1, ""
10 B2 = B1 + 459.7
15 S = 141.5 / (A1 + 131.5)
20 K = (B2 ^ (1 / 3)) / S
25 M1 = -12272.6 + 9486.4 * S + (4.6523 - 3.3287 * S) * B2
30 M2 = (1 - .77084 * S - .02058 * S * S) * (1.3437 - 720.79 / B2) *
(1E+07) / B2
35 M3 = (1 - .80882 * S + .02226 * S * S) * (1.8828 - 181.98 / B2) *
(1E+12) / (B2 ^ 3)
42 M = M1 + M2 + M3
44 CH1 = 5.316 + 5478 / B1 + .554 * (B1 / 100)
45 CH2 = .8 * S * S - S
46 CH3 = (17598.1 / B1) + 2.03 * (B1 / 100)
47 CH = CH1 + CH2 * CH3
50 T1 = 341.7 + 811 * S + (.4244 + .1174 * S) * B2
55 T2 = (.4669 - 3.2623 * S) * (100000) / B2
70 T = T1 + T2
75 P1 = 8.3634 - .0566 / S
80 P2 = (.24244 + 2.2898 / S + .11857 / (S * S)) * (.001) * B2
85 P3 = (1.4685 + 3.648 / S + .47227 / (S * S)) * (.0000001) * (B2 *
B2)
90 P4 = (.42019 + 1.6977 / (S * S)) * (1E-10) * (B2 ^ 3)
95 P = EXP(P1 - P2 + P3 - P4)
100 R1 = (LOG(P / 14.7)) / 2.303
105 R2 = T / B2
110 W = (3 / 7) * (R1 / (R2 - 1)) - 1
115 T7 = T - 459.7
117 PRINT #1, "PC,PSIA", "TC,F", "W", "MW"
118 PRINT #1, P, T7, W, M
119 PRINT #1, ""
120 PRINT #1, "KW", "S.G.", "C/H"
122 PRINT #1, K, S, CH
123 PRINT #1, ""
127 PRINT #1, "T,F", "P,PSIA", "H0,BTU/LB", "H-H0,BTU/LB", "H,BTU/LB"
130 READ T0, P0, F
135 REM F=1 LIQUID; F=2 VAPOR
140 T0 = T0 + 459.7
145 R = 1.9872
150 T9 = T0 / 100
155 H1 = 1044.336 - 7.802478 * T9 + 3.406409 * T9 * T9
160 H2 = -(4.867539E-02) * (T9 ^ 3) - 63.24663 / T9
165 H3 = H1 + H2
170 H4 = 1066.963 - 9.936141 * T9 + 4.082524 * T9 * T9
175 H5 = -(5.743644E-02) * (T9 ^ 3) - 71.30033 / T9
180 H6 = H4 + H5
```

```
185 H7 = 1045.532 - 3.645153 * T9 + 3.890683 * T9 * T9
190 H8 = -(.0485823) * (T9 ^ 3) - 48.05258 / T9
195 H9 = H7 + H8
200 G1 = 1200.242 - 47.1735 * T9 + 8.967712 * T9 * T9
205 G2 = -.2259742 * (T9 ^ 3) - 230.1361 / T9
210 G3 = G1 + G2
215 IF K > 11 THEN 230
220 H0 = H3 + (K - 10) * (H6 - H3)
225 GOTO 250
230 IF K > 11.8 THEN 245
235 H0 = H6 + ((K - 11) / .8) * (H9 - H6)
240 GOTO 250
245 H0 = H9 + ((K - 11.8) / .7) * (G3 - H9)
250 M0 = .551088 + 1.452291 * W
255 A0 = 1 + M0 * (1 - (T0 / T) ^ .5)
260 S1 = (27 / 64) * A0 * A0 * (R * R * T * T / P)
265 S2 = .125 * R * T / P
270 A = (S1 * P0) / (R * R * T0 * T0)
275 B = (S2 * P0) / (R * T0)
280 GOSUB 760
282 PRINT #1, "Z="; Z
285 V = Z * R * T0 / P0
290 S3 = -M0 * A0 / SQR(T * T0)
295 S4 = (27 / 64) * S3 * R * R * T * T / P
300 L1 = (S1 - T0 * S4) / V
305 L2 = P0 * V - R * T0
310 U5 = (L2 - L1) / M
315 U7 = H0 + U5
320 T8 = T0 - 459.7
325 PRINT #1, T8, P0, H0, U5, U7
330 GOTO 130
760 REM SUBROUTINE TO CALCULATE 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
1200 DATA 70,109.2
1220 DATA 50,3.644,1,50,3.644,2
3000 CLOSE #1
9999 END
```

APPENDIX II
(continued)

API= 70

TB,F= 109.2

PC,PSIA	TC,F	W	MW
560.3616	419.2358	.2432042	71.12146

KW	S.G.	C/H	
11.79951	.7022333	5.811809	

T,F	P,PSIA	H0,BTU/LB	H-H0,BTU/LB	H,BTU/LB
Z= 1.618964E-03				
50	3.644	1112.163	-180.3463	931.8163
Z= .9892319				
50	3.644	1112.163	-.4252366	1111.737