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A COMPARISON OF EXISTING ENTHALPY CORRELATIONS FOR PETROLEUM FRACTIONS

By

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ABSTRACT

A study is made of existing enthalpy correlations for petroleum fractions in the hope that these correlations can be applied to coal-derived liquids. No one correlation is assessed to be the best for petroleum fractions as the area of enthalpy prediction for naturally occurring crudes is constantly being improved.

A section containing sample calculations and the error between calculated and experimental enthalpy values is included for each correlation.

Difficulties which might be encountered in applying petroleum fraction correlations to coal-derived liquids are mentioned. Suggestions are made to provide a better comparison of existing petroleum fraction correlations and to continue the nature of this work in the future.

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DEDICATION

I dedicate this thesis to the memory of my aunt, Audry Karls Schroer.

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INTRODUCTION

In order to provide a comparison between the enthalpies of petroleum fractions and coal-derived liquids, studies are now being conducted to measure the enthalpies of coal-derived liquids calorimetrically. However, it is impossible to measure the enthalpy for every hydrocarbon liquid, whether it is naturally occurring or synthetic, so it is desirable to be able to predict enthalpies by a generalized correlation.

The correlation of enthalpies for coal-derived liquids has as its logical basis the correlations already in existence for petroleum fractions. It is assumed at this point that the same equations used to estimate the enthalpies and physical properties of the petroleum fractions can also be applied to coal-derived liquids. It must be remembered that the conditions under which the coal-derived liquids are formed and the hydrocarbon type distribution often differ radically from those of the petroleum fractions. This could affect the usefulness of any petroleum-fraction empirical correlation for coal-derived liquids. Also, as coal-derived liquids are undefined mixtures of hydrocarbons, it is difficult to apply a mixing rule with a pure component correlation to these liquids. Recognizing these difficulties, various petroleum-fraction enthalpy correlations are investigated as a possible foundation for a coal-derived liquid correlation. Consequently, this thesis is divided into four main sections:

1) investigation of existing enthalpy correlations for petroleum fractions,
2) estimation of physical properties,
3) comparison of the different correlations' accuracies,
4) discussion of how existing correlations might apply to coal-derived liquids.

EXISTING PETROLEUM-FRACTION CORRELATIONS

This section reviews the existing correlations in chronological order of development. Not all of the correlations which have been developed are covered, but the most significant ones are included. At the beginning of each correlation synopsis the physical properties required in the correlation are listed. The references which provide methods for estimating these physical properties can be found in the section, "Physical Properties of Petroleum Fractions."

It should be noted that most of the correlations follow the same procedure for predicting enthalpies. The first step is to determine empirical equations at the reference state pressure for the specific heats of the liquid and vapor states and the heat of vaporization as functions of temperature. By integrating the specific heat equation between the reference temperature and the temperature of the liquid, the enthalpy of the liquid phase is determined. If the petroleum fraction exists as a gas, the liquid heat capacity is integrated normal boiling point, the heat of vaporization added, and the gas phase specific heat equation integrated between the limits of the normal boiling point and the temperature of the petroleum fraction. Correction terms are then added to compensate for the effect of the system's pressure on the enthalpy. Often the effect of pressure on a liquid that exists below 1000 psia can be neglected.

Summarizing the above steps mathematically:

$$H = \int_{T_{ref}}^{T_b} C_{pl}\,dT + \int_{T_b}^{T} C_{pv}\,dT + H_{pres} + \lambda \qquad (1)$$

where:

H = enthalpy, Btu/lb, relative to T_{ref}

C_{pl} = liquid heat capacity at reference pressure

λ = heat of vaporization at one atmosphere, Btu/lb.

C_{pv} = heat capacity of vapor at reference pressure

H_{pres} = pressure correction term for deviation from the reference pressure

T_{ref} = reference temperature

T_b = normal boiling point temperature

T = system temperature (if a gas, T is above T_b)

1933 - K.M. Watson and E.F. Nelson (1)

Physical Properties Required:

(refer to section entitled, "Physical Properties of Petroleum Fractions" for references which define and estimate the physical properties for a petroleum fraction)

Normal boiling point, specific gravity at 60/60°F, molecular weight, critical pressure, critical **temperature**

Region of Correlation's Applicability:

Liquid heat capacity
- Temperature: 0-100°F
- Specific gravity: 10-70°API

Latent heat of vaporization at 1 atm
- Temperature range of molal average boiling point: 0-675°F
- Molecular weight: 75-300
- Watson's Characterization Factor, K: 10-12

Vapor heat capacity at 1 atm
- Temperature: 50-900°F
- Specific gravity: 0.55 gas-10°API

Isothermal enthalpy departure from ideal gas
- Temperature: T_r between 0.8 and 1.5
- Pressure: P_r between .1 and 6

Some of the earliest petroleum-fraction correlational work was done by Watson and Nelson of Universal Oil Products in 1933. One of their main contributions was the definition of the so-called Watson Characterization Factor, K. K provided an overall correlation parameter which was defined as:

$$K = \frac{(T_b)^{1/3}}{SG} \qquad (2)$$

where:

T_b = molal average boiling point, $^{\circ}R$

SG = specific gravity at 60/60°F

The K factor serves as an index of paraffinicity, with high values of 12.5-plus indicating a high degree of saturation. Severely cracked stocks have K's of 10-11.

Watson and Nelson used this characterization factor to improve existing correlations which had been based on temperature and specific gravity alone. Since each previous correlation had been based on data with different K values, Watson and Nelson observed that by multiplying existing correlations by a factor involving K, differences between correlations diminished. Two generalized specific heat correlations, applicable to all stocks, were the net result:

$$C_{pl} = (0.6811 - 0.308*SG + T(0.000815 - 0.000306 *SG)) * (0.055*K + 0.35) \qquad (3)$$

$$C_{pv} = (4.0 - SG)/6450. * (T + 670.) * (0.12*K - 0.41) \qquad (4)$$

where:

C_{pl}, C_{pv} = specific heats of liquid and vapors respectively, at 1 atm, Btu/lb/°F

T = temperature, °F

The reference state chosen was liquid at 32°F.

To compute the latent heat of vaporization at 1 atm, Watson and Nelson proposed using Kistyakowski's equation which was originally intended for pure, nonpolar compounds:

$$L = T_b/M * (7.58 + 4.57/\log T_b) \qquad (5)$$

where:

L = latent heat of vaporization, Btu/lb

T_b = boiling point, ^oR

M = molecular weight, lb/lb-mole

The above equation was assumed to be applicable to polar and nonpolar mixtures if T_b was equal to the molal average boiling point and M was equal to the average molecular weight.

No correction for pressure from the reference state was given for the liquid phase enthalpy. However, there is considerable deviation in C_{pl} in the critical state. The liquid phase specific heat capacity equation applies where the pressure is well below that required to prevent vaporization but may give results too low at lower pressures. A pressure correction term for enthalpy is necessary however in the vapor phase.

$$\left(\frac{\partial H}{\partial P}\right)_T = V - T\left(\frac{\partial V}{\partial T}\right)_P \qquad (6)$$

where:

H = enthalpy

V = volume

T = absolute temperature

P = absolute pressure

However,

$V = ZRT/P$

Z = compressibility factor

R = gas constant

Z was fitted to the chart of Brown, Souders and Smith(20) by the following equations which are applicable to a reduced temperature of 1.5:

for low values of reduced pressure, $P_r < 2.5$

$$Z = 1.0 - (0.73(T_r)^{-3} - 0.18) * P_r \qquad (7)$$

for high values of reduced pressure, $2.5 \leq P_r \leq 6$

$$Z = 1.0 - (0.24 - 0.14*T_r) * (8.0 - P_r) \qquad (8)$$

where:

P_r = reduced pressure

T_r = reduced temperature

By differentiating the volume equation with respect to T and substituting this expression into the differential for enthalpy, equation 6, the following equations were derived:

at low P_r, $P_r < 2.5$

$$\Delta \frac{HM}{T} = -4.4 * P_r/(T_r)^3 \qquad (9)$$

at high P_r, $2.5 \leq P_r \leq 6$

$$\Delta \frac{H'M}{T} = 0.28*T_r * (P'_r - P_{ro} - 8.*\ln(P'_r/P_{ro})) \qquad (10)$$

where: M = molecular weight

ΔH = change in enthalpy due to change in pressure from the reference pressure to P_r, where P_r is in the range of the low P_r equation

$\Delta H'$ = change in enthalpy due to a change from P_{ro} to P_r', where P_{ro} is the limit of the range for the low P_r equation and P_r' is any pressure above the P_{ro} limit

The graph, figure 10(1), which is a plot of these two equations has as its range of applicability, T_r from 0.8-1.5 and P_r from .1-6.

Included in the section, "Comparison of the Petroleum-Fraction Correlations", is a sample calculation using the methods of Watson and Nelson to predict the enthalpy of a petroleum fraction. The enthalpy of this example petroleum fraction is predicted by all of the different correlations reviewed for comparison.

It should be noted that the difference in enthalpy due to a pressure change from zero pressure to 1 atm is neglected in Watson's and Nelson's correlations, as in most of the earlier correlations.

1942 (correction, 1944) - D.E. Holcomb and G.R. Brown (2,3)

Physical Properties Required:

Specific gravity at 60/60°F and °API, critical temperature and pressure

Region of Correlation's Applicability:

Liquid heat capacity at 1 atm
Temperature: -100-1000°F
Specific gravity: 10-70°API
K: 10-12.5
Vapor heat capacity at 1 atm
Temperature: -200-1200°F
Specific gravity: 0-70°API
Isothermal enthalpy departure from ideal gas
Temperature: T_r between .75-1.00
Pressure: P_r between 0-.9

Much of the work done by Holcomb and Brown was applicable to specific pure light hydrocarbons. The reference state chosen was 32°F, 0 psia, liquid. However, at zero pressure the enthalpy of a vapor mixture is obtained by summing up the products of each component and its molal enthalpy at zero pressure. At higher pressures, the vapor mixtures are not ideal, so the effect of pressure on enthalpy must be evaluated.

Charts correlating the specific heats of hydrocarbon liquids as a function of specific gravities are included in the original article. The charts are based on data measured at 32°F and the hydrocarbon's vapor pressure, however the enthalpy change from 32°F and the vapor pressure to 32°F and zero pressure can not be more than on the order of .07 Btu/lb, as calculated for pentane.

The van't Hoff equation was used to calculate the latent heat of vaporization at 32°F and zero pressure for a component i in a mixture:

$$2.303 * \frac{d(\log_{10}K_i)}{d(T)} = \frac{\Delta H_{vap_i}}{RT^2} \qquad (11)$$

where:

$d(\log_{10}K_i)/d(T)$ = slope of curve of $\log_{10}K_i$ vs. temperature at constant pressure where K_i is the vaporization equilibrium constant for a component i, defined as y_i/x_i where y_i is the mole fraction in the vapor phase, x_i is the mole fraction in the liquid phase of component i

R = gas law constant

A table was presented in the 1942 article which represented the results of this equation on current data. The reference conditions were at 32°F and 0 psia. The 1944 article corrected the results based on this equation as it was found that the K's were unreliable. The 1944 charts were correlated in terms of total vapor enthalpy for pure components at zero pressure which incorporated the corrected heats of vaporization. However, this correlation is not very useful for petroleum fractions which are undefined mixtures of hydrocarbons normally.

A chart based on curve-fitting of data was presented to calculate the specific heat of gaseous paraffins. The heat capacity charts and heat of vaporization chart were used to determine overall enthalpy charts at zero pressure for pure components.

To calculate the isothermal effect of pressure on the enthalpy of liquid, the following equation was used:

$$\Delta H = 144./778. \int_0^P (V - T(\partial V/\partial T)_p)\, dp \qquad (12)$$

where:

ΔH = change of enthalpy due to pressure

V = volume

p = system pressure

where pressure-volume-temperature relations for liquid paraffins can be found in the literature.

To calculate the isothermal effect of pressure on vapor enthalpy:

$$-\frac{\Delta H}{T} = R\left(\frac{(\partial \ln(f/p))}{(\partial \ln(T_r))}\right)_{P_r}, \quad \frac{f}{p} = \text{activity coefficient} \qquad (13)$$

First a chart was plotted for the f/p relation and then this was used to determine an overall change in enthalpy using pseudocritical properties of the mixture as correlating parameters.

1944 - J.F. Fallon and K.M. Watson (4)

Physical Properties Required:

API gravity, K factor, critical temperature, molecular weight

Region of Correlation's Applicability:

Liquid heat capacity at critical pressure
- Temperature: 0-1000°F
- Specific gravity: 0-90°API

Latent heat of vaporization
- Temperature range of average boiling point: 100-1000°F
- Specific gravity: -5-90°API
- Molecular weight used in preference to specific gravity: 80-400

Vapor heat capacity at 0 psia
- Temperature: 0-1400°F
- K: 10-13

The empirical specific heat equations which formed the basis of the correlations of Watson and Nelson were a result of averaging existing petroleum-fraction calorimetric data. In 1944, heat capacities for the ideal vapor state were developed from spectroscopic data and statistical calculations by Spencer and Flannagan(21). With proper frequency assignments, the correlation applied over a wide range of temperatures. Values for normal paraffins up to octane could be correlated, along with isobutane, ethylene, and acetylene. Dobratz attempted to estimate the constraints for this correlation from the structural formula of a compound. However, errors resulted at high temperatures and if the compounds to which the correlation was applied were very different in structural type from those on which the correlation was based. In 1944, Fallon and Watson presented correlations in agreement with spectroscopic data and thermodynamically consistent with those based on the generalized relations of Watson(22).

Fallon and Watson combined the correlations of Spencer and Flannagan(21), Dobratz(23), and Watson(22) to yield a specific heat of vapor equation at 0 psia:

$$C_{pv} = (0.045*K - 0.233) + (0.44 + 0.0177*K)(10^{-3}T) - 0.153(10^{-6}T^2) \qquad (14)$$

where:

K = Watson's Characterization Factor

T = temperature, ^{o}F

This correlation is different from the previously described method of Watson and Nelson(1) in that only the characterization factor is used to characterize the stock. No systematic variation was found from this correlation with wide variations in specific gravity and boiling point.

Specific heats of the liquid were calculated from the vapor specific heat capacity by using the generalized thermodynamic method described by Watson(22). A generalized thermodynamic method of obtaining specific heat capacities of saturated liquids from ideal gas specific heat capacities was described by Hougen and Watson(5), in 1947.

The calculations for the specific heat capacities of liquids obtained by Watson's approach(22), were restricted to reduced temperatures less than 0.85 where pressure effects are negligible. However, at these lower temperatures, the petroleum fractions were not well represented by the liquid specific heat capacity obtained by the above method.(22) This is due to the fact that the generalized thermodynamic approach is in doubt in this region. Consequently, for heavier stocks a new C_{pl} was correlated:

$$C_{pl} = ((0.355 + 0.128 * 10^{-2} \,^{o}API) + (0.503 + 0.117 * 10^{-2} \,^{o}API)\, 10^{-3} T) * (0.05K + 0.41) \tag{15}$$

To calculate the latent heat of vaporization at one atm pressure, a modified form of the Clausius-Clapeyron equation was used:

$$\lambda = ZRT^2/P * \frac{d(P)}{d(T)} = \frac{ZRT_r^2 T_c^2}{P} * \frac{d(P)}{d(T)} \tag{16}$$

$\frac{d(P)}{d(T)}$ can be found by differentiating the vapor pressure equation proposed by Gamson and Watson(24):

$$\frac{d(P)}{d(T)} = \frac{P * A}{T_c * T_r^2} + \frac{40P(T_r - b)}{T_c} e^{-20(T_r - b)^2} \tag{17}$$

where:

Z = compressibility factor

R = gas constant

T = temperature, ^{o}R

P = pressure

T_r = reduced temperature

T_c = critical temperature, ^oR

b, A = constants in vapor pressure equations

The constant b can be found in the original article by Gamson and Watson(24). A can be evaluated by substituting the critical point and mean average boiling point into equation (17). The article by Fallon and Watson(4) contains a graph which summarizes these results, figure 4(4), along with C_{pv} and C_{pl} graphs, figures 2 and 3 respectively(4). The values for heats of vaporization predicted in this way are in close agreement with the Kistyakowski equation, used by Watson and Nelson(1), for low-boiling compounds, but is considerably higher for high-boiling compounds.

Any pressure correction necessary for the deviation of enthalpy from zero pressure is computed in the same manner as in the Watson and Nelson correlation(1). As the charts of Fallon and Watson were prepared from pure hydrocarbon data, these charts should not be used to predict the enthalpies of mixtures except under conditions where ideal solutions are formed. Balzhiser, Samuels, and Eliassen defined an ideal solution as one that obeys the Lewis and Randall rule,(25)

$$\bar{f}_i = n_i f_i \tag{18}$$

where:

$\bar{f}_i$ = partial fugacity of component i

f_i = fugacity of the pure component in the same phase and at the same temperature and pressure as the mixture.

n_i = mole fraction of component i in mixture

Ideal gases are ideal solutions, however liquids often are not ideal solutions because of intermolecular interaction in the condensed phase. If the solution is ideal, there is no heat of mixing.

<u>1947</u> - O.A. Hougen and K.M. Watson(5)

Physical Properties Required:

Critical pressure and temperature

Region of Correlation's Applicability:

Isothermal enthalpy departure from ideal gas
Temperature: T_r between 0.575 and 15
Pressure: P_r between .01 and 20

Fallon and Watson used generalized thermodynamic equations to estimate the heat capacity of a liquid from that of a gas. Hougen and Watson have summarized many useful thermodynamic relations which are applicable to hydrocarbons, including estimating saturated liquid heat capacities from the specific heat capacity of an ideal gas. As Hougen and Watson pointed out, data on the heat capacities of liquids, particularly at temperatures other than atmospheric are scanty and frequently unreliable. However, data is available for the heat capacities of ideal gases over wide temperature ranges.

$$(c_{sl}-c_p^*)_T = \frac{-d\,\lambda}{d\,T} - \frac{d(H^* - H_{sG})}{dT} \qquad (19)$$

where:

c_{sl} = specific heat capacity of the saturated liquid

c_p^* = specific heat capacity of ideal gas

H = enthalpy

$sG,*$ = saturated gas and ideal gas, respectively

However,

$$\left(\frac{d(H^* - H_{sG})}{dT}\right)_s = \left(\frac{\partial(H^* - H_{sG})}{\partial T}\right)_P + \left(\frac{\partial(H^* - H_{sG})}{\partial P}\right)_T \left(\frac{dp}{dT}\right)_s \qquad (20)$$

The enthalpy difference derivatives can be calculated from the enthalpy departure graphs of Hougen and Watson(5). $\left(\frac{dp}{dT}\right)_s$ can be found by differentiating the vapor pressure equation. Hougen and Watson chose the Calingaert-Davis equation to represent the vapor pressure. The term $\frac{d\lambda}{dT}$ is obtained by differentiation of the latent heat of vaporization equation:

$$\frac{d\lambda}{dT_r} = -0.361 * R * \frac{B(T_b)^2}{(T_b - 43)^2} \frac{(1 - T_{rb})^{-.38}}{(1 - T_r)^{.62}} \qquad (21)$$

where:

R = gas constant

B = constant of Calingaert-Davis equation

T_b = normal boiling point, degrees Kelvin

The c_{sl} computed in this manner is applicable at zero pressure or approximately, 1 atm. From the relation presented above, along with suitable corrections derived by Hougen and Watson(5), the heat capacity of a liquid at any condition may be predicted from this saturated liquid heat capacity.

Hougen and Watson also updated the pressure correction chart of Watson and Nelson(1) for the deviation of enthalpies from the ideal state. The chart of Hougen and Watson(5) represents the data calculated by Edmister(26) and York and Weber.(27) York and Weber(27) found that in the temperature range above $T_r = 1$, where T_r represents the reduced temperature, the enthalpy corrections varied systematically with the critical temperature of the substance. Therefore, the chart's values of Hougen and Watson(5) should be corrected by multiplying these values by ϕ:

$$\text{where } \phi = (T_c/470)^n \qquad (22)$$

n is a function of reduced temperature. A table summarizing these n's is presented in the original article by Hougen and Watson.(5)

<u>1953</u> - C.R. Bauer and J.F. Middleton(6)

Physical Properties Required:

Mean average boiling point at 1 atm, molecular weight, K factor, °API gravity

Region of Correlation's Applicability:

Liquid heat capacity
Extended gravity range to 0°API for Nelson and Watson correlation(1)
Latent heat of vaporization at 1 atm
Temperature range of mean average boiling point: 0-1000°F
Molecular weight: 70-500
Specific gravity: -10-90°API
Vapor heat capacity at 1 atm
Temperature: 0-1200°F
K factor: 10-13

Bauer and Middleton used the same specific heat equations as Watson and Nelson(1) to calculate liquid enthalpies, the same Kistyakowski equation to calculate latent heats of vaporization at atmospheric pressure, and the correlation of Fallon and Watson(4) to calculate vapor enthalpies. However, the charts of Bauer and Middleton improved the original correlational charts which were a result of the above equations(1),(4) to relect more recent data.

The liquid specific heat equation of Watson and Nelson(1) was thoroughly checked by Gaucher(28) for a wide variety of petroleum fractions and pure hydrocarbons and was found to give very satisfactory results. The data of Hyman and Kay(29) for a -11°API crude water gas tar indicated that extrapolating the original correlation to 0°API was justified. The original Watson and Nelson(1) chart for latent heat of vaporization was based on a correlation for molecular weights of petroleum fractions which has since been revised. The chart of Bauer and Middleton(6) reflects this revision.

The specific heat equation of Fallon and Watson(4) for vapors gives close agreement for petroleum fractions which have a K=11.8, but at characterization factors other than 11.8, large deviations occur. Bauer and Middleton empirically determined the deviation from Fallon and Watson's chart(4) which resulted from K not being equal to 11.8. Consequently, their chart for specific heats of petroleum vapors gives better results than that of Fallon and Watson for K's other than 11.8.

When using the charts of Bauer and Middleton, it should be noted that their chosen reference state was liquid, saturated, $0^{\circ}F$. The alignment chart for the pressure effect on enthalpy represents basically a refinement of the Hougen-Watson(5) chart, except that pseudocritical and critical properties have been eliminated as variables. However, this simplification results in increased error.

<u>1961</u> - R.L. Johnson and H.G. Grayson(7)

Physical Properties Required:

Specific gravity at 60/60°F, critical pressure and temperature

Region of Correlation's Applicability:

Correlated in terms of total enthalpy
Temperature: 0-1200°F
Specific gravity: 0-90°API
K= 11.8

The enthalpy charts presented by Johnson and Grayson(7) were developed from data presented by Bauer and Middleton(30) and Lydersen, Greenkorn, and Hougen(31). The enthalpy of vapor at zero absolute pressure and liquid at one atmosphere is taken directly from the Bauer-Middleton data(30) except that the basis is changed from liquid at 0°F to -200°F. The pressure correction for the enthalpy of liquid petroleum fractions below 1000 psia is negligible. However, for pressures above 1000 psia, a pressure-correction chart(7) which corrects for the deviation of liquid enthalpy from 1 atm is presented, using specific gravity as the correlating parameter. A pressure correction chart for the enthalpy of vapor was presented for a K of 11.8. An additional chart for a petroleum fraction with a compressibility factor (critical) of 0.27 is presented(7). The reduced properties of the petroleum fraction are necessary.

Enthalpy charts often do not include a visual means of representing the liquid and vapor regions, and the saturation envelopes. Previous charts failed to predict enthalpy in the critical region because of the difference in critical behavior between mixtures and pure compounds. It is possible for an actual fraction to have a latent heat of vaporization where a pseudocritical correlation would indicate none. In this region, Johnson and Grayson developed saturated vapor-liquid domes which are included on the enthalpy chart(7). The domes are convenient because they present a visual picture of the given petroleum fraction's phase condition at certain operating conditions, in relation to the pseudocritical point of the material. No pressure corrections are necessary because these domes represent saturated conditions. Latent heats of vaporization can be estimated directly from the domes.

1974 - J.G. Jacks, J.H. Dluzniewski and S.B. Adler(8)

Physical Properties Required:

Depends on which correlations previously described are used to estimate ideal gas enthalpy

Region of Correlation's Applicability:

Depends on which correlations previously described are used to estimate ideal gas enthalpy
Isothermal enthalpy departure from ideal gas(9)
Temperature: T_r between .8 and 4.0
Pressure: P_r between .2 and 9.0

Enthalpies can be calculated using an application of the Curl-Pitzer corresponding states correlation. A brief synopsis of the original article which was revised in 1961 by Pitzer and Brewer, is given below(9).

Statistical theory shows that a group of substances will conform to the principle of corresponding states only if their intermolecular potentials are identical except for distance and energy-scale factors characteristic of each substance. The principle of corresponding states was originally proposed by van der Waals and assumes that all substances would have the same equation of state when expressed in terms of the reduced variables. Quantum effects must be negligible. Simple fluids are those which conform accurately to corresponding states behavior. Molecules of large dipole moments can not be correlated by corresponding states.

To provide a measure of a fluid's deviation from simple fluids, an acentric factor was defined:

$$\omega = -\log_{10}(P_s/P_c) - 1.0 \qquad (23)$$

where:

P_s = vapor pressure at reduced temperature, .7 T_r

P_c = critical pressure

$\omega = 0.$ for simple fluids such as Ar, Kr and other spherical molecules. Non-spherical molecular normal fluids have low positive acentric factors. However, normal fluids do not have strong intermolecular interactions such as hydrogen bonding, acid-base association, etc.

At low pressures, the virial equation of state through the second virial coefficient would apply leading to the following equation to calculate the departure of enthalpy from the ideal gas state's enthalpy:

$$\frac{H - H^o}{RT_c} = P_r * ((0.1445 + .073\,\omega) - (0.66 - .92\,\omega) T_r^{-1} - (.4155 + 1.5\,\omega)T_r^{-2} - (0.0484 + .388\,\omega)T_r^{-3} - .0657\,\omega\, T_r^{-8}) \qquad (24)$$

where:

H^o = ideal gas enthalpy at 1 atm.

R = ideal gas law constant

T_c = critical temperature

Note: The correlation for the second virial coefficient is given by a modified form of the Berthelot equation(9).

The ideal gas enthalpy can be calculated from the previous correlations.

At higher pressures, where the second virial coefficient no longer applies, the following equation is used:

$$\frac{H_T^o - H_T}{RT_c} = \left(\frac{H_T^o - H_T}{RT_c}\right)^0 + \omega\left(\frac{H_T^o - H_T}{RT_c}\right)^1 \quad (25)$$

where:

$\frac{H_T^o - H_T}{RT_c}$ = dimensionless isothermal enthalpy departure from ideal gas

$\left(\frac{H_T^o - H_T}{RT_c}\right)^0$ = dimensionless isothermal enthalpy departure from ideal gas for a simple fluid, plotted as a function of T_r and P_r

$\left(\frac{H_T^o - H_T}{RT_c}\right)^1$ = dimensionless isothermal enthalpy departure correction term for molecular acentricity, plotted as a function of T_r and P_r

Pitzer and Brewer published tables(9) for the enthalpy departure terms as a function of T_r and P_r.

The above corresponding state correlation involving T_r, P_r, and ω as parameters, formed the basis of the Adler, Jacks, and Dluzniewski correlation(8). They were able to improve existing correlations to predict the needed input data for the Pitzer-Curl correlation(9), namely, molecular weight and critical properties. However, their work was proprietary. Their findings did demonstrate the importance of the three-parameter corresponding states correlation to give isothermal pressure corrections to enthalpy.

1974 - P.K. Huang and T.E. Daubert(10)

Physical Properties Required:

Depends on which correlations previously described are used to estimate ideal gas enthalpy

Region of Correlation's Applicability:

Depends on which correlations previously described are used to estimate ideal gas enthalpy

Huang and Daubert of the Pennsylvania State University have developed a method of predicting the enthalpies of unknown mixtures of hydrocarbons. It is called the pseudocompound method because it is based on the idea that if a petroleum fraction can be described by pure compounds(called pseudocompounds) which characterize each of the hydrocarbon types present in an undefined mixture, then prediction methods for the defined mixtures can be applied directly to petroleum fractions.

After performing an ASTM distillation, the petroleum fraction is analyzed for volume percentages of the four hydrocarbon types, (n-paraffins, n-alkylcyclopentanes, n-1-olefins, and n-alkyl-benzenes). The 50% boiling point(B.P. when 50% of the petroleum fraction has boiled away) from the ASTM distillation is taken as the characteristic boiling point. Two pseudocompounds are chosen to represent each hydrocarbon type present. These two pseudocompounds chosen have boiling points which bracket the 50% boiling point. The weight fractions of these two pseudocompounds are determined by defining a characteristic boiling point of this mixture equal to the 50% boiling point. It is assumed that weight percent and volume percent are equal.

The amount of each pseudocompound in the petroleum fraction is determined by multiplying the weight fractions of the two pseudocompounds by the corresponding hydrocarbon's compsition found above. From the API 44 tabulations of ideal gas enthalpies which have resulted from the previously described correlations, a linear relationship can be derived for each hydrocarbon type at a definite temperature if the boiling point range is not too large. This relationship is expressed below:

$$H^{o} = a*T_b + b \qquad (26)$$

where:

H^{o} = ideal gas enthalpy of a pure hydrocarbon (reference point: H^{o} equals 0 Btu/lb at $0^{o}R$)

T_b = boiling point of a pure hydrocarbon in ^{o}F

a,b = coefficients to be determined for each hydrocarbon type

$$H^{o}_{mix} = a\left(\sum_{i=1}^{n} T_{bi}x_{wi}\right) + b \qquad (27)$$

where:

$T_{bi}x_{wi}$ = weight average boiling point where x_{wi} is weight fraction of component i, n components

The Pitzer three-parameter correlation for corresponding states as outlined previously is used to correct for isothermal pressure changes. The critical properties required are defined by the pseudocritical properties of the pseudomixtures, as is the molecular weight of the mixture.

1975, 1976 - M.G. Kesler and B.I. Lee(11),(12)

Physical Properties Required:

Normal boiling point, K factor, specific gravity, critical temperature, critical pressure

Region of Correlations's Applicability:

Enthalpies presented by overall enthalpy charts(12)
Temperature: 0-1200°F
Specific gravity: 0-70°API
K factor: 10,11,11.8, 12.5
Isothermal enthalpy departure from ideal gas
Temperature: T_r between 0.3-4.
Pressure: P_r between 0-10

Kesler and Lee developed an analytical representation of the Pitzer three-parameter corresponding states correlation. Pitzer's original correlation was limited to reduced temperatures greater than 0.8. Lee and Kesler's correlation extended the range for reduced temperatures from 0.3-4, and reduced pressures from 0-10.

The enthalpy departure function was represented by:

$$\frac{(H - H^o)}{RT_c} = \left(\frac{(H - H^o)}{RT_c}\right)^0 + \frac{\omega}{\omega^r}\left(\frac{(H - H^o)^r}{RT_c} - \frac{(H - H^o)^0}{RT_c}\right) \quad (28)$$

where:

$\frac{(H - H^o)}{RT_c}$ = dimensionless isothermal enthalpy departure from ideal gas

$\frac{(H - H^o)^0}{RT_c}$ = dimensionless isothermal enthalpy departure from ideal gas for a simple fluid

ω = acentric factor

$\frac{(H - H^o)^r}{RT_c}$ = dimensionless isothermal enthalpy departure from ideal gas for the reference fluid

To calculate the $\frac{(H - H^o)}{RT_c}$, one can use the Benedict, Webb and Rubin equation of state to represent the compressibility factor, z, which is used in the following:

$$\frac{(H - H^o)}{RT_c} = -T_r^2 \int_0^{P_r} \frac{1}{P_r} * \left(\frac{\partial z}{\partial T_r}\right) dP_r \quad (29)$$

The constants used in the Benedict, Webb, and Rubin equation of state for the simple fluid and the reference fluid, n-octane are given in the original article.(12) n-octane was chosen as the heavy reference fluid because it is the heaviest hydrocarbon for which there are accurate P-V-T and enthalpy data over a wide range of conditions. The acentric factor for the reference fluid is taken to be 0.3978.

Briefly, the method entails using the simple fluid contants(12) to determine z^0 and the reference constants to determine z^r, giving ultimately the enthalpy departure for a simple fluid from ideal gas, and for the reference fluid. Kesler and Lee presented correlations to estimate T_r, P_r and ω analytically. By analytically representing the physical properties and enthalpy departure, one can implement this method for the computer, as outlined in the appendix.

In March, 1976, Kesler and Lee presented this correlation in graphical form, basing the liquid enthalpy on Watson and Nelson's(1) correlation and the pressure effect on enthalpies separately on the basis of the 1975 Lee-Kesler correlation.

PHYSICAL PROPERTIES OF PETROLEUM FRACTIONS

This section lists references which can be used to estimate the physical properties of petroleum fractions and pure hydrocarbons which are required in the enthalpy correlations described in the previous section. The physical properties section is divided into two parts: correlations by individuals, and the API's compilation which often includes many of these same correlations.

The individual correlations are grouped according to physical properties, with a chronological list of references. The API's correlations are grouped by pure substances and petroleum fractions.

K Factor

1. 1933 - Watson and Nelson(1)

K factor defined in terms of molal average boiling point where $MABP = \sum_{i=1}^{n} x_i T_{bi}$, T_{bi} = normal boiling point of component i

x_i = mole fraction of component i (30)

2. 1937 - Smith and Watson(13)

K factor defined in terms of cubic average boiling point where $CABP = (\sum_{i=1}^{n} x_{vi} T_{bi})^3$, x_{vi} = volume fraction of component i (31)

3. 1974 - Huang and Daubert(10)

K factor defined by mean average boiling point which is defined in terms of molal average boiling point and cubic average boiling point where $MeABP = \frac{MABP + CABP}{2}$ (32)

Note: Either $^{\circ}F$ or $^{\circ}R$ may be used for MABP. $^{\circ}R$ must be used for CABP. MABP and CABP must be in the same units to calculate MeABP. See API Data for characterizing boiling points for petroleum fractions(16).

Molecular Weight of Petroleum Fractions

1. 1933 - Watson and Nelson(1)

MW, molecular weight, correlated graphically as a function of K's (10.0-12.5) and molal average boiling point (100-650°F), and a graph for MW as a function of boiling point (100-700°F) and specific gravity (15-70°API)

2. 1957 - Winn(14)

   Nomogram using API gravity and mean average boiling point as correlative parameters

3. 1976 - Kesler and Lee(12)

   Equation involving specific gravity and boiling point as variables.

Acentric Factor

1. 1961 - Pitzer and Brewer(9)

   $$\omega = -\log(P_s/P_c) - 1.000 \text{ at } T_r = .700 \quad (33)$$

   Presented tables of ω as function of T_r and P_r

2. 1958 - Edmister(15)

   Approximate equation of ω

   $$\omega = 3/7 * (\log P_c/(T_c/T_b - 1)) - 1 \quad (34)$$

   P_c, T_c, T_b are variables where T_b is the normal boiling point, P_c is in atm

3. 1976 - Kesler and Lee(12)

   Analytical equation involving Riedel's vapor pressure equation

Critical properties

Critical Temperatures and Reduced Temperatures

Reduced Temperature, $T_r = T/T_c$

If the substance is pure, then T_c is the true critical temperature. If it is a mixture, then a pseudocritical temperature, defined by Kay, is needed for a corresponding states T_r.

For a defined mixture, the pseudocritical temperature, T_{pc} is:

$$T_{pc} = \sum_{i}^{n} x_i T_{ci}$$. A similar relation holds for P_{pc}.(35)

Therefore, if the correlations previously described are applied to a mixture and a critical property is required to compute a reduced property, the pseudocritical property is used.(13)

1. 1933 - Watson and Nelson(1)

   T_c chart presented as a function of molal average boiling point (100-700°F, 15-70°API)

2. 1937 - Smith and Watson(13)

   Graphs of critical temperature as functions of boiling point, specific gravity, (300-1000°F), (0-400°API)

3. 1976 - Kesler and Lee(12)

   Equation for T_c using specific gravity and boiling point as variables.

Critical Pressures and Reduced Pressures

1. 1933 - Watson and Nelson(1)

   Expresses critical pressure as a function of average boiling point, critical temperature and slope of the ASTM distillation curve

2. 1937 - Smith and Watson(13)

   Graph of pseudocritical pressure as a function of mean average boiling point (100-900°F) and API gravity (0-

90°API) and a graph as a function of molecular weight (10-100) and specific gravity (30-450°API)

3. 1957 - Winn(14)

Nomogram of pseudocritical pressure using API gravity and mean average boiling point to correlate

4. 1961 - Johnson and Grayson(7)

Pseudocritical pressures as correlated by K (10-13) and specific gravity (10-91°API)

5. 1976- Kesler and Lee(12)

Equation for P_c with specific gravity and boiling point as variables.

API Data - 1970(16)

This is a handy reference book which contains correlations for pure hydrocarbons and petroleum fractions and their physical properties, namely:

PURE:

1. Acentric factor
2. Watson Characterization Factor
3. Critical compressibility factor
4. Critical properties

PETROLEUM FRACTIONS

1. Characterizing boiling points
2. Molecular weight
3. Watson Characterization Factor
4. Acentric factor
5. True critical pressures and temperatures
6. Pseudocritical temperatures and pressures

COMPARISON OF THE PETROLEUM-FRACTION CORRELATIONS

In the appendix are included sample calculations for the enthalpy of the vapor for a California naphtha(17) with the given properties:

	ASTM distillation, D-86					Sp. Gr.	°API
Vol. %	10	30	50	70	90	60/60°F	
°F	174	184	196	210	231	0.7365	60.6

This petroleum fraction was selected because the molecular type analysis, in vol %, necessary for the pseudocompound method of Huang and Daubert was available.

Molecular Type Analysis, Vol%

Paraffin	Naphthene	Olefin	Aromatic	S Compound
36.2	58.2	0.0	5.6	0.0

The sample calculations performed for the enthalpy are suggested as examples of how to manipulate the data and carry out the calculations, rather than as a comparison of the correlations' accuracies. The correlations' accuracies are included in appendix B.

However, it is difficult on the basis of the results found in the literature for the different correlations to say any one correlation is best. This is due to the fact that not all of the enthalpy deviations calculated from the correlations from experimental data were based on the same data set or calculated at the same conditions. The correlations which employ the 3-parameter corresponding states enthalpy departure term also must incorporate the error in the ideal gas enthalpy. This error depends on which correlation is used to estimate ideal gas enthalpy.

Some general observations concerning a comparison of the correlations can be made:

1) All of the correlations have maximum deviation in the critical region.
2) The correlations which incorporate a K deviation term correlate best for a K of 11.8.
3) An isothermal pressure correction for a change from saturated conditions, liquid, to 0 psia can be neglected.

Some suggestions:

1) A comparison of all of the correlations needs to be carried out on the same data set; for example, the Lenoir data set used for comparison purposes in the Johnson-Grayson and Huang and Daubert correlations needs to be used in all correlations. The comparison should use the same number of points and at the same conditions.
2) The comparison should be divided into three areas:
    a) Comparison of specific heat capacities for vapor and liquid.
    b) Comparison of heats of vaporization

c) Comparison of the ideal gas enthalpy calculatted by the same thermodynamic path above some basic reference condition

3) After the above comparison is made, chose the correlations for specific heat capacity of vapor and liquid and heat of vaporization to calculate the ideal gas enthalpy, and then select the isothermal pressure correction to produce the least deviation from experimental data.

4) It must be remembered that the correlations used to estimate the physical properties of the petroleum fraction would affect the accuracy of any results.

The above suggestions were made to demonstrate the complexity of determining which correlation is the "best". The program outlined above would take a great deal of time, a factor which also must be taken into consideration. But it is reasonable to assume that the "best" correlation for petroleum fractions would also be the "best" for coal-derived liquids.

Based on the accuracies of the correlations given in the appendix, it would appear that a first approach to an overall enthalpy correlation would be one which employs the 3-parameter corresponding states isothermal pressure correction term for enthalpy and the specific heat capacity equations of Kesler and Lee. The computer program in appendix

E incorporates this approach to predict enthalpies.

APPLICATION TO COAL-DERIVED LIQUIDS

A comparison of the distillates of similar boiling ranges from three syncrudes on a weight-percent of distillate basis is included in the appendix D. The comparison shows that aromatics account for a considerable amount of the distillate(18). As noted by Bauer and Middleton, the existing correlations were empirically derived from paraffinic petroleum fractions, and are not as reliable for aromatics(6). This is evident from the Johnson-Grayson correlation deviation from experimental data presented in appendix B. This correlation especially had problems correlating liquid enthalpies for the aromatic naphtha, with a maximum error of 24 Btu/lb, with 19 of 54 points in excess of 10 Btu/lb.

Another point of interest is the amount of heteroatomics present in the distillates. These heteroatomics, containing sulfur, nitrogen and oxygen compounds, can increase the polarity of the syncrudes. The correlations were applicable to non-polar to slightly polar fractions as noted by McCracken and Smith(19). Therefore, applying existing correlations to syncrudes could be difficult.

The pseudocompound method of Huang and Daubert did give good results for the liquid and vapor enthalpies of an aromatic naphtha, but more comparisons are needed. This method has the advantage of taking the molecular type analysis of the petroleum fraction into account.

This is all speculation however as no enthalpy data for coal-derived liquids exists at this time. Therefore, it is best to reserve judgment on which of the existing correlations would best represent coal-derived liquids and vapors. A factor, similar to the K factor, might have to be developed to reflect aromaticity, and existing correlations might have to be modified to account for this or new correlations derived.

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SUGGESTIONS

1) After collecting reliable enthalpy data for coal-derived liquids, apply the Kesler-Lee equations outlined in appendix E to predict the enthalpies at experimental conditions.

2) If the error between calculated and experimental enthalpy values exceed 10 Btu/lb consistently, this suggests modifying the existing correlations.

3) Modifying existing correlations:

   a) As the specific heat capacity equations were empirically determined for paraffinic stocks, a characterization factor, similar to Watson's K factor, could be developed to reflect aromaticity and would modify existing specific heat capacity equations to fit enthalpy data for coal-derived liquids.

   b) Calculate the isothermal enthalpy departure from ideal gas by a 3-parameter corresponding states approach. The first two parameter, T_r and P_r, could be used in a generalized correlation. However, the deviations from experimental values observed by Curl and Pitzer(32) in using the acentric factor as the third parameter to estimate isothermal enthalpy departure for benzene at a

P_r of 2.0 and T_r between 0.8 and 1.3 suggests that a different third parameter might have to be developed for correlating aromatics such as coal-derived liquids.

APPENDIX A

Sample calculations are carried out on the California naphtha referred to in the section, "Comparison of the Petroleum-Fraction Correlations". The vapor enthalpy at 500°F and 300 psia, based on a reference state of 75°F saturated liquid, was experimentally determined as 332.8 Btu/lb.

Any values obtained from graphs are in doubt as the graphs in the literature were often too small to read accurately.

1933 - Nelson and Watson(1)

Estimation of molal average boiling point:

Take average of ASTM distillation data

$$\frac{174 + 184 + 196 + 210 + 231}{5} = 199^{\circ}F$$

Correction from this average for molal average boiling point:

Need to get slope of distillation curve in order to get correction term from Fig. 1

$$\frac{231-174}{80} = .7125$$

From fig. 1

$$199-3 = 196^{\circ}F$$

Calculate K:

$$K = \frac{T_b^{1/3}}{SG} = \frac{(196 + 460)^{1/3}}{.7365} = 11.8$$

Nelson and Watson calculated the enthalpy by:

$$H = \int_{T_{ref}}^{T_b} C^*_{pl}dT + \Delta H^*_{vap} + \int_{T_b}^{T} C^*_{pv}dT + \Delta\frac{HM}{T}$$

where $\Delta\frac{HM}{T}$ represents change of enthalpy from ideal gas state to system pressure (* representing 0 psia, approximately 1 atm)

Find mean specific heat of liquid

$$T = \frac{32 + 196}{2} = 144^{\circ}F$$

$$C^*_{pl} = (.6811 - .308(.7365) + 114(.00815 - .000306(.7365)) * (.055(11.8) + .35)$$

Enthalpy of liquid:

$$H_1^* = .5215(196 - 32) = 85.5 \text{ Btu/lb}$$

For vapor:

$$\frac{196 + 500}{2} = 348^{\circ}F$$

$$C_{pv}^* = (4 - .7365)/6450 * (348 + 670)(.12(11.8) - .41)$$

Enthalpy of vapor

$$.5181668(500 - 196) = 157.5 \text{ Btu/lb}$$

Latent heat of vaporization

$$\Delta H_{vap}^* = \frac{196 + 460}{95} * (7.58 + 4.571(\log(196+460)))$$

$$\Delta H_{vap}^* = 141.3 \text{ Btu/lb}$$

Estimate T_c

From fig. 4(1) for a molal average boiling point of 196°F and 60.6°API

$$T_c = 510^{\circ}F$$

Estimate P_c:

The slanting lines on the Cox chart, fig. 5(1), are the vapor pressure curves of the paraffin hydrocarbons having the number of carbon atoms indicated at the tops of the lines. Line FC is the critical temperature abscissa at 510°F. AB is the average boiling point line drawn through the atmospheric average boiling point A, at 196°F and the point of convergence of the pure hydrocarbon lines. Point D is located by measuring along line AB a distance equal to .2 times the distance of AC. Point E is the ASTM 10% point, 174°F. The critical temperature and pressure are represented by point F, corresponding to a p_c of 530 psia.

$$\frac{P}{P_c} = \frac{300}{530} = .5660377 = P_r$$

$$\Delta\frac{HM}{T} = \frac{-4.4P_r}{T_r}$$

$$\frac{T}{T_c} = \frac{500+460}{510+460} = .9896907$$

Calculate enthalpy departure:

$$\Delta\frac{HM}{T} = \frac{95\,\Delta H}{960} = \frac{-4.4(.5660377)}{(.9896907)^3}$$

$$\Delta H = -25.3 \quad \text{Btu/lb}$$

$$H = 85.5 + 157.5 + 141.3 - 25.3$$

$H = 359.0$ Btu/lb, referenced to liquid at 32°F

Referenced to 75°F

$$T = \frac{32+75}{2} = 53.5°F$$

$$C_{pl} = (.6811 - .308(.7365) + 53.35(.000815 - .000306 * (.7365))$$

enthalpy is 20.9 Btu/lb.

H is 359.0 - 20.9 = 338.1 Btu/lb.

1942 - Holcomb and Brown(2)

Only correlational plots for mixtures were presented, referenced to 32°F liquid.

Using the same mean average temperatures as before:

$C_{pl}{}^{*} = .525$ (fig. 1(2))

$\Delta H_{vap} = 141.3$ Btu/lb (Smith and Nelson)

$C_{pv}{}^{*} = .505$ (fig. 7(2))

Enthalpy of liquid

.525(196-32)

Enthalpy of vapor

.505(500-196)

Adding:

$H^{*} = 380.9$ Btu/lb.

Subtracting pressure correction term from figure 12(2):

$H = 380.9 - 16.2$

To correct for a new reference of 75°F:

$C_{pv} = .48$

$H = 380.9 - 16.2 - .48(75-32)$

$H = 344.1$ Btu/lb

1944 - Fallon and Watson(4)

Fallon suggested first vaporizing the liquid at the reference temperature, 0 psia, integrating the C_{pv}^* equation, and then adding pressure effects.

$$\lambda = \lambda_B \left(\frac{1-T_r}{1-T_{rb}}\right)^{.38}$$ (neglect change from vapor pressure to 1 atm.)

where:

λ, λ_B are the heats of vaporization at the reference temperature and the normal boiling point respectively

T_r, T_{rb} are the corresponding reduced temperatures

Using Nelson and Watson's critical properties and the heat of vaporization at one atm. from fig. 4(4), 145 Btu/lb:

$$\lambda = 145 * \left(\frac{1 - \frac{75 + 460}{510 + 460}}{1 - \frac{196 + 460}{510 + 460}}\right)^{.38}$$

$$\lambda = 164.1 \text{ Btu/lb.}$$

Calculate average temperature for C_{pv}^* equation:

$$\frac{500 + 75}{2} = 288^{\circ}F$$

$$C_{pv}^* = (.0450(11.8) - .233) + (.44 + .0177(11.8)) * (10)^{-3}(288) - .153(10^{-6})(288)^2$$

Enthalpy of vapor:

$$H^* = 164.1 + .4721813(500-75)$$

$$H^* = 364.8 \text{ Btu/lb}$$

Using correction of Nelson and Watson's for pressure effects:

$$H = 339.5 \text{ Btu/lb.}$$

If the approach used by Smith and Nelson is employed, a different enthalpy results(the approach referred to is first calculating the enthalpy of the liquid to the boiling point, then adding the heat of vaporization, and finally adding the vapor enthalpy and pressure effects):

$$C^*_{pl} = ((.355 + .128*10^{-2}\,°API) + (.503*.117*10^{-2}\,°API)10^{-3}t) *(.05K + .41)$$

$t_{av} = 114$

$H^*_l = 71.6$ Btu/lb

$H_{vap} = 145$ Btu/lb

$$C_{pv}^* = (.045(11.8) - .233) + (.44 + .0177(11.8))(10^{-3})(348) -.153(10^{-6})(348)^2$$

where 348 is t_{av} °F

$H^*_v = (.5052744)(500-196) = 153.6$ Btu/lb

Adding(using smith and Nelson's pressure correction enthalpy term):

$H_{32} = 145. + 153.6 + 71.6 - 25.3 = 344.9$

Subtracting to account for change of reference:

$344.9 - 18.7 = 326.2$ Btu/lb

1947 - Hougen and Watson(5)

Since the correlation presented was only for an isothermal pressure correction to enthalpy, this correction will be applied to Fallon's result:

Using Watson and Nelson's reduced properties:

From fig. 106(5), enthalpy departure is

$2 \frac{\text{g-cal}}{\text{gmole-K}}$

$H = 364.8 - 20.2$

$H = 344.6$ Btu/lb

Applied to Fallon's second result:

$H = 331.3$ Btu/lb

1953 - Bauer and Middleton(6)

From Nelson and Watson, ideal liquid enthalpy	85.5
Heat of vaporization, fig. 1(6)	145.
From Fallon, and Watson	153.6
From fig. 3(6), pressure correction	-30.
	354.1 Btu/lh
Change of reference from 32°F to 75°F	-20.9
	333.2 Btu/lb.

1961 - Johnson and Grayson(7)

Estimate critical properties:

From fig. 6(7) -

T_c 970°R

P_c 470 psia

Calculate reduced properties:

T_r .9896907

P_r .6382979

From fig. 3(6):

Estimate ideal enthalpy of vapor (reference at -200°F, liquid)	475.
Change of reference to 75°F	-125.
Pressure correction	-20.
	330. Btu/lb.

1974 - Pitzer(9)

From the Pitzer tables, estimate $\left(\frac{H^o - H}{RT_c}\right)^o$ and $\left(\frac{H^o - H}{RT_c}\right)^1$:

by double interpolation for T_r and P_r

$$\left(\frac{H^o - H}{RT_c}\right)^o = .92$$

$$\left(\frac{H^o - H}{RT_c}\right)^1 = 1.38$$

Estimate an acentric factor:

Use Edmister's approximation(15):

$$3/7 * \left(\frac{\log(470/14.7)}{\frac{970}{196\quad 460} - 1}\right) - 1. = .3473$$

$$\left(\frac{H^o - H}{RT_c}\right) = \left(\frac{H^o - H}{RT_c}\right)^o + \omega\left(\frac{H^o - H}{RT_c}\right)^1 = 1.4$$

$$H^o - H = \frac{1.4}{96}(1.986)(970) = 28.1 \text{ Btu/lb.}$$

Apply this correction to previous correlations

1974 - Huang and Daubert(17)

Molecular Type Analysis, Vol. %

Paraffin	Napthene	Olefin	Aromatic
36.2	58.2	0.0	5.6

50% BP is 196°F

Select the pseudocompounds:

	BP	MW	Sp.Gr.	T_c	P_c	acentric factor
PARAFFIN						
n-hexane	155.7	86.2	.6640	453.7	436.9	0.3498
n-heptane	209.2	100.2	.6882	512.8	396.8	0.2306
NAPHTHENE						
methylcyclo-pentane	161.3	84.2	.7536	299.4	548.9	0.2709
ethylcyclo-pentane	218.2	98.2	.7710	565.5	492.8	0.2125
AROMATIC						
benzene	176.2	78.1	.8844	552.2	710.4	0.2596
methylbenzene	231.1	92.1	.8718	605.5	595.9	0.2836

The weight fractions of n-pentane and n-heptane in the paraffin are obtained by solving

$$155.7X + 209.2Y = 196$$

$$X + Y = 1$$

Thus, $X = 0.247$, $Y = 0.753$. These are also considered to be equal to the volume fractions. Then the volume fractions of n-hexane and n-heptane in the whole system will be

$$X_{v1} = (0.362)(0.247) = 0.0892$$

$$X_{v2} = (0.362)(0.753) = 0.2728$$

Assuming the volume fractions equal the weight fractions:

compute the pseudomixture's properties by additive mixture rules

MW	T_{pc}	P_{pc}	ω_p
93.6	526.4	484.2	0.2836

The ideal gas enthalpy for each pseudocompound at 500°F can be obtained from API 44 tables or calculated from polynomials. Then the ideal gas enthalpy for this mixture will be:

$$H^o_{mix} = \sum_i X_{vi} H^o_i = 310.1 \text{ Btu/lb at } 500^oF$$

Since $T_r = \dfrac{500 + 459.6}{526.4 + 459.6} = .97$, $P_r = \dfrac{300}{484.2} = .62$

From the Pitzer table,

$$\left(\frac{H^o - H}{RT_c}\right)^o = 0.85 \qquad \left(\frac{H^o - H}{RT_c}\right)^1 = 0.97$$

Therefore, calculate the overall enthalpy departure:

$$\left(\frac{H^o - H}{RT_c}\right) = 0.85 + (0.2836)(0.97) = 1.13$$

$$H^o - H = \left(\frac{H^o - H}{RT_c}\right) \frac{RT_c}{M} = 1.13(1.987)\frac{(526.4 + 459.6)}{93.60}$$

$$H^o - H = 23.7 \text{ Btu/lb}$$

The enthalpy at 500°F and 300 psia is 310.1 - 23.7 = 286.4 Btu/lb, which is based on 0°R and 0 psia. The enthalpy at 75°F saturated liquid having the same basis is -45.3 Btu/lb. Therefore, the enthalpy at 500°F and 300°F based on 75°F saturated liquid will be

$$286.4 - (-45.3) = 331.7 \text{ Btu/lb}$$

The experimental value is 332.8 Btu/lb.

1975 - Kesler and Lee(11),(12)

In appendix E, sample clculations for this method are performed by means of a computer program.

The value computed by the program was 339.3 Btu/lb.

APPENDIX B

Deviations of the correlations' calculated enthalpy values from experimental values are presented.

Comparison of Correlations for Smith and Watson, Holcomb and Brown, and Hougen and Watson

1) In the original 1933 article, the only example given was a naphtha (K 11.9) at 800°F and 1014.7 psia which agreed within 5 Btu/lb of the experimental value.
2) Nothing was given in terms of reliability in the original 1942 article of Holcomb and Brown or the corrected 1944 article.
3) No reliability was presented for the enthalpy departure correction term of Hougen and Watson.

Fallon and Watson Correlation Compared to Experimental Enthalpy

1) Comparison of Calculated and Observed Specific Heats and

Enthalpies in the Liquid State, Btu/lb (4)

SUBSTANCE	^{o}API	K	t, ^{o}F	enthalpy Exp.	Calculated
Gas Oil	34.8	11.86	766	457	454
			859	537	532
Vapor-phase furnace charge	25.3	11.0	751	406	411
			853	496	491
Refractory gas oil	18.4	10.4?	825	446	445
Cross furnace charge	28.1	11.24	748	420	418
			827	483	478
				specific heat	
n-octane	68.6	12.65	77	.505	.508
Benzene	29	9.7	50	.394	.375
			140	.444	.418
Tridecane	54.5	12.75	77	.500	.491

2) Comparison of Calculated and Observed

Enthalpies in the Vapor State, Btu/lb. (4)

SUBSTANCE	^{o}API	K	av. BP, ^{o}F	t, ^{o}F	Exp.	Calculated
Naphtha	58	11.9	250	438	344	340
				949	705	685
Cross furnace charge	28.1	11.24	530	746	516	502
				863	596	584

SUBSTANCE	°API	K	av. BP, °F	t, °F	Exp.	Calculated
Refractory gas oil	18.4	10.4	490	826	550	534
	15.3	10.3	505	738	471	474
				1003	607	615
Vapor-phase furnace charge	25.3	11.0	510	750	506	503
				951	661	641
Gas oil	34.8	11.86	570	749	522	516
				958	671	674

Comparison of ideal gas state heat capacities(12)

SUBSTANCE	# of pts	Temp., °F	% Deviations Avg.	% Deviations Max.
n-Hexane	7	0-1200	2.5	5.0
n-Decane	7	0-1200	2.7	2.5
n-Hexadecane	7	0-1200	4.5	8.1
n-Eicosane	7	0-1200	6.3	9.8
I-Decene	7	0-1200	4.5	8.5
I-Eicocene	7	0-1200	7.3	11.3
Benzene	7	0-1200	8.7	16.1
Ethylbenzene	7	0-1200	6.5	12.1
m-Xylene	7	0-1200	8.0	13.7
n-Heptylbenzene	7	0-1200	5.6	10.9
Cyclohexane	7	0-1200	5.5	7.2
Ethylcyclohexane	7	0-1200	5.2	6.5
n-Decylcyclohexane	7	0-1200	1.3	3.7
Cyclohexane	18	320-660	6.9	8.6

SUBSTANCE	# of pts	Temp., °F	% Deviations Avg.	Max.
n-Octane	10	400-580	0.5	1.5
n-Hexadecane	12	420-640	5.0	5.8
trans-Decalin	7	480-600	2.4	6.3
Calif. naphtha	14	320-580	2.9	6.7
Alaska naphtha	9	440-600	2.7	5.8
Jet naphtha	9	420-580	5.2	7.5
Aromatic naphtha	5	420-500	2.2	2.8
Low-boiling naphtha	8	480-620	1.7	4.1
High-boiling "	4	500-560	3.5	6.7
Kerosine	5	500-580	4.9	6.3
Naphtha C	13	413-893	1.3	3.3
Refined oil	19	560-920	1.0	2.8
Gas Oil	8	675-815	3.3	5.6
Ref. gas oil	12	758-978	11.9	18.1

Reliability of Bauer and Middleton(6)

LIQUIDS

Liquid enthalpies read from figure 3(6) reproduce the experimental data corrected to the same datum with an average deviation of about 3%, except within 50°F of the pseudocritical temperature. Lines of constant API gravity are terminated at the corresponding pseudo-critical temperature for fractions with ASTM distillation slopes of 1.5 and K of 11.8. Deviations for these fractions may exceed 10% within 50°F of T_c. As the K varies from 11.8 and the distillation slope increases above 2.0, the liquid enthalpies read from the curves decreases greatly in the critical region.

VAPOR ENTHALPIES AT 1 ATM.

When corrected to the same datum, the average deviation is ±10 Btu/lb. for petroleum fractions. For ten normal hydrocarbons, the average deviation is ± 5 Btu/lb. Figure 3(6) does not give reliable values for isomers of normal paraffins lighter than octane. Better values for these isomers result if the API gravity of the corresponding normal paraffin is used instead of that of the isomer because the vapor specific heats of normal and isomeric paraffins are nearly the same for the same molecular weights, while their densities differ. Since data obtained from straight-run Mid-Continent type fractions predominate among the data available for developing figure 3(6), the correlation gives the most reliable results for that type of hydrocarbon mixture and the greatest deviation for highly aromatic fractions.

The correlation for vapor enthalpy at 1 atm applies within the deviations above for the following ranges of °API gravity:

K	°API
10	10-40
11	15-60
11.8	25-80
12.5	50-88
13	82-95

Average deviation between experimental and calculated enthalpy for Johnson-Grayson correlation (see Pitzer comparison for fractions' properties)(8)

PETROLEUM FRACTION	# of pts.	Phase	Average deviation, Btu/lb. H(calc)-H(exptl)
Alaskan naphtha	54	Liquid	2.3
	60	Vapor	4.9
	22	Critical	7.5
Aromatic naphtha	50	Liquid	6.0
	41	Vapor	6.8
	10	Critical	3.7
Jet naphtha	70	Liquid	6.1
	60	Vapor	5.8
	0	Critical	-
Low-boiling naphtha	50	Liquid	10.0
	64	Vapor	5.2
	70	Critical	14.5
High-boiling naphtha	65	Liquid	7.2
	47	Vapor	6.1
	2	Critical	16.8
California kerosine	48	Liquid	2.7
	35	Vapor	4.7
	0	Critical	-
Fuel oil	39	Liquid	2.8
	0	Vapor	-

PETROLEUM FRACTION	# of pts.	Phase	Average deviation, Btu/lb. H(calc)-H(exptl)
Fuel Oil	0	Critical	-
Gas oil	72	Liquid	1.9
	0	Vapor	-
	0	Critical	-
Averages	448	Liquid	4.9
	307	Vapor	5.6
	104	Critical	12.1

Results of the Johnson-Grayson Correlation for Liquid Enthalpy(17)

PETROLEUM FRACTIONS	# of pts.	Max.	Avg.	Bias	RMS	>10 Btu/lb.
1. California naphtha	99	21.2	9.1	9.1	10.3	39
2. Alaska naphtha	29	11.7	6.0	6.0	6.4	1
3. Aromatic naphtha	54	24.6	9.1	9.1	10.8	19
4. Jet naphtha	39	14.7	6.4	6.4	7.4	8
5. Low-boiling naphtha	30	20.4	9.4	9.4	10.2	11
6. High-boiling naphtha	58	19.6	10.6	10.6	11.3	28
7. Kerosene	90	7.3	3.4	3.4	3.5	0
8. Fuel oil	79	-18.0	2.2	1.6	3.2	1
9. Gas oil	73	4.4	1.2	0.4	1.6	0
Totals	551	24.6	6.0	5.8	7.7	107

Errors in Btu/lb.

Results of the Johnson-Grayson Correlation for Vapor Enthalpy(17)

PETROLEUM FRACTION	# of pts.	Errors in Btu/lb. Max.	Avg.	Bias	RMS	> 10 Btu/lb.
1. California naphtha	138	25.8	11.5	11.4	13.1	60
2. Alaska naphtha	21	11.8	6.3	6.0	6.6	1
3. Aromatic naphtha	6	7.0	5.5	5.5	5.6	0
4. Jet naphtha	28	11.7	8.5	8.5	8.8	7
5. Low-boiling naphtha	89	33.2	10.5	10.5	14.4	30
6. High-boiling naphtha	31	11.8	5.5	5.5	6.0	1
7. Kerosene	19	9.5	5.6	5.6	5.9	0
Totals	332	33.2	9.6	9.6	11.9	99

Comparison of Pitzer 3-Parameter Corresponding States Correlation Using Fallon and Watson Ideal Gas Enthalpy(8)

Properties of hydrocarbon fractions

Property	Alaskan naphtha	Jet "	Aromatic "	Low-BP "	High-BP "	Cal. Kerosine	Fuel oil	Gas oil
API grav.	50.5	44.4	34.5	59.9	54.2	43.5	33.0	35.3
VABP, ^{o}F	283.0	321.6	254.8	266.6	317.6	407.2	547.2	538.8
ASTM D-86 10-90 slope	0.29	0.46	1.31	2.40	0.99	1.49	1.43	1.03
K	11.63	11.48	10.5	12.1	12.1	11.8	11.68	11.8

PETROLEUM FRACTION	# of pts.	Phase	Average deviation, Btu/lb. H(calc)-H(exptl)
Alaskan naphtha	54	Liquid	3.7
	60	Vapor	5.3
	22	Critical	11.8
Aromatic naphtha	50	Liquid	4.5
	41	Vapor	6.2
	10	Critical	7.7
Jet naphtha	70	Liquid	2.0
	60	Vapor	4.8
	0	Critical	-
Low-boiling naphtha	50	Liquid	2.3
	64	Vapor	2.0
	70	Critical	11.7
High-boiling naphtha	65	Liquid	3.9

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PETROLEUM FRACTION	# of pts.	Phase	Average deviation, Btu/lb. H(calc)-H(exptl)
High-boiling naphtha	47	Vapor	3.6
	2	Critical	3.0
California kerosine	48	Liquid	1.7
	35	Vapor	3.1
	0	Critical	-
Fuel oil	39	Liquid	3.2
	0	Vapor	-
	0	Critical	-
Gas oil	72	Liquid	2.6
	0	Vapor	-
	0	Critical	-
Averages	448	Liquid	3.1
	307	Vapor	4.1
	104	Critical	11.2

Results of the Pseudocompound Correlation for Liquid Enthalpy Using Simple Composition - Huang and Daubert(17)

		Errors in Btu/lb.				
PETROLEUM FRACTION	# of pts.	Max.	Avg.	Bias	RMS	> 10 Btu/lb.
1. California naphtha	127	10.1	3.3	-1.1	3.7	1
2. Alaska naphtha	77	11.1	4.0	-2.7	4.4	3
3. Aromatic naphtha	89	4.4	2.1	-1.9	2.3	0
4. Jet naphtha	40	-4.5	1.8	-1.7	2.2	0
5. Low-boiling naphtha	73	-23.7	3.1	-1.5	4.3	1
6. High-boiling naphtha	53	-6.0	2.6	-2.6	2.9	0
7. Kerosene	85	-4.5	1.8	-1.7	2.1	0
8. Fuel oil	64	5.1	2.1	1.9	2.5	0
9. Gas oil	25	3.2	0.7	0.7	0.9	0
Totals	633	-23.7	2.6	-1.3	3.2	5

Error = Calculated enthalpy - actual enthalpy, Btu/lb

Avg. $= \Sigma|\text{Error}|/N$

Bias $= \Sigma\,\text{Error}/N$

RMS $= (\Sigma(\text{Error})^2/N)^{\frac{1}{2}}$

N = # of points

Results of the Pseudocompound Correlation for Vapor Enthalpy Using Simple Composition - Huang and Daubert(17)

PETROLEUM FRACTION	# of pts	Max. (Errors in Btu/lb.)	Avg. (Errors in Btu/lb.)	Bias (Errors in Btu/lb.)	RMS (Errors in Btu/lb.)	Pts. > 10 Btu/lb.
1. California naphtha	137	-12.6	3.1	-0.3	4.0	4
2. Alaska naphtha	21	-12.2	1.6	-0.7	3.0	1
3. Aromatic naphtha	6	-2.0	1.1	-0.9	1.2	0
4. Jet naphtha	28	4.2	2.0	1.4	2.3	0
5. Low-boiling naphtha	89	-12.1	2.7	-1.7	3.7	3
6. High-boiling naphtha	31	5.7	1.9	1.4	2.3	0
7. Kerosene	19	9.0	5.6	5.6	5.9	0
Totals	331	-12.6	2.8	-0.1	3.7	8

Deviation of Kesler and Lee Correlation for Ideal Gas State Heat Capacities (12)

1) Using equation(43) in appendix E

SUBSTANCE	# of pts.	Temp., ^{o}F	% deviations Avg.	Max.
n-Hexane	7	0-1200	1.3	2.7
n-Decane	7	0-1200	1.5	3.2
n-Hexadecane	7	0-1200	3.5	5.8
n-Eicosane	7	0-1200	5.1	7.4
I-Decene	7	0-1200	3.6	6.3
I-Eicocene	7	0-1200	6.2	8.9
Benzene	7	0-1200	1.8	3.2
Ethylbenzene	7	0-1200	2.0	3.5
m-Xylene	7	0-1200	3.9	5.2
n-Heptylbenzene	7	0-1200	4.6	6.6
Cyclohexane	7	0-1200	6.5	10.6
Ethylcyclohexane	7	0-1200	4.2	7.4
n-Decyclcylohexane	7	0-1200	1.0	2.4
Cyclohexane	18	320-660	5.1	7.8
n-Octane	10	400-580	0.5	0.8
n-Hexadecane	12	420-640	3.9	4.5
trans-Decalin	7	480-600	2.2	4.5
Calif. naphtha	14	320-580	1.1	4.0
Alaska naphtha	9	440-600	1.9	2.7
Jet naphtha	9	420-580	3.8	5.7

SUBSTANCE	# of pts.	Temp., °F	% deviations Avg.	Max.
Aromatic naphtha	5	420-500	0.7	1.0
Low-boiling naphtha	8	480-620	1.2	3.4
High-boiling naphtha	4	500-560	3.6	5.8
Kerosine	5	500-580	3.7	5.0
Naphtha C	13	413-893	2.0	3.3
Refined oil	19	560-920	1.4	3.6
Gas oil	8	675-815	2.9	5.0
Ref. gas oil	12	758-978	7.2	10.1

2) Using equation(42) in appendix E

Note: over a temperature range from 0-1200°F with 200°F interval

SUBSTANCE	% deviations Avg.	Max.
n-Hexane	1.3	2.0
n-Octane	1.8	2.1
n-Decane	1.4	1.7
n-Tridecane	0.2	0.5
n-Hexadecane	1.1	1.5
n-Eicosane	2.7	3.4
1-Hexene	3.1	4.2
1-Octene	1.2	1.9
1-Decene	0.7	1.3
1-Tridecene	1.3	2.0
1-Hexadecene	2.4	3.0
1-Eicosene	3.8	4.1
Benzene	1.1	1.9

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SUBSTANCE	% deviations Avg.	Max.
Toluene	1.1	1.6
Ethylbenzene	0.8	2.0
M-Xylene	1.9	2.7
n-Heptylbenzene	0.8	2.2
n-Tetradecylbenzene	3.6	5.3
Cyclohexane	0.7	2.1
Methylcyclohexane	0.7	1.5
Ethylcyclohexane	2.4	3.3
1,1-Dimethylcyclohexane	1.4	2.0
n-Decylcyclohexane	2.8	4.0
n-Hexadecylcyclohexane	1.6	5.6

Deviations of calculated enthalpies from literature data for Kesler-Lee

PETROLEUM FRACTION	# of pts	t, °F	p, psia	Deviations, Btu/lb. Avg.	Max.
Calif. naphtha	64	300-600	0-500	3.7	5.9
Alaska "	56	420-620	0-400	1.4	8.3
Jet "	44	389-600	0-200	2.4	5.2
Aromatic "	37	324-600	0-300	2.7	3.8
Low-boiling "	47	368-640	0-400	0.9	1.9
High-boiling "	25	390-600	0-200	2.1	4.9
Kerosine "	22	480-600	0-50	4.2	6.4
VAPOR TOTAL	295			2.4	8.3
Liquid					
Calif. naphtha	36	120-600	100-1400	3.4	7.0
Alaska "	54	75-626	30-1400	2.4	10.2
Jet "	32	75-600	30-1400	0.7	2.3
Aromatic "	45	75-600	20-1400	1.3	2.9
Low-boiling "	33	75-600	30-1000	3.1	4.8
High-boiling "	33	75-600	30-1400	3.2	5.7
Kerosine	24	75-600	20-1400	0.9	2.7
Fuel oil	24	75-600	20-1400	0.7	1.5
Gas oil	39	75-600	40-1400	0.8	2.0
LIQUID TOTAL	320			1.91	10.2

APPENDIX C

The Lenoir Data Set used for the comparison for deviation of the calculated enthalpy from experimental enthalpy is presented. This Data Set was used for the pseudocompound and Johnson-Grayson correlations' deviations.(17)

The Lenoir Data Set for Enthalpies of Petroleum Fractions Used for Pseudocompound and Johnson-Grayson Correlations

PETROLEUM FRACTIONS	Range of Conditions T, °F	P, (psia)	# of pts.
1. California naphtha	120-600	25-1400	128(L), 138(V), 70(T)
2. Alaska naphtha	275-625	30-1400	85(L), 21(V), 43(T)
3. Aromatic naphtha	160-600	30-1400	89(L), 6(V), 24(T)
4. Jet naphtha	155-600	20-1400	46(L), 28(V), 32(T)
5. Low-boiling naphtha	270-645	30-1400	77(L),89(V), 57(T)
6. High-boiling naphtha	220-645	30-1400	62(L), 31(V), 39(T)
7. Kerosene	300-605	30-1400	90(L), 19(V), 8(T)
8. Fuel oil	300-600	20-1400	79(L), 4(T)
9. Gas oil	75-600	40-1400	73(L)

L = Liquid

V = Vapor

T = Two-phase region

The Lenoir Data Set for Enthalpies of Petroleum Fractions Used for Pseudocompound and Johnson-Grayson Correlations

PETROLEUM FRACTIONS	ASTM Distillation, D-86, °F 10%	30%	50%	70%	90%	Sp. gr. 60/60	°API
1. California naphtha	174	184	196	210	231	0.7365	60.6
2. Alaska naphtha	272	278	282	288	295	0.7774	50.5
3. Aromatic naphtha	206	230	252	275	311	0.8520	34.5
4. Jet naphtha	304	313	321	329	341	0.8046	44.4
5. Low-boiling naphtha	172	226	260	311	364	0.7395	59.8
6. High-boiling naphtha	271	310	322	335	350	0.7624	54.2
7. Kerosene	350	380	404	433	469	0.8083	43.5
8. Fuel oil	490	526	547	569	604	0.8616	33.0
9. Gas oil	503	518	535	553	585	0.8475	35.3

The Lenoir Data Set, contd.

	K	M.W.	T_c, °F	P_c, psia	Molecular Type Analysis, vol % Paraffin	Naphthene	Olefin	Aromatic	S Compound
1.	11.94	102.4	536.7	532	36.2	58.2	0.0	5.6	0.0
2.	11.63	131	526.5	414.7	39.7	39.6	0.0	20.5	0.0
3.	10.5	126	626	709	0.0	0.0	16.9	83.1	0.0
4.	11.48	144	665	440	18.6	69.8	0.0	10.6	1.0
5.	12.1	120	605	463	61.9	30.6	0.0	7.6	0.0
6.	12.1	142.4	646	371	59.3	30.8	0.0	9.9	0.0
7.	11.8	162.3	739	361	30.9	64.3	0.0	4.8	0.0
8.	11.68	227.5	879	290	29.8	45.6	0.0	22.4	1.3
9.	11.8	214	868	280	38.8	41.5	0.0	17.2	2.4

APPENDIX D

This appendix contains results from an analysis of a synthoil from West Virginia coal from an ERDA installation in Bartlesville Energy Research Center.(18)

Comparison of distillates of similar boiling ranges from three syncrudes on a weight-percent of distillate basis

	W.Va. 207°-363°	W.Ky. 205°-380°	Utah 204°-381°	W.Va. 363°-531°	W.Ky. 380°	Utah 381°
Saturates	16.0	25.0	27.8	9.7	23.8	25.8
Monoaromatics	27.8	42.0	25.1	4.7	25.1	14.4
Diaromatics	21.6	13.0	17.5	22.6	24.3	18.4
Polyaromatics	7.9	5.4	7.1	41.1	20.0	25.1
Heteroaromatics	22.2	4.4	15.2	15.6	4.5	7.4
Distillate weight-% of syncrude	42.6	54.2	45.4	27.3	24.2	40.3

Note: Temperature in degrees centigrade.

APPENDIX E

The program based on Kesler and Lee's correlation(11), (12) is presented. A sample calculation is performed on the California naphtha correlated in appendix A.

Equations Used by Kesler and Lee:(11),(12)

Physical properties:

$$T_c = 341.7 + 811*SG + (0.4244 + 0.1174*SG)T_b + (0.4669 - 3.2623*SG) *10^5/T_b \quad (36)$$

$$\ln P_c = 8.3634 - 0.0566/SG - (0.24244 + 2.2898/SG + 0.11857/SG^2) 10^{-3}*T_b + (1.4685 + 3.648/SG + 0.47227/SG^2)10^{-7}T_b^2 - (0.42019 + 1.6977/SG^2)\ 10^{-10}T_b{}^3 \quad (37)$$

$$MW = -12272.6 + 9486.4*SG + (4.6523 - 3.3287*SG)T_b + (1 - 0.77084*SG - 0.02058*SG^2)*(1.3437 - 720.79/T_b)\ 10^7/T_b + (1 - 0.80882*SG + 0.02226*SG^2)*(1.8828 - 181.98/T_b)\ 10^{12}/T_b{}^3 \quad (38)$$

$$\omega = -7.904 + 0.1352*K - 0.007465*K^2 + 8.359*T_{br} + (1.408 - 0.01063*K)/T_{br} \quad (\text{for } T_{br} > 0.8) \quad (39)$$

T_{br} = reduced n.b.p.

otherwise,

$$\omega = \frac{\ln P_{cr} - 5.92714 + 6.09648/T_{br} + 1.28862*\ln T_{br} - 0.169347*T^6{}_{br}}{15.2518 - 15.6875/T_{br} - 13.4721*\ln T_{br} + 0.43577*T^6{}_{br}} \quad (40)$$

If this acentric factor is used:

the specific heat capacity of ideal gas is

$$C_{pv}{}^* = -0.33886 + 0.02827*K - (0.9291 - 1.1543*K + 0.0368*K^2)10^{-4}T - 1.6658*10^{-7}T^2 - CF(0.26105 - 0.59332\omega - (4.56 - 9.48\omega) *10^{-4}T - (0.536 - 0.6828\omega)10^{-7}T^2) \quad (41)$$

where CF is $((12.8 - K)(10 - K)/(10\omega))^2$ (42)

If $T_{br} > 0.8$:

$$C_{pv}{}^* = -0.32646 + 0.02648*K - (1.3892 - 1.2122*K + 0.03803*K^2) 10^{-4}T - 1.5393*10^{-7}T^2 - CF(0.084773 - 0.080809*SG - (2.1773 - 2.0826*SG)10^{-4}T + (0.78649 - 0.70423*SG)10^{-7}T^2) \quad (43)$$

H-H° / H = Sepdo

where CF is $(12.8/K-1)(10/K-1)*100)^2$ (44)

$C_{pl}^{*} = (0.35 + 0.055*K)(0.6811 - 0.308*SG + (.000815 + .000306*SG)t)$ (45)

where:

the enthalpy departure is calculated by:

$$Z = \frac{P_r V_r}{T_r} = 1 + \frac{B}{V_r} + \frac{C}{V_r^2} + \frac{D}{V_r^5} + \frac{c_4}{T_r^3 V_r^2}\left(\frac{\gamma}{V_r^2} + \beta\right)\exp\left(-\frac{\gamma}{V_r^2}\right) \quad (46)$$

where $B = b_1 - b_2/T_r - b_3/T_r^2 - b_4/T_r^3$ (47)

$C = c_1 - c_2/T_r + c_3/T_r^3$ (48)

$D = d_1 + d_2/T_r$ (49)

Enthalpy departure:

$$\frac{H - H^o}{RT_c} = T_r\left(Z - 1 - \frac{b_2 + 2b_3/T_r + 3b_4/T_r^2}{T_r V_r} - \frac{c_2 - 3c_3/T_r^2}{2T_r V_r^2} + \frac{d_2}{5T_r V_r^5} + 3E\right) \quad (50)$$

where $E = \frac{c_4}{2T_r^3 \gamma}\left(\beta + 1 - \left(\beta + 1 + \frac{\gamma}{V_r^2}\right)\exp\left(-\frac{\gamma}{V_r^2}\right)\right)$ (51)

$$\frac{H - H^o}{RT_c} = ((H - H^o)/RT_c)^0 + \frac{\omega}{\omega^r}\left(((H - H^o)/RT_c)^r - ((H - H^o)/RT_c)^0\right) \quad (52)$$

r represents reference fluid

0 represents simple fluid

Steps in program:

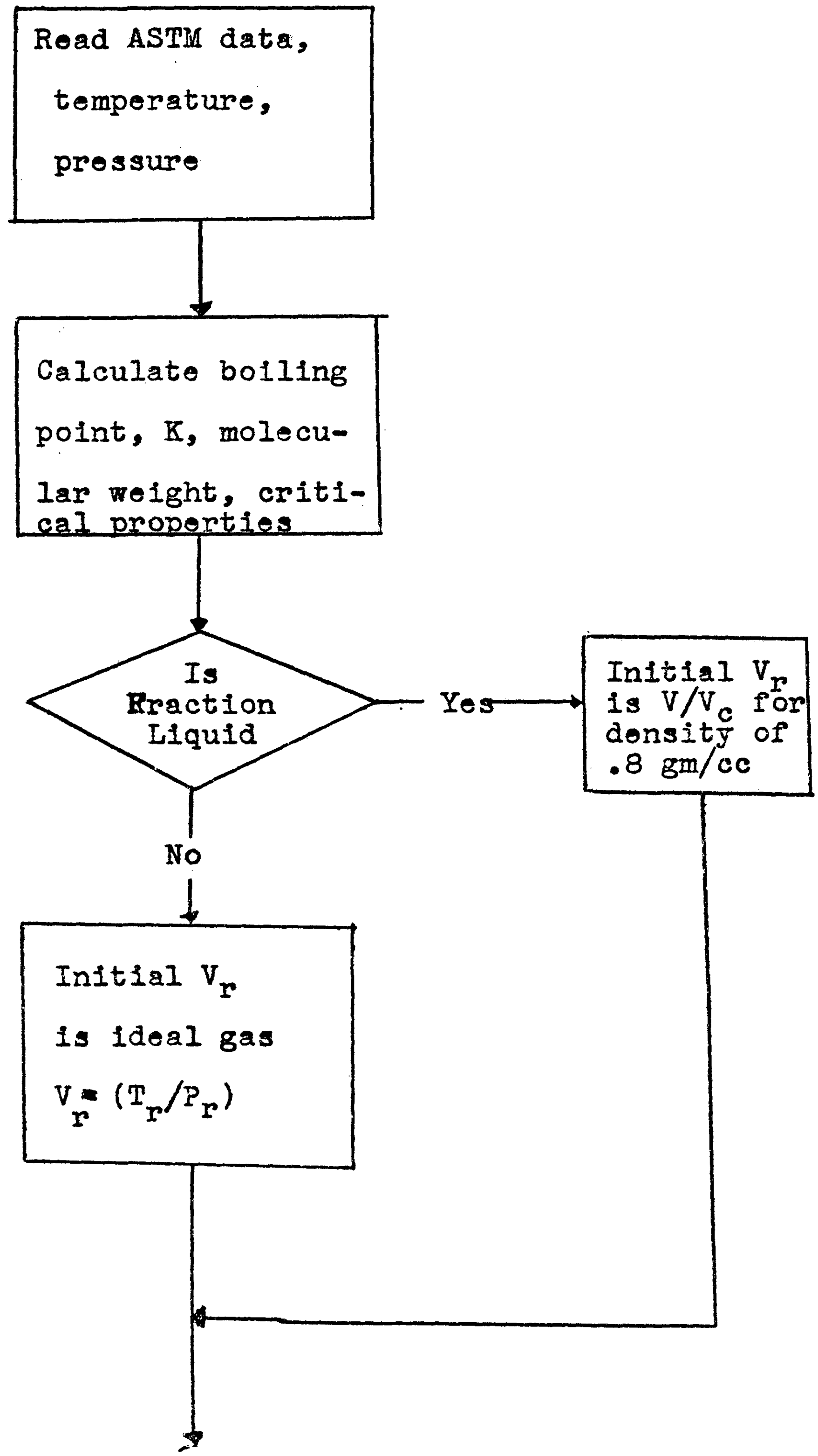
1) Determine V_r and Z^0 for the simple fluid at the T_r and P_r. Calculate $\frac{(H - H^o)}{RT_c}$ for the simple fluid.
2) Repeat the previous step, except for the reference fluid.
3) Determine the overall enthalpy departure term for

isothermal pressure effects.

4) Calculate ideal gas enthalpy.

5) Add isothermal pressure enthalpy departure term to find enthalpy.

See the flow diagram on the next page.


Read ASTM data, temperature, pressure
Calculate boiling point, K, molecular weight, critical properties
Is Fraction Liquid
Yes
Initial V_r is V/V_c for density of .8 gm/cc
No
Initial V_r is ideal gas $V_r = (T_r/P_r)$

Solve for V_r from BWR equation by Newton-Raphson

↓

Calculate enthalpy departure for pressure

↓

Calculate ideal gas enthalpy:

1) $H_{vap} = \frac{H^* - H}{RT_c} \frac{RT_c}{M}$ at ref. of 75° liquid.
2) Integrate C_p to temperature

↓

Calculate enthalpy by adding ideal gas enthalpy and isothermal pressure enthalpy term

↓

Print Results

Documentation

The program currently exists on disk, under the file name DAVE.F10. The input parameters and readout values are in real free-field format.

READING PARAMETERS INTO THE PROGRAM

Read(4,11) P1,T1,T10,T30,T50,T70,T90,SG,TB

where:

P1 = system pressure, psia

T1 = system temperature, °F

T10-T90 = ASTM Distillation Volumetric Boiling Points, °F, used to estimate a mixture's boiling point. If the mixture's boiling point has already been determined, read in 5 0.'s for these values

SG = specific gravity

TB = if the mixture's boiling point has already been determined, it is fed in by this parameter; if the mixture's boiling point has to be estimated by ASTM data, read in a 0. for this value

Read(4,12) ALIQ

where:

ALIQ = indicates whether the fraction exists as a vapor or liquid. A 0. indicates that the fraction is a vapor, a 1.

indicates it is a liquid.

OUTPUT

The following values are output:

```
211     FORMAT(1X,'ENTHALPY=',F,5X,'MW=',F,5X,'TC=',5X,'PC=',F,/
      1 ,X,'ACENTRIC FACTOR=',F,5X,'IDEAL VAPOR=',F)
```

where:

ENTHALPY	=	enthalpy of fraction at system's temperature and pressure in Btu/lb referenced to liquid, 75°F
MW	=	molecular weight, lb/lb-mole
TC	=	critical temperature, °R
PC	=	critical pressure, psia
ACENTRIC FACTOR	=	acentric factor, dimensionless
IDEAL VAPOR	=	ideal gas enthalpy at system's temperature

SAMPLE CALCULATIONS

Performed on the California naphtha used for sample calaulations in appendix A, having a specific gravity of 0.7365.

Conditions: vapor at 500°F and 300 psia; the experimentally determined enthalpy value referenced to 75°F is 332.8 Btu/lb.

READ-IN

```
                  10
300.,500.,174.,184.,196.,231.,.7365,0.
0.
```

OUTPUT

ENTHALPY = 339.2547500 MW = 99.0607910 TC = 981.9159300

PC = 468.2372700

ACENTRIC FACTOR = 0.3056040 IDEAL VAPOR = 361.8919300

COMMENTS

More fractions need to be tested, and at a wide range of conditions. The program is capable of predicting liquid enthalpies but needs to be tested. Problems are encountered near the pseudocritical point, as liquid volumes and vapor volumes approach one another, values which are calculated in the program by the BWR equation of state. A better way of estimating the mixture's boiling point can be incorporated. A listing of the program follows.

```
      DIMENSION E(2),C(2),B1(2),B2(2),B3(2),B4(2),B(2),DELH(2)
      DIMENSION C1(2),C2(2),C3(2),C4(2)
      DIMENSION VR(2),D1(2),D2(2),BET(2),GAM(2),D(2),Z(2)
      READ(4,11) P1,T1,T10,T30,T50,T70,T90,SG,TB
      READ(4,12) ALIQ
      T=T1
      P=P1
      IF(TB.GT.0.) GO TO 911
C     CALCULATE BOILING POINT
      TB=(T10+T30+T50+T70+T90)/5.+460.
C     CALCULATE WATSON FACTOR
911.  AK=(TB)**(1./3.)/SG
C     READ IN SIMPLE AND REFERENCE FLUID CONSTANTS
      B1(1)=.1181193
      B1(2)=.2026579
      B2(1)=.265728
      B2(2)=.331511
      B3(1)=.154790
      B3(2)=.027655
      B4(1)=.030323
      B4(2)=.203488
      C1(1)=.0236744
      C1(2)=.0313385
      C2(1)=.0186984
      C2(2)=.0503618
      C3(1)=0.0
      C3(2)=.016901
      C4(1)=.042724
      C4(2)=.041577
      D1(1)=.155488/10.**4.
      D1(2)=.48736/10.**4.
      D2(1)=.623689/10.**4.
      D2(2)=.0740336/10.**4.
      BET(1)=.65392
      BET(2)=1.226
      GAM(1)=.060167
      GAM(2)=.03754
C     CALCULATE CRITICAL PROPERTIES
      TC=341.7+811.*SG+(.4244+.1174*SG)*TB
      TC=TC+(0.4669-3.2623*SG)*10.**5./TB
      PC=EXP(8.3634-.0566/SG-(.24244+2.2898/SG
     1+.11857/SG**2.)*10.**(-3.)*TB
     1+(1.4685+3.648/SG+.47227/SG**2.)*10.**(-7.)
     1*TB*TB-(0.42019+1.6977/SG/SG)*10.**(-10.)
     1*TB*TB*TB)
C     CALCULATE MOLECULAR WEIGHT
      AMW=-12272.6+9486.4*SG+(4.6523-3.3287*SG)*TB
     1+(1.-.77084*SG-.02058*SG**2.)*(1.3437-
     1720.79/TB)*10.**7./TB+(1.-.80882*SG+.02226*SG**2.)
     1*(1.8828-181.98/TB)*10.**12./TB/TB/TB
      J=1
      T=T+460.
      TR=T/TC
      PR=P/PC
      VR(1)=TR/PR
      IF(ALIQ.EQ.1.) VR(1)=AMW*7.12*10.**(-4.)
      VR(2)=VR(1)
C     CALCULATE ENTHALPY DEPARTURE FROM IDEAL GAS
7     DO 2 I=1,2
      B(I)=B1(I)-B2(I)/TR-B3(I)/TR/TR-B4(I)/TR**3.
```

```
      C(I)=C1(I)-C2(I)/TR+C3(I)/TR**3.
      D(I)=D1(I)+D2(I)/TR
4     BB=-PR+TR/VR(I)+B(I)*TR/VR(I)**2.+C(I)*TR/VR(I)**3.
     1 +D(I)*TR/VR(I)**6.
     1 +C4(I)/TR**2./VR(I)**3.*(BET(I)+GAM(I)/VR(I)**2.)*EXP(-GAM(I)
     1 /VR(I)**2.)
      AA=C4(I)/TR**2.*VR(I)**(-3.)*(BET(I)+GAM(I)*VR(I)**(-2.))
     1 *EXP(-GAM(I)*VR(I)**(-2.))*
     1 (2.*GAM(I)*VR(I)**(-3.))*C4(I)/TR**2.*VR(I)**(-3.)*EXP
     1 (-GAM(I)*VR(I)**(-2.))
     1 *(-2.*GAM(I)*VR(I)**(-3))-3.*(BET(I)+GAM(I)*VR(I)**(-2.))
     1 *EXP(-GAM(I)*VR(I)**(-2.))
     1 *C4(I)/TR**2.*VR(I)**(-4.)
      AB=-TR*VR(I)**(-2.)-2.*B(I)*TR*VR(I)**(-3.)
     1 -3.*C(I)*TR*VR(I)**(-4.)-6.*D(I)*TR*VR(I)**(-7.)
      AB=AB+AA
      VR(I)=VR(I)-BB/AB
      IF(ABS(BB).LE..00001) GO TO 3
      GO TO 4
3     E(I)=C4(I)/2./TR**3./GAM(I)*(BET(I)+1.-
     1 (BET(I)+1.+GAM(I)/VR(I)**2.)*EXP(-GAM(I)/VR(I)**2.))
      Z(I)=VR(I)*PR/TR
      DELH(I)=(Z(I)-1.-(B2(I)+2.*B3(I)/TR+3.*B4(I)/TR
     1 **2.)/TR/VR(I)-(C2(I)-3.*C3(I)/TR/TR)/(2.*TR*VR(I)**2.)
     1 +D2(I)/5./TR/VR(I)**5.+3.*E(I))*TR
2     CONTINUE
      WR=.3978
      PBR=14.7/PC
      TBR=TB/TC
      IF(TBR.GT.0.8) GO TO 5
C     CALCULATE ACENTRIC FACTOR
      W=(ALOG(PBR)-5.92714+6.09648/TBR+1.28862*
     1 ALOG(TBR)-.169347*TBR**6.)/(15.2518-15.6875/TBR
     1 -13.4271*ALOG(TBR)+.43577*TBR**6.)
      GO TO 6
5     W=-7.904+.1352*AK-.007465*AK*AK+8.359*TBR
     1 +(1.408-.01063*AK)/TBR
6     ENTH=DELH(1)+W/WR*(DELH(2)-DELH(1))
      IF(J.EQ.1) ENTH1=ENTH
      IF(J.EQ.2) ENTH2=ENTH
      IF(J.EQ.2) GO TO 8
C     CALCULATE HEAT OF VAPORIZATION
      T=75.+460.
      PR=.01
      TR=T/TC
      VR(1)=AMW*7.12*10.**(-4.)
      VR(2)=VR(1)
      J=2
      GO TO 7
8     CF=((12.8/AK-1.)*(10./AK-1.)*100.)**2.
      IF(TBR.LE..8) GO TO 18
      T=T1+460.
C     CALCULATE VAPOR ENTHALPY ABOVE 75 DEGREES
19    VAP=-.32646*T+.02678*AK*T-(1.3892-1.2122*AK
     1 +0.03803*AK**2.)*10.**(-4.)*T*T/2.-1.5393*10.**(-7.)*T**3./3.
     1 -CF*(.084773*T-.080809*SG*T-(2.1773-2.0826*SG)*T*T/2.
     1 *10.**(-4.)+(.78649-.70423*SG)*10.**(-7.)*T**3./3.)
      IF(M.EQ.1) GO TO 811
      VAP1=VAP
      T=75.+460.
```

```
            M=1
            GO TO 19
            GO TO 811
   18       CF=((12.8-AK)*(10.-AK)/(10.0*W))**2.
            T=T1+460.
  119       VAP=-.33886*T+.02827*AK*T-(.9291-1.1543*AK
        1   +.0368*AK**2.)*T*T/2.*10.**(-4.)-1.6658*10.**(-7.)
        1   *T*T*T/3.-CF*(.26105*T-.59332*W*T-(4.56-9.48*W)
        1   *10.**(-4.)*T*T/2.-(.536-.6828*W)*10.**(-7.)*T**3./3.)
            IF(M.EQ.1) GO TO 811
            VAP1=VAP
            T=75.+460.
            M=1
            GO TO 119
  811       AI=VAP1-VAP
            R=1.9869
            RTC=R*TC
   C        CALCULATE IDEAL GAS ENTHALPY
            VIDEAL=-ENTH2*RTC/AMW+AI
            ENTHAL=VIDEAL+ENTH1*RTC/AMW
  211       FORMAT(1X,'ENTHALPY=',F,5X,'MW=',F,5X,'TC=',F,5X,'PC=',F,/
        1   ,X,'ACENTRIC FACTOR=',F,5X,'IDEAL VAPOR=',F)
            WRITE(4,211) ENTHAL,AMW,TC,PC,W,VIDEAL
   11       FORMAT(9F)
   12       FORMAT(F)
            STOP
            END
```

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