THE EFFECT OF PRESSURE AND COMPOSITION ON THE ENTHALPY

OF METHANE BINARIES/IN THE VAPOR PHASE

By

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PREFACE

The effect of pressure on the mixture enthalpy and the partial enthalpies of methane binary systems is studied. The effect of pressure on the enthalpies is calculated by using experimental pressure-volume-temperature-composition data and by using an equation of state. General correlations for the effect of pressure on the mixture enthalpy of methane binaries and the effect of pressure on the partial enthalpy of methane in binary systems are presented.

CHAPTER I

INTRODUCTION

Mixture enthalpy data are of utmost importance for the accurate design of process equipment. Inaccurate enthalpy data could lead to an "underdesign" or "overdesign" of the equipment. The "underdesigned" equipment would cause the operating costs to be higher than expected because the expected output could not be met. The "overdesigned" equipment would cause the equipment costs to be higher than necessary thus hurting the economics of the process.

There are very few mixture enthalpy data or partial enthalpy data for mixture components in the vapor phase. However, there are limited enthalpy data for four methane binary systems. Some partial enthalpies for the methane – ethane, methane – n–butane and methane – n–pentane binaries have been calculated by Sage and Lacey (15). Sage and Lacey processed experimental pressure–volume–temperature–composition (PVTx) data by graphical methods to obtain the effect of pressure on the partial enthalpies of the components. Some partial enthalpies have been calculated for the methane – propane binary system by using experimental Joule–Thomson coefficients (1). None of the calculated partial enthalpy data covers the complete composition range of the binaries.

The effect of pressure on the mixture enthalpy and the partial enthalpies of the components in a mixture can also be calculated by using an equation of state. This approach has been used by several

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investigators (2,8,11,19,20) to calculate the vapor phase enthalpy of light hydrocarbon mixtures. The form of the equation of state used to calculate mixture enthalpies and partial enthalpies can be programmed on a digital computer. Fast and numerically accurate calculations are the advantage of this method. However, the equation of state fits the data with a somewhat pre-shaped curve. Hence any error in the equation of state enters into the calculated enthalpy value. The graphical treatment using the experimental data works with curves that fit the data.

The system studied primarily in this work is the methane - propane binary. The effect of pressure on the mixture enthalpy and the partial enthalpies of methane and propane in the superheated vapor region were calculated from PVTx data by graphical methods. Using the enthalpy data from this binary and the other methane binaries, correlations were developed for the mixture enthalpy and the partial enthalpy of methane in the different solvents. The mixture enthalpy and the partial enthalpy of methane were correlated as functions of the pseudo reduced temperature, pseudo reduced pressure and a pseudo acentric factor.

Mixture enthalpies and partial enthalpies of light hydrocarbons for binary mixtures in the superheated vapor region were calculated using the Redlich-Kwong equation of state. This equation has been programmed for use on the IBM 650 digital computer (7). The superheated vapor enthalpy values calculated using the Redlich-Kwong equation of state were compared with enthalpies calculated by the Benedict-Webb-Rubin equation of state (10,11), Sage and Lacey (15), Edmister's generalized correlation (6) extended to mixtures by the pseudo critical concept and this work. The Redlich-Kwong equation of state was also used to

calculate some saturated vapor enthalpies for binary mixtures, although the equation was meant to be applied only to superheated vapor. These saturated vapor enthalpies were compared with enthalpies calculated by the Benedict-Webb-Rubin equation (19,20) and Edmister's generalized correlation.

CHAPTER II

METHANE - PROPANE BINARY CALCULATIONS

Data Used in Calculations

PVTx data used in calculating the effect of pressure on mixture enthalpy and partial enthalpies of the methane - propane system in the superheated vapor region were obtained from Sage and Lacey (15). Sage and Lacey do not estimate the variation in the smoothed PVTx data that they present. However, an estimate based on variations in PVTx data that they report for other binaries (16,17) gives a variation in the PVTx data for the methane - propane system of 0.2 to 0.3%.

Enthalpy data for superheated methane and propane are presented by Sage and Lacey (15). The effect of pressure on the enthalpy of the pure components was calculated from PVT data. Sage and Lacey estimate the isothermal variations in enthalpy for propane as 0.8% and the variations in the enthalpy of methane as 1.5%.

Some limited partial enthalpy data on the methane - propane binary system are available (1). These partial enthalpies were calculated from heat capacities and experimental Joule-Thomson coefficient data for the mixture. The mixture heat capacities were calculated as a function of state starting with the ideal gas state heat capacities of methane and propane. The calculated partial enthalpies of methane and propane were tabulated at 0.40, 0.60 and 0.80 weight fraction methane. These partial

enthalpies were not used in the calculations, but were used to compare
the two methods of obtaining enthalpy data.

Derivation of Equations

For a closed system, the First Law of Thermodynamics is

$$dU = \delta'Q + \delta'W \tag{1}$$

where   dU is the change in internal energy of a system with units of
energy/mole, which is an intensive property.

$\delta'Q$ is an infinitesimal quantity of heat put into the system,
energy/mole.

$\delta'W$ is an infinitesimal amount of work done on the system,
energy/mole.

Internal energy is a property of the system. This means that the value
of U is fixed by the state of the system and is a point function. How-
ever, the work and heat terms are not properties of the system and are
not perfect differentials. This is indicated by the δ' to show the
infinitesimal change.

When pressure is the only force acting on the system, only
pressure-volume work is considered. For a reversible process, $\delta'W = -PdV$
and

$$dU = \delta'Q - PdV \tag{2}$$

where   P is the absolute pressure of the system.

V is the volume of the system, volume/mole.

For a reversible process, the Second Law of Thermodynamics is

$$dS = \delta'Q/T \tag{3}$$

where S is the entropy of the system, energy/degree-mole.

T is the absolute temperature.

The combined statement of the First and Second Laws for a reversible process is

$$dU = TdS - PdV \tag{4}$$

The enthalpy per mole of the system is $H = U + PV$, or

$$dH = dU + PdV + VdP \tag{5}$$

Substituting equation 4 into equation 5 gives

$$dH = TdS + VdP \tag{6}$$

The Gibbs free energy per mole of a system is $G = H - TS$, or

$$dG = dH - TdS - SdT \tag{7}$$

Substituting equation 6 into equation 7 gives

$$dG = VdP - SdT \tag{8}$$

Since the Gibbs free energy is a property of the system it is an exact differential,

$$dG = \left(\frac{\delta G}{\delta T}\right)_P dT + \left(\frac{\delta G}{\delta P}\right)_T dP \tag{9}$$

or

$$- S = \left(\frac{\delta G}{\delta T}\right)_P \qquad \text{and} \qquad V = \left(\frac{\delta G}{\delta P}\right)_T$$

It follows that

$$-\left(\frac{\delta S}{\delta P}\right)_T = \frac{\delta^2 G}{\delta P \delta T} \quad \text{and} \quad \left(\frac{\delta V}{\delta T}\right)_P = \frac{\delta^2 G}{\delta T \delta P}$$

For a function f of two variables, if the partial derivative of the function with respect to one variable, $D_1(f)$, and the partial derivative of the function with respect to the other variable, $D_2(f)$, exist and are continuous and if the second partial derivative $D_{1,2}(f)$ exists and is continuous, then $D_{1,2}(f) = D_{2,1}(f)$. In a one phase region the thermodynamic quantities meet these specifications (5), therefore

$$\left(\frac{\delta S}{\delta P}\right)_T = -\left(\frac{\delta V}{\delta T}\right)_P \tag{10}$$

By taking the partial derivative of equation 6 with respect to pressure the following equation is obtained.

$$\left(\frac{\delta H}{\delta P}\right)_T = T\left(\frac{\delta S}{\delta P}\right)_T + V \tag{11}$$

Substituting equation 10 into equation 11,

$$\left(\frac{\delta H}{\delta P}\right)_T = V - T\left(\frac{\delta V}{\delta T}\right)_P \tag{12}$$

Equation 12 was derived for a closed system. Since no matter can flow into or out of a closed system, equation 12 is true only at constant composition. This constant composition will be indicated by the subscript y. The symbol y is the mole fraction of a component in the vapor phase.

The residual volume α is defined as

$$\alpha = \frac{RT}{P} - V \tag{13}$$

Thus

$$\left(\frac{\delta V}{\delta T}\right)_{P,y} = \frac{R}{P} - \left(\frac{\delta \alpha}{\delta T}\right)_{P,y} \tag{14}$$

Substituting equations 13 and 14 into equation 12 gives

$$\left(\frac{\delta H}{\delta P}\right)_{T,y} = \left(\frac{RT}{P} - \alpha\right) - T\left[\frac{R}{P} - \left(\frac{\delta \alpha}{\delta T}\right)_{P,y}\right] \tag{15}$$

or

$$\left(\frac{\delta H}{\delta P}\right)_{T,y} = \left(\frac{RT}{P} - \alpha\right)\left[1 - \frac{\frac{RT}{P} - T\left(\frac{\delta \alpha}{\delta T}\right)_{P,y}}{\frac{RT}{P} - \alpha}\right] = V(1 - \theta) \tag{16}$$

letting θ be defined by equation 16.

The partial molal enthalpy of component i is defined as

$$\overline{H}_i = \left(\frac{\delta H'}{\delta n_i}\right)_{T,P,n_j} \quad (j \neq i) \tag{17}$$

where $\overline{H}_i$ is the partial molal enthalpy of component i with units of energy/mole, which is an intensive property.

H' is the total enthalpy of the system with units of energy, which is an extensive property.

n_i is the moles of component i.

For a general change in enthalpy for a binary mixture (components 1 and 2),

$$dH' = \left(\frac{\delta H'}{\delta T}\right)_{P,n} dT + \left(\frac{\delta H'}{\delta P}\right)_{T,n} dP + \left(\frac{\delta H'}{\delta n_1}\right)_{T,P,n_2} dn_1 + \left(\frac{\delta H'}{\delta n_2}\right)_{T,P,n_1} dn_2 \tag{18}$$

which at constant temperature and pressure reduces to

$$dH' = \left(\frac{\delta H'}{\delta n_1}\right)_{T,P,n_2} dn_1 + \left(\frac{\delta H'}{\delta n_2}\right)_{T,P,n_1} dn_2 \tag{19}$$

Consider a total enthalpy H' in a mixture of n_1 moles of component 1 and n_2 moles of component 2. The ratio of component 1 to component 2 is n_1/n_2. Allow both n_1 and n_2 to increase (decrease) to $n_1 + \Delta n_1$ and $n_2 + \Delta n_2$, but require that $(n_1 + \Delta n_1)/(n_2 + \Delta n_2) = n_1/n_2$. Under these conditions H' will be increased (decreased) to $H' + \Delta H'$, where $(H' + \Delta H')/H' = (n_1 + \Delta n_1)/n_1$, since H' is an extensive property or is homogeneous to the first degree in n_1, n_2. However, both $\bar{H}_1$ and $\bar{H}_2$ will remain constant as the number of moles are increased (decreased) because they are intensive properties or are functions of n_1, n_2 to the zero degree. This means that the partial enthalpy of a component is independent of the mass but is dependent on the mass ratios or composition. Thus one may write

$$dn_1 = n_1 d\xi, \quad dn_2 = n_2 d\xi, \quad dH' = H' d\xi$$

where $d\xi$ is the increase (decrease) of n_1, n_2 and H'.

Substituting the above into equation 19 gives

$$H' d\xi = \bar{H}_1 n_1 d\xi + \bar{H}_2 n_2 d\xi \tag{20}$$

Dividing both sides of equation 20 by $d\xi$ leaves the expression

$$H' = n_1 \bar{H}_1 + n_2 \bar{H}_2 \tag{21}$$

To make equation 21 consistent with equations 1 through 16, the extensive property H' must be changed to an intensive property. This can be done by dividing equation 21 by the total number of moles in the

system, n_t. Since $H'/n_t = H$ and $n_i/n_t = y_i$ for a vapor mixture, equations 19 and 21 become

$$dH = \bar{H}_1 dy_1 + \bar{H}_2 dy_2 \tag{22}$$

and

$$H = y_1 \bar{H}_1 + y_2 \bar{H}_2 \tag{23}$$

The two mole fractions y_1 and y_2 are not independent since $y_1 + y_2 = 1$ and $dy_1 = - dy_2$. Substituting this into equation 22 gives

$$dH = (\bar{H}_1 - \bar{H}_2)dy_1 \tag{24}$$

In equation 24 dy_1 is independent, thus

$$\left(\frac{\delta H}{\delta y_1}\right)_{T,P} = \bar{H}_1 - \bar{H}_2 \tag{25}$$

Substituting $y_2 = 1 - y_1$ into equation 23 gives the expression

$$H = y_1 \bar{H}_1 + (1 - y_1)\bar{H}_2 = \bar{H}_2 + y_1(\bar{H}_1 - \bar{H}_2) \tag{26}$$

Equation 25 can be substituted into equation 26 giving

$$H = \bar{H}_2 + y_1\left(\frac{\delta H}{\delta y_1}\right)_{T,P} \tag{27}$$

or, by rearranging equation 27

$$\bar{H}_2 = H - y_1\left(\frac{\delta H}{\delta y_1}\right)_{T,P} \tag{28}$$

From equation 25

$$\bar{H}_2 = \bar{H}_1 - \left(\frac{\delta H}{\delta y_1}\right)_{T,P} \tag{29}$$

Eliminating $\bar{H}_2$ between equation 29 and equation 28 gives

$$\bar{H}_1 = H + (1 - y_1)\left(\frac{\delta H}{\delta y_1}\right)_{T,P} \tag{30}$$

Equations 28 and 30 are useful in that partial enthalpies may be evaluated without using the definition given by equation 17.

Another useful equation can be obtained by differentiating equation 26 with respect to y_1 holding T and P constant.

$$\left(\frac{\delta H}{\delta y_1}\right)_{T,P} = \bar{H}_1 - \bar{H}_2 + y_1\left(\frac{\delta \bar{H}_1}{\delta y_1}\right)_{T,P} + (1 - y_1)\left(\frac{\delta \bar{H}_2}{\delta y_1}\right)_{T,P} \tag{31}$$

Substituting equations 28 and 30 into equation 31 gives

$$\left(\frac{\delta H}{\delta y_1}\right)_{T,P} = H + (1 - y_1)\left(\frac{\delta H}{\delta y_1}\right)_{T,P} - H + y_1\left(\frac{\delta H}{\delta y_1}\right)_{T,P}$$

$$+ y_1\left(\frac{\delta \bar{H}_1}{\delta y_1}\right)_{T,P} + (1 - y_1)\left(\frac{\delta \bar{H}_2}{\delta y_1}\right)_{T,P} \tag{32}$$

or

$$y_1\left(\frac{\delta \bar{H}_1}{\delta y_1}\right)_{T,P} + (1 - y_1)\left(\frac{\delta \bar{H}_2}{\delta y_1}\right)_{T,P} = 0 \tag{33}$$

Calculation of Mixture Enthalpy

Sage and Lacey (15) tabulate smoothed values of the compressibility factor z and volume in the superheated vapor region for the methane – propane binary. The tabulations are for nine equally spaced mole fractions between pure methane and pure propane. The temperature ranges from 100 to 460°F at 60° intervals. The pressure range for the tabulation varies from 200 to 10,000 psia. However, the pressure range used in this work is 200 to 2000 psia. The PVTx values used in this work are tabulated in Table XIII, Appendix B.

The compressibility data was used to calculate values of the residual volume α. This residual quantity was suggested by Deming and Shupe (4) as a correction term to the ideal gas volume. The calculated values of α were plotted against temperature with a pressure parameter at each mole fraction. A smooth curve was drawn through the points in preparation for numerical differentiation as shown in Figure 1. The residual volume was used for numerical differentiation since an error in the slope of an α–curve at any point will introduce much smaller errors into the derivatives of V. This is evident from equation 14. A 1% error in $(\delta\alpha/\delta T)_{P,y}$ may mean only a few hundredths of 1% error in $(\delta V/\delta T)_{P,y}$ since $(\delta\alpha/\delta T)_{P,y}$ enters as a correction term to the slope of an ideal gas just as α is a correction term to RT/P.

The slope of the tangent to the α–curve (Figure 1) was calculated by numerical differentiation at 60°F intervals between 100 and 460°F for each isobar on the constant composition plots. Three numerical differentiation equations were necessary. A forward differences equation was required for the temperatures on the left terminal of the isobars in Figure 1. The left terminal is 100°F for the 200, 400 and 600 psia

isobars and 160°F for the 800, 1000, 1250, 1500, 1750 and 2000 psia isobars. A backward differences equation was required for the temperature on the right terminal of the isobars, 460°F in Figure 1. One equation was used for the temperatures between the two terminal temperatures. The equations used are shown below with the approximate error functions for each equation (18).

Forward Differences

$$\left(\frac{\delta\alpha_0}{\delta T}\right)_{P,y} = \frac{1}{2h}(-3\alpha_0 + 4\alpha_1 - \alpha_2) \qquad e = \frac{1}{3}h^2\left(\frac{\delta^3\alpha_0}{\delta T^3}\right)_{P,y} \qquad (34)$$

Backward Differences

$$\left(\frac{\delta\alpha_2}{\delta T}\right)_{P,y} = \frac{1}{2h}(\alpha_0 - 4\alpha_1 + 3\alpha_2) \qquad e = \frac{1}{3}h^2\left(\frac{\delta^3\alpha_2}{\delta T^3}\right)_{P,y} \qquad (35)$$

Interior Temperatures

$$\left(\frac{\delta\alpha_2}{\delta T}\right)_{P,y} = \frac{1}{120h}(6\alpha_0 - 60\alpha_1 - 40\alpha_2 + 120\alpha_3 - 30\alpha_4 + 4\alpha_5)$$

$$e = -\frac{h^5}{60}\left(\frac{\delta^6\alpha_2}{\delta T^6}\right)_{P,y} \qquad (36)$$

where h is the distance between equally spaced temperatures on the
      abscissa.

α_i is the residual volume for temperature i of the abscissa.

The calculated values of $(\delta\alpha/\delta T)_{P,y}$ were used to calculate the dimensionless Θ of equation 16. Θ was plotted against pressure with a temperature parameter for the nine equally spaced mole fractions as shown in Figure 2. This plot was used to smooth the partial derivatives at low pressure since Θ approaches unity as pressure approaches zero.
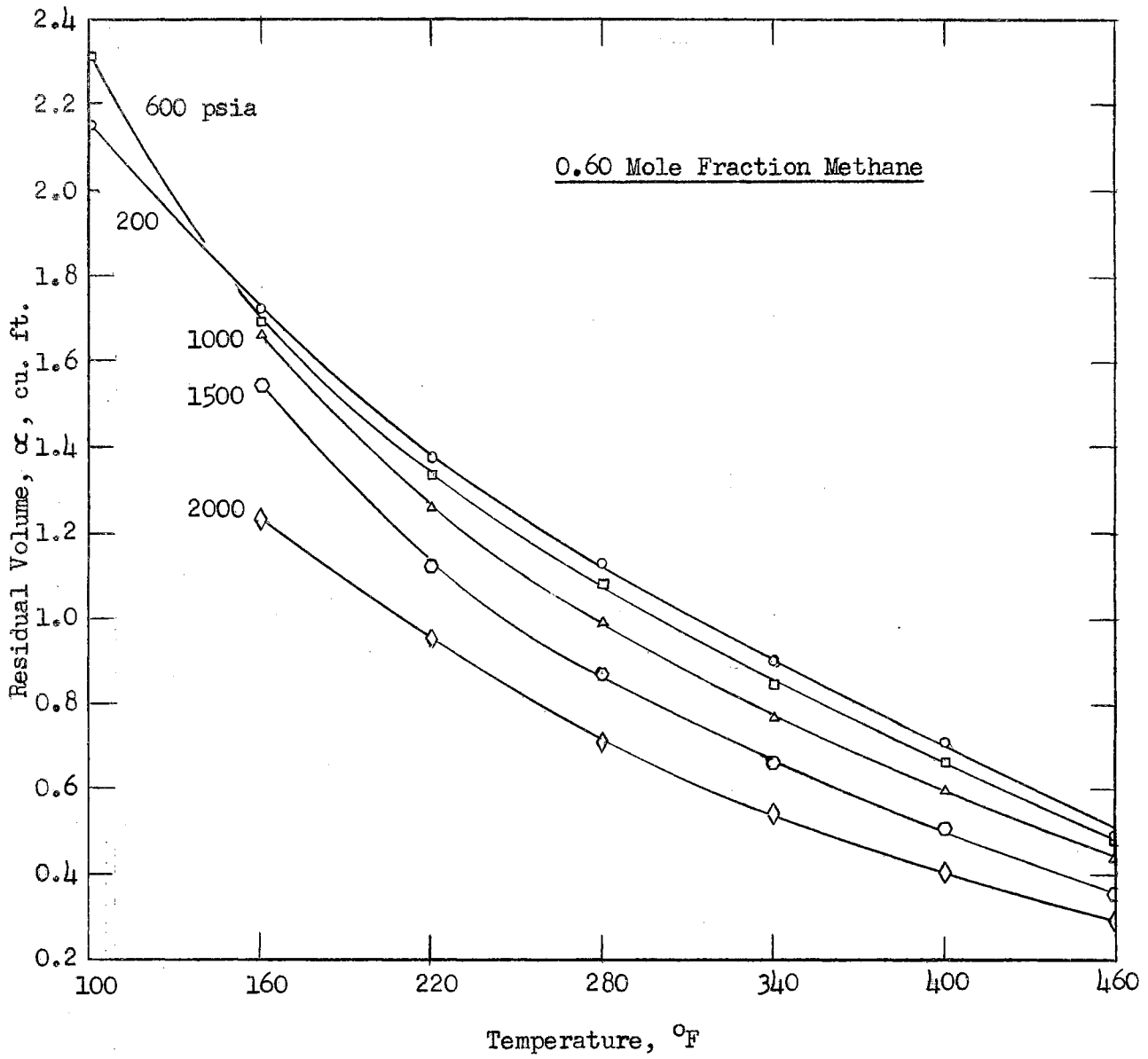
Figure 1

Residual Volume – Temperature Diagram
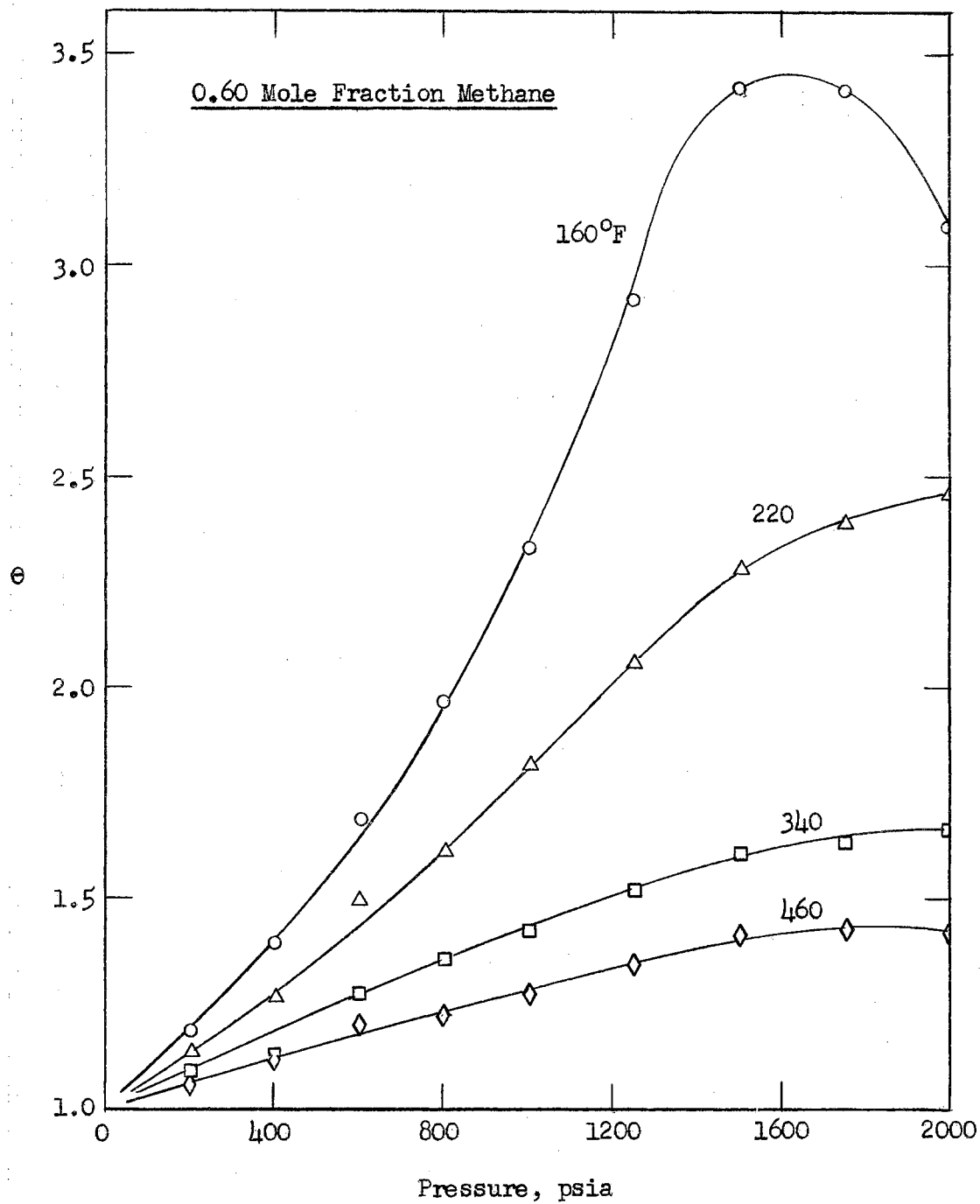
Figure 2

Smoothing Plot of Θ Against Pressure

$$\underset{P \to 0}{\text{Lim}} \left[\frac{\dfrac{RT}{P} - T\left(\dfrac{\delta\alpha}{\delta T}\right)_{P,y}}{\dfrac{RT}{P} - \alpha} \right] = 1, \quad \text{since} \quad T\left(\frac{\delta\alpha}{\delta T}\right)_{P,y} \quad \text{and } \alpha \text{ become small as } P \to 0$$

The smoothed values of Θ were used to calculate the pressure correction to the ideal gas enthalpy of the binary mixture at each mole fraction by integrating equation 16.

$$\Delta H = (H^P - H^O)_{T,y} = \int_{P=0}^{P} dH = \int_0^P V(1 - \Theta) dP \qquad (37)$$

The integral was evaluated by plotting $V(1 - \Theta)$ against pressure with a temperature parameter at each mole fraction as shown in Figure 3. A smooth curve was drawn through the points and was extrapolated to zero pressure. The pressure correction to the ideal gas enthalpy at a given pressure and temperature was found by graphical integration using an Ott planimeter. The area under the given isotherm from zero pressure to the given pressure determined the value of the pressure correction to the ideal gas enthalpy.

The pressure correction to the ideal gas state enthalpy is tabulated in Table I. The temperature range is 100 to 460°F and the pressure range is 200 to 2000 psia for each of the nine equally spaced mole fractions between the pure components. The tabulated values have been smoothed by plotting the enthalpy difference from an ideal gas, ΔH, against composition with a temperature parameter for each pressure as shown in Figure 4. The terminal points of the isotherms, 0 and 1.0 mole fraction methane, were drawn to the pure component propane and methane enthalpy differences, respectively. This method gives mixture enthalpy differences that are consistent with available pure component data.
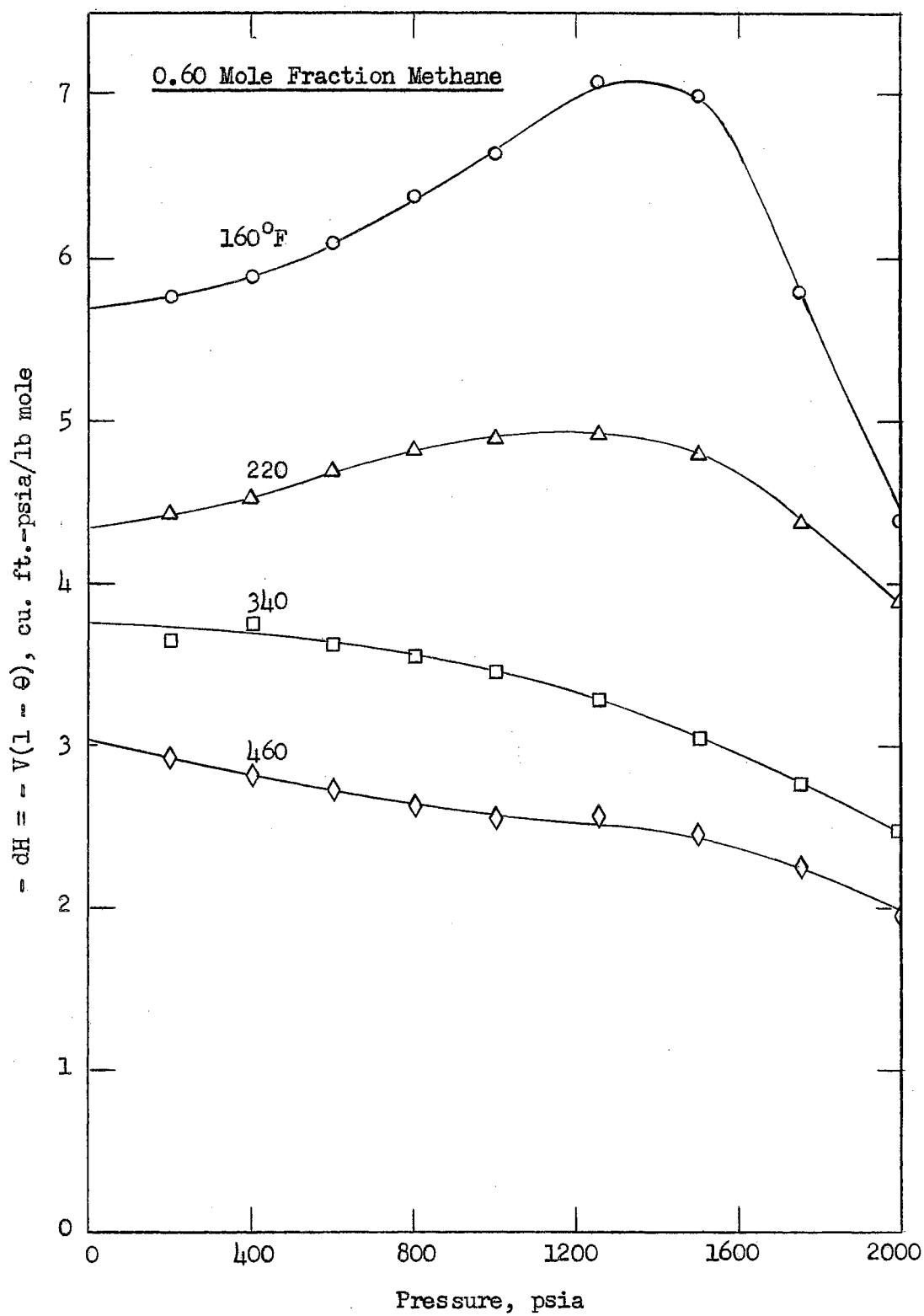
Figure 3

Graphical Integration Plot to Obtain the Mixture Enthalpy Difference
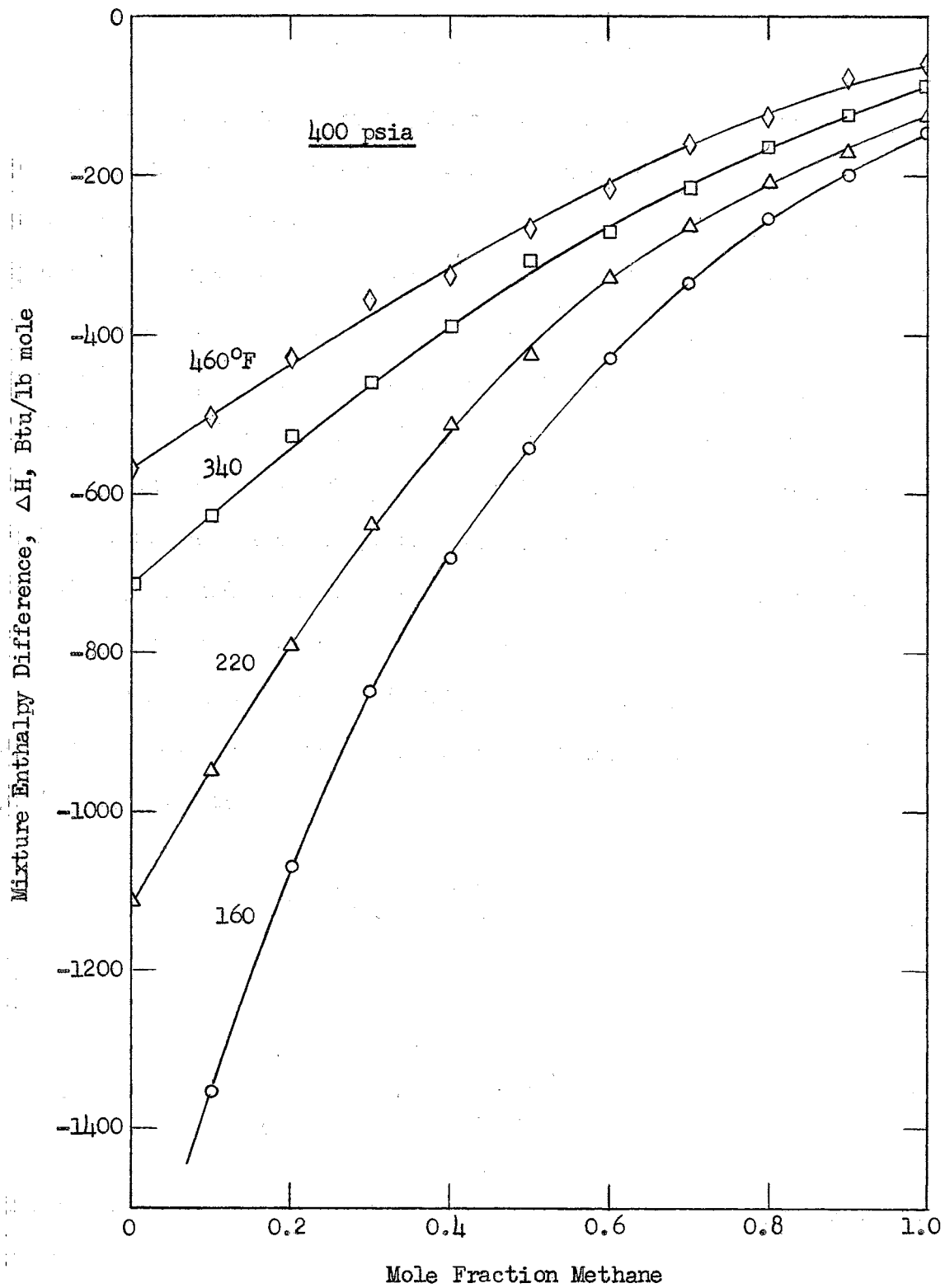
Figure 4

Mixture Enthalpy Difference as a Function of Composition

Calculation of Partial Enthalpies

The effect of pressure on the partial enthalpies of methane and propane in the binary mixture were calculated by equations 30 and 28, respectively. In these equations the enthalpy difference from an ideal gas, ΔH, was substituted for the enthalpy H. Using the substituted form of the equation, the partial molal enthalpy difference from an ideal gas, $\Delta \overline{H}_i = (\overline{H}_i^P - H_i^O)_{T,y}$, is obtained. The slope of the tangent, $(\delta \Delta H / \delta y_1)_{T,P}$, (let subscript 1 refer to methane and 2 refer to propane) to the smooth curves as shown in Figure 4 was obtained by numerical differentiation. Equation 36 was used to obtain the slope at each equally spaced mole fraction over the temperature range 100 to 460°F and the pressure range 200 to 2000 psia.

The partial derivative $(\delta \Delta H / \delta y_1)_{T,P}$ was smoothed by plotting against composition using the following method. From equations 28 and 30 it follows that

$$\frac{\Delta \overline{H}_2}{\Delta H} = 1 - \frac{y_1 \left(\frac{\delta \Delta H}{\delta y_1}\right)_{T,P}}{\Delta H} \tag{38}$$

and

$$\frac{\Delta \overline{H}_1}{\Delta H} = 1 - \frac{(y_1 - 1) \left(\frac{\delta \Delta H}{\delta y_1}\right)_{T,P}}{\Delta H} \tag{39}$$

However, as y_1 approaches zero the right side of equation 38 approaches unity

$$\lim_{y_1 \to 0} \left[1 - \frac{y_1 \left(\frac{\delta \Delta H}{\delta y_1}\right)_{T,P}}{\Delta H}\right] = 1 \tag{40}$$

and as y_1 approaches unity the right side of equation 39 approaches unity.

$$\underset{y_1 \to 1}{\text{Lim}} \left[1 - \frac{(y_1 - 1)\left(\frac{\delta \triangle H}{\delta y_1}\right)_{T,P}}{\triangle H} \right] = 1 \qquad (41)$$

Thus the right side of equation 38 was used to smooth the partial derivative at mole fractions of methane from 0.50 to 0.10. The right side of equation 39 was used to smooth the partial derivative at mole fractions of methane from 0.50 to 0.90. These curves are shown in Figures 5 and 6. The values obtained from the two plots at 0.50 mole fraction methane for a given temperature and pressure were equal or very nearly equal. In the cases where a difference between the two values existed, the average of the values was used.

Since a second partial derivative of the volumetric data was required to obtain partial enthalpies, more smoothing was done to assure that no large deviations existed. The partial enthalpy difference from an ideal gas, $\triangle \bar{H}_i$, was plotted against pressure with a temperature parameter at each equally spaced mole fraction for each component. At zero pressure $\triangle \bar{H}_i = 0$ since the partial enthalpy of a component in an attenuated gaseous mixture is equal to the enthalpy of the pure substance in the same state. Therefore the partial enthalpy difference of each component can be drawn to zero at zero pressure as shown in Figures 7 and 8. This facilitates smoothing at low pressures. These smoothed values of $\triangle \bar{H}_i$ were plotted against temperature for further smoothing. In this smoothing plot a mole fraction methane parameter was used for each pressure as shown in Figures 9 and 10. The final smoothed values for methane and propane are tabulated in Table I.
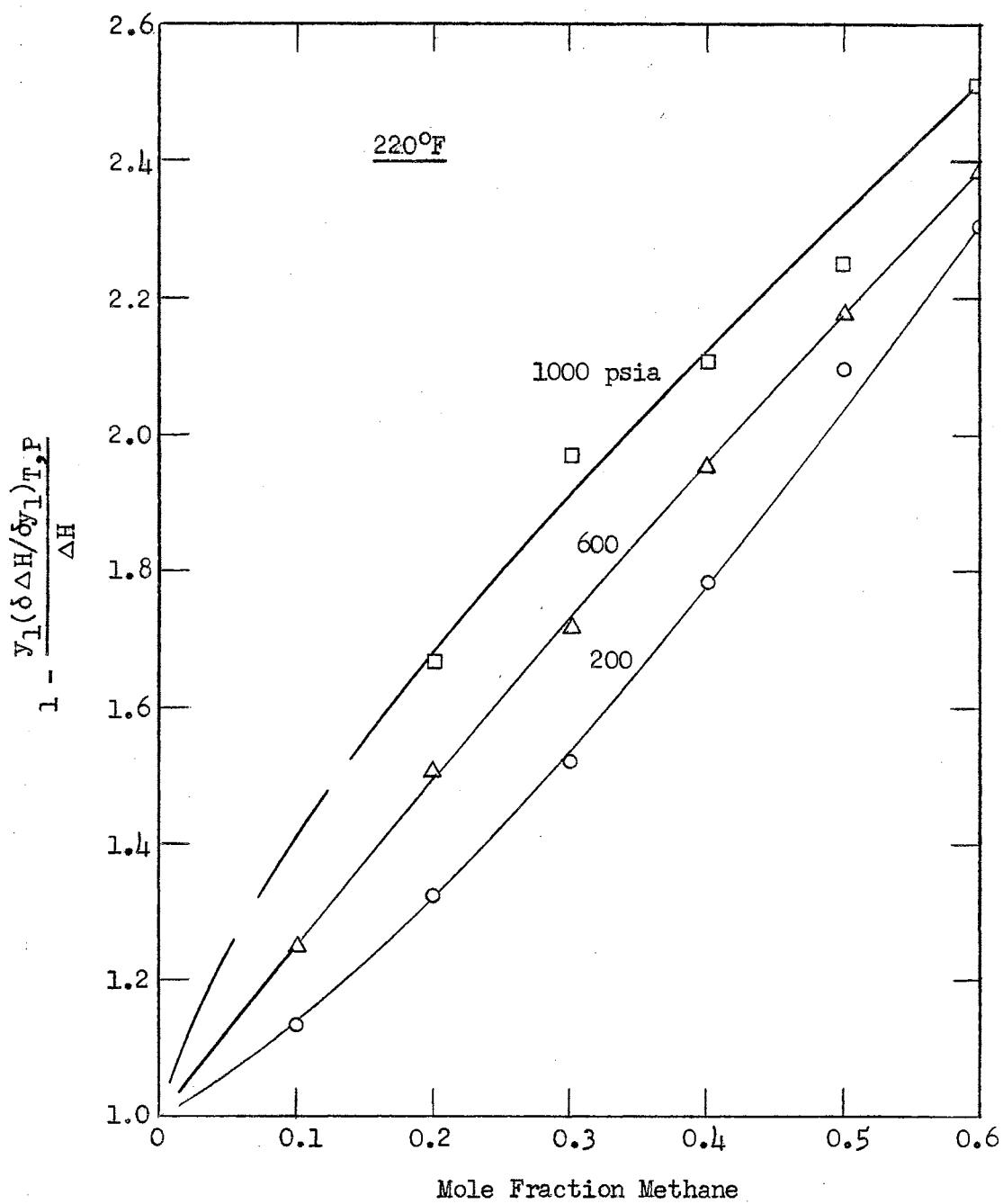
Figure 5

Smoothing of $(\delta \Delta H/\delta y_1)_{T,P}$ at Low Mole Fractions of Methane
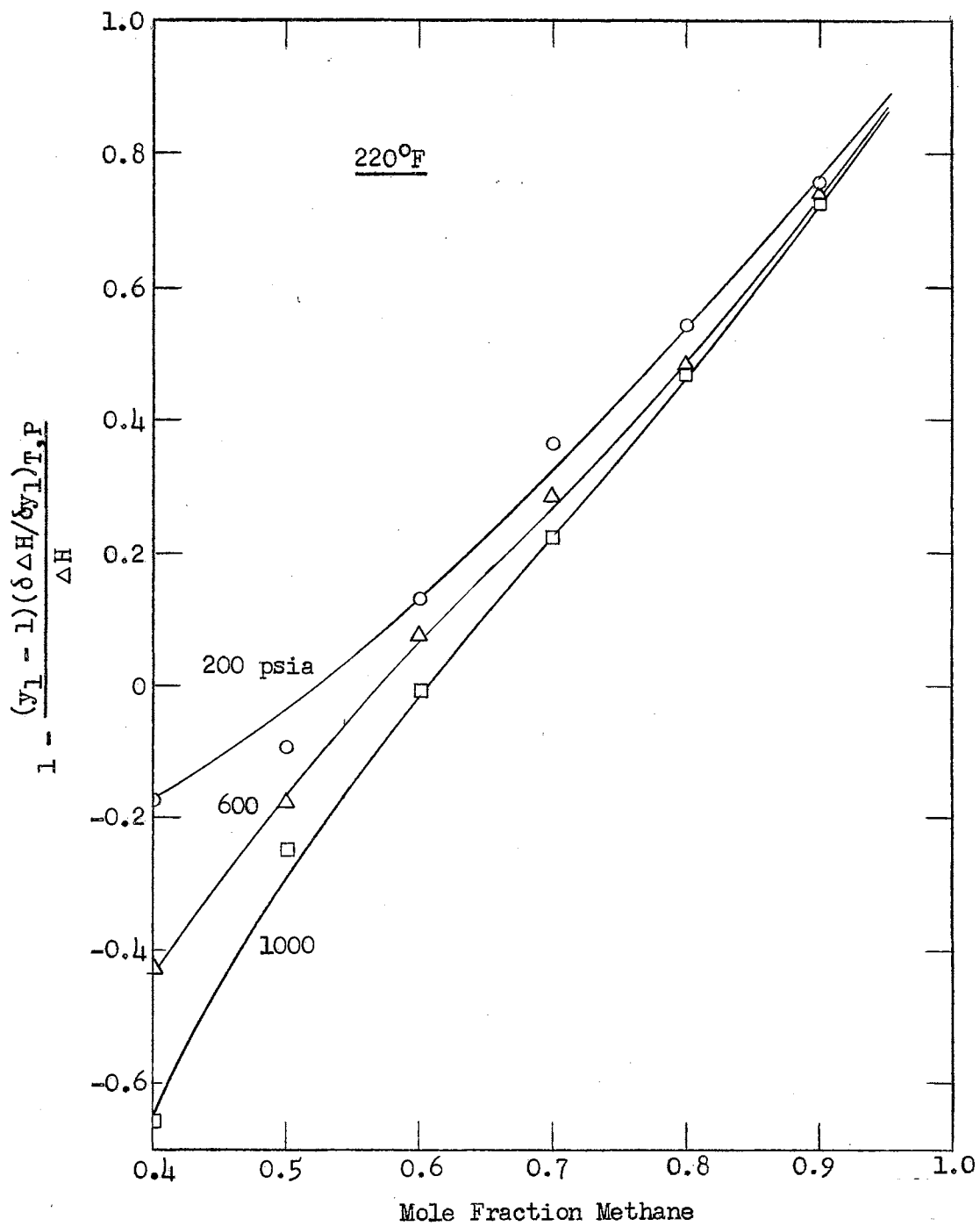
Figure 6

Smoothing of $(\delta \triangle H/\delta y_1)_{T,P}$ at High Mole Fractions of Methane
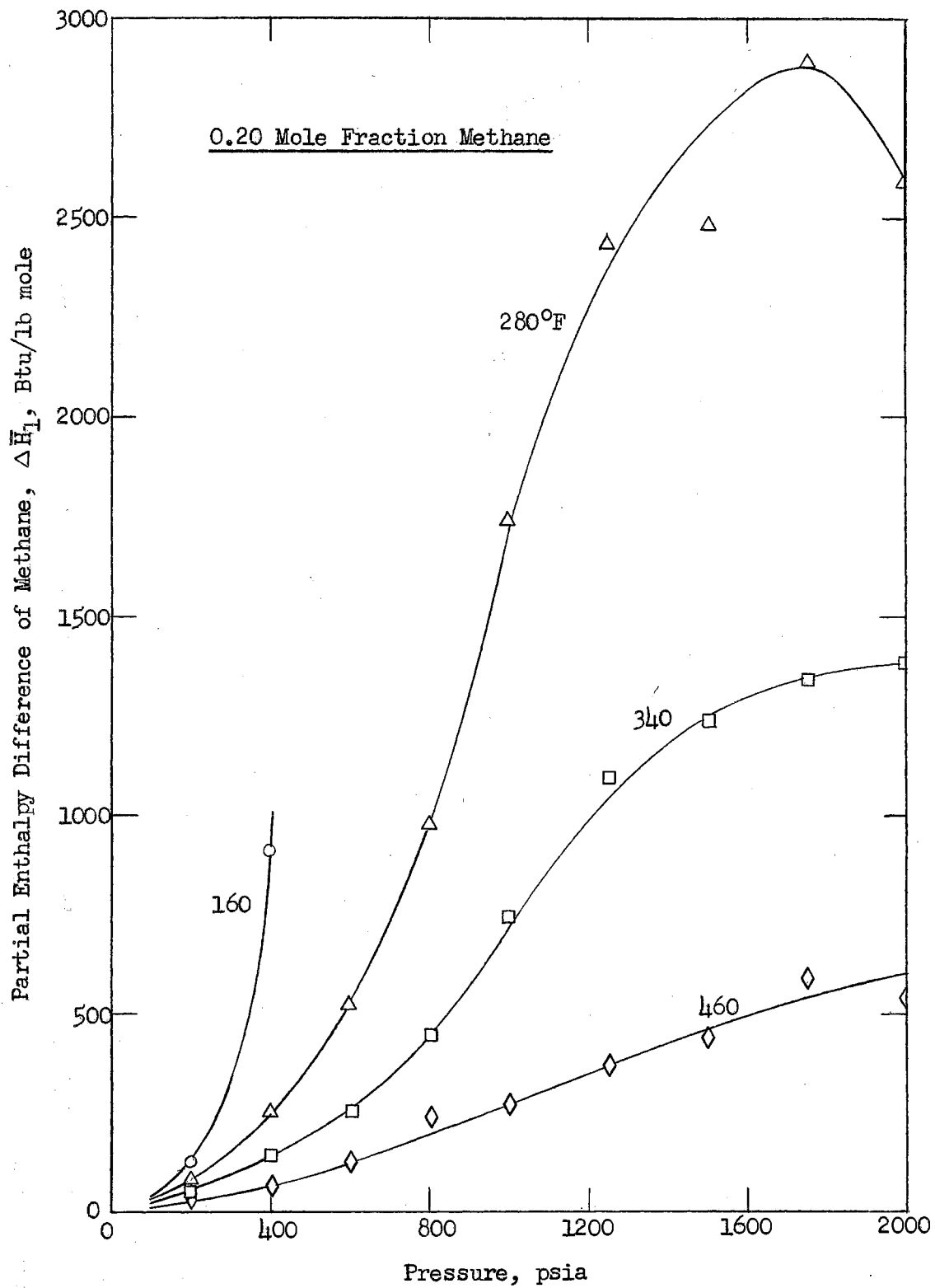
Figure 7

Partial Enthalpy Difference of Methane as a Function of Pressure
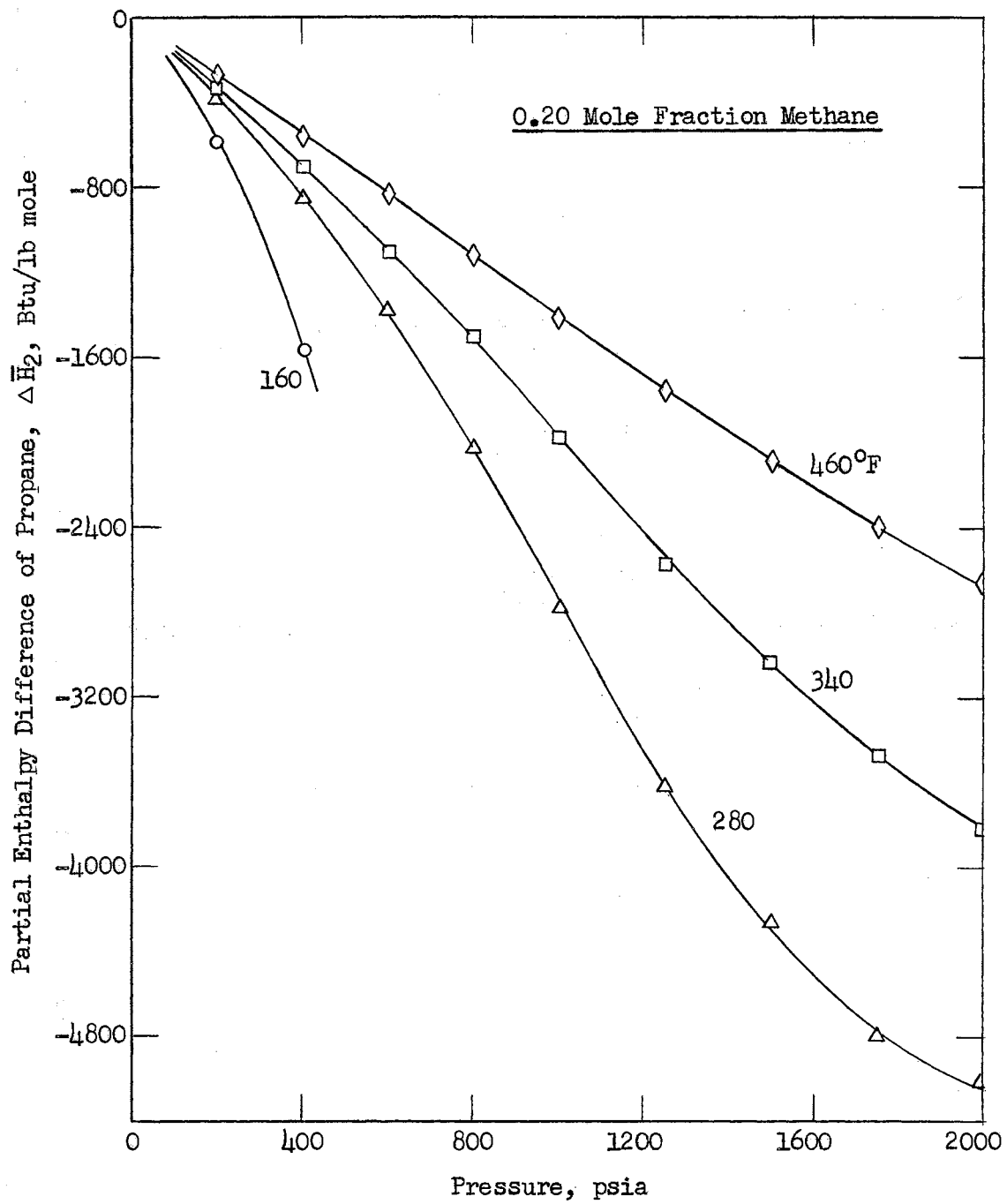
Figure 8

Partial Enthalpy Difference of Propane as a Function of Pressure
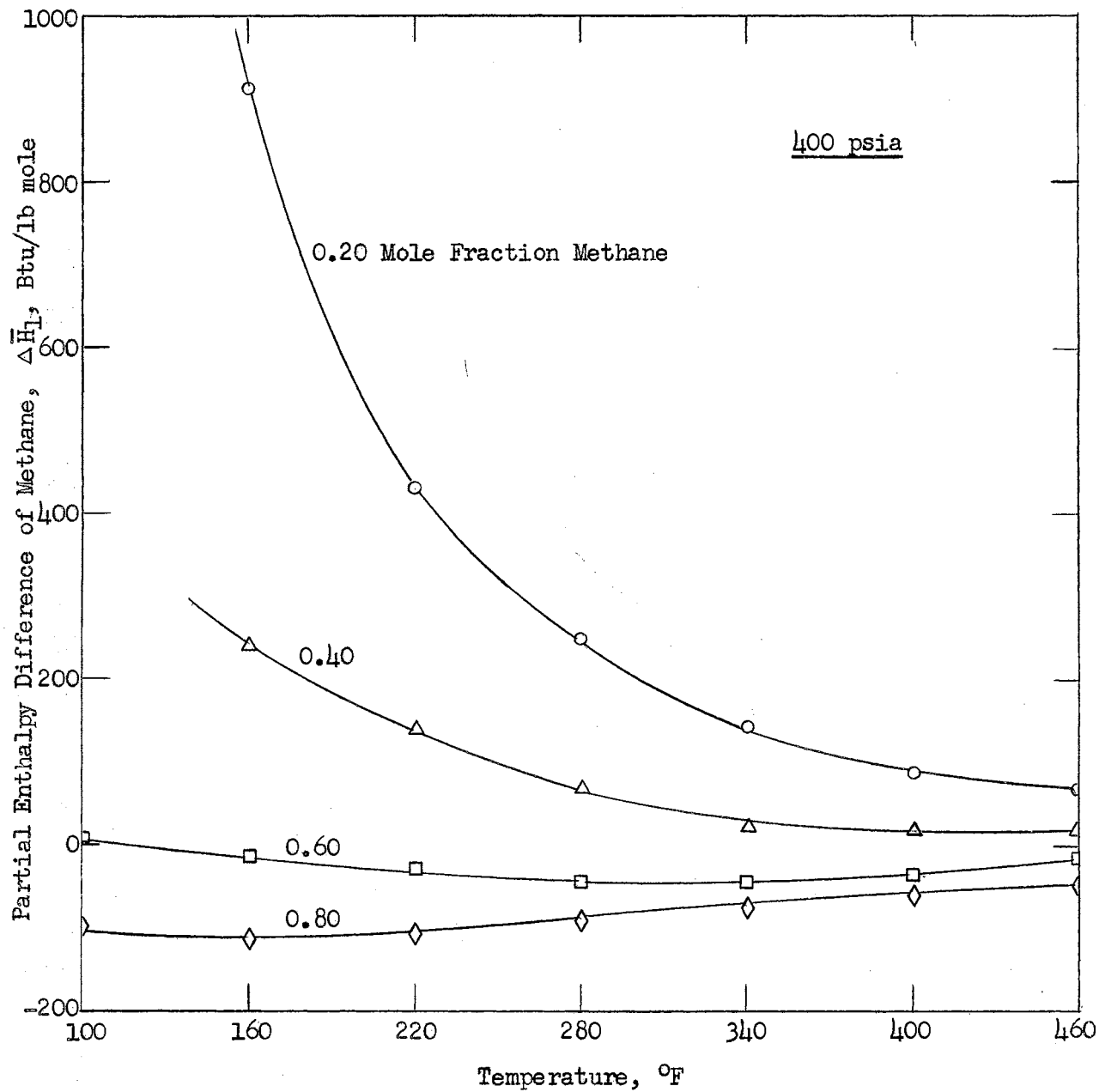
Figure 9

Partial Enthalpy Difference of Methane as a Function of Temperature
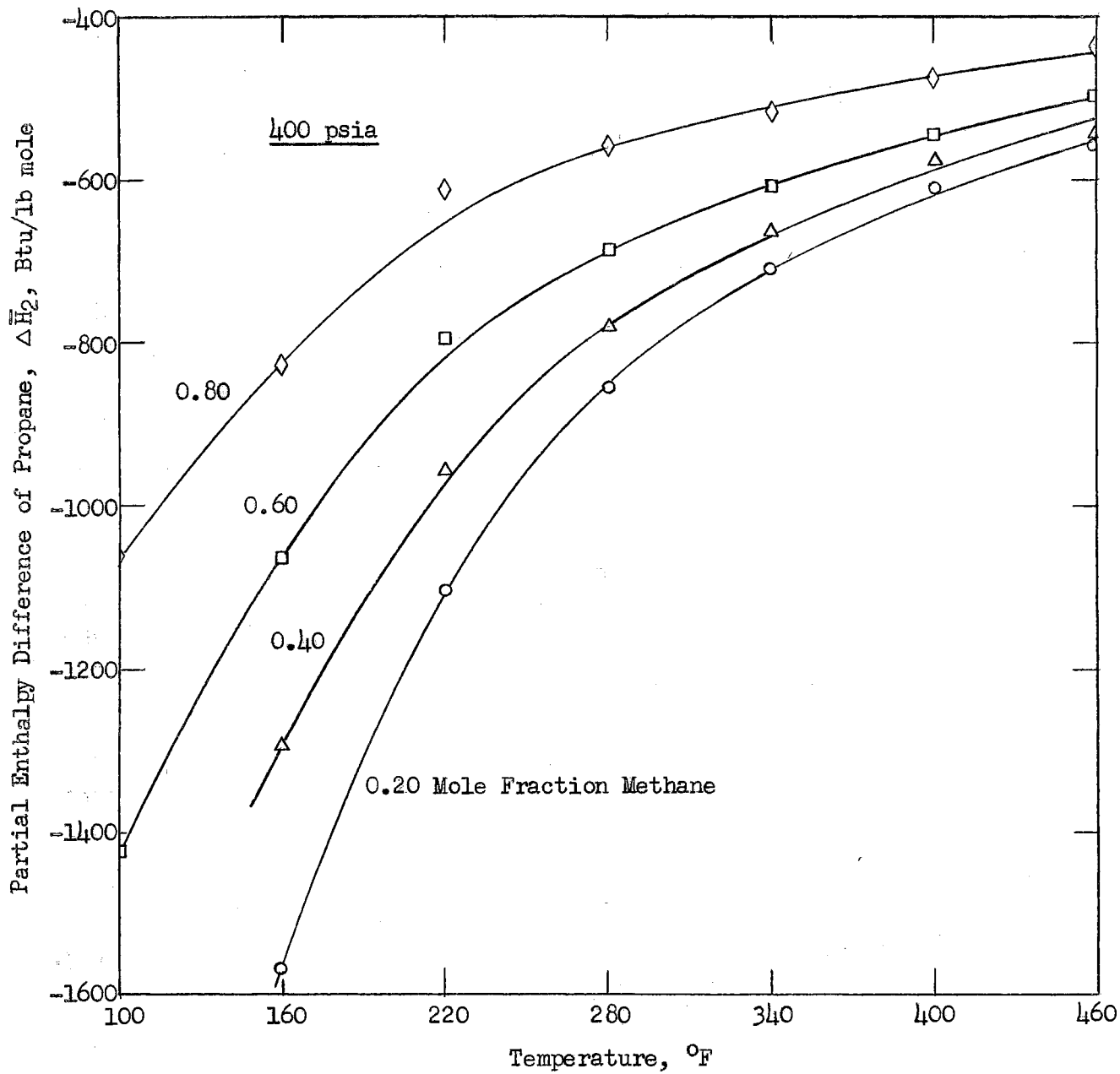
Figure 10

Partial Enthalpy Difference of Propane as a Function of Temperature

Accuracy of Mixture Enthalpy Values

The accuracy of the mixture enthalpy values is limited by the errors in the original data, errors introduced in calculating the partial derivative, errors in smoothing the data and errors in graphical integration. The error introduced in calculating the partial derivative can be estimated by the error functions of the equations used.

At a constant temperature and pressure the slope of the residual volume versus temperature curve decreases as the composition of methane in the binary increases. The errors introduced in using equations 34, 35 and 36 were calculated for each equation at different compositions. This gave the per cent error that each numerical differentiation equation would introduce in the right side of equation 37 at different values of $(\delta\alpha/\delta T)_{P,y}$. The errors calculated using the error functions were averaged arithmetically for each equation used to obtain the partial derivative. The average error introduced by using the forward differences equation was 2.33%. The average error inherent in the backward differences equation was 3.68%. The equation used for the interior temperatures introduced an average error of 1.02%.

The equation used to obtain the partial derivative for the interior temperatures is a more accurate equation than the equations used for the terminal temperatures. This is evident since more terms are used in this equation and points are taken on both sides of the point at which the slope is calculated. The backward differences equation was used in a region of smaller slope than was the forward differences equation as can be seen in Figure 1. This difference in slope caused the difference in error for the forward and backward difference equations.

The errors introduced by smoothing and by graphical integration were assumed to be negligible. The smoothing plot was used to reduce errors and to make the data conform to theoretical considerations at zero pressure. The graphical integration using the Ott planimeter was performed twice for each area. The two tracings were done using different but symmetrically opposed positions of the planimeter. The mean value of the two areas was used as the correct area. This method compensates for any mechanical errors introduced by using the planimeter.

Values of the mixture enthalpy difference were calculated at 492 separate combinations of temperature, pressure and composition. The deviation of each calculated value from the smoothed value of the enthalpy difference was calculated by the formula

$$\% \text{ deviation} = \frac{\triangle H_{\text{smoothed}} - \triangle H_{\text{calculated}}}{\triangle H_{\text{smoothed}}} 100 \qquad (42)$$

Of the 492 calculated values, 238 were positive deviations, 52 had no deviation and 202 were negative deviations from the smoothed values. The average positive deviation was 1.60% and the average negative deviation was 1.86%.

The deviation defined by equation 42 was compared with the error of the original data and the errors introduced in taking the partial derivatives in the following way. Of the 492 calculated partial derivatives, 330 were calculated using equation 36 while equations 34 and 35 each were used to calculate 81 partial derivatives. The fraction of partial derivatives calculated using equation 36 was 0.670 and the fraction for equations 34 and 35 was 0.165 for each. The overall average error introduced by the numerical differentiation equations was assumed to be

the sum of the fraction of partial derivatives taken by each equation times the average error calculated for that equation. Then the overall average error introduced by the numerical differentiation equations is

$$0.670(1.02\%) + 0.165(2.33\% + 3.68\%) = 1.68\%$$

The overall average error of the calculated mixture enthalpy difference should be the error of the original data plus the average error introduced in the numerical differentiation. A value of 0.2 to 0.3% for the variation of the original data would give an overall average error in the calculated mixture enthalpy difference of 1.9 to 2.0%. The average deviation of the calculated mixture enthalpy difference from the smooth curve is within this error. The difference between the two deviations probably is due to smoothing the partial derivatives.

Accuracy of Partial Enthalpy Values

The accuracy of the partial enthalpy difference is less than that of the mixture enthalpy difference. This is evident since a numerical differentiation of the mixture enthalpy difference is required to obtain the partial enthalpy difference. Equation 36 was used to calculate the partial derivative $(\delta \triangle H/\delta y_1)_{T,P}$ from curves of the type shown in Figure 4. The error function was used to calculate the error introduced in the partial derivatives by using equation 36.

To obtain the average error introduced by equation 36, the error in the partial derivative was calculated at several points. The points were selected so the error was calculated for large values, small values and intermediate values of the partial derivative. The arithmetic average error in the partial derivative was 0.81%, which was assumed to be

the average error introduced by using equation 36. The overall average error of the partial derivative $(\delta\triangle H/\delta y_1)_{T,P}$ should be the sum of the error of the mixture enthalpy difference and the error introduced in the partial derivative. This would give an overall average error between 2.5 and 3.0%.

For the methane - propane binary, the mixture enthalpy difference was always a negative quantity. The partial derivative $(\delta\triangle H/\delta y_1)_{T,P}$ was always a positive quantity. Thus from equation 30 the partial enthalpy difference of methane is a difference between two numbers. The partial enthalpy difference of methane is positive for low concentrations of methane and negative for high concentrations of methane at a given temperature and pressure. This means that for a given composition range, usually 0.40 to 0.70 mole fraction methane, the partial enthalpy difference of methane is a small difference between two large numbers. In this case a per cent deviation could be a large number while the numerical deviation could be small relative to the deviation at a lower or higher composition. For this reason a per cent error in the partial enthalpy difference values of methane is not given. Due to the three smoothing plots, the average deviation of the partial enthalpy difference of methane probably does not exceed 20 Btu/lb mole except near the two phase region or at low mole fractions of methane (0.10 or 0.20).

The partial enthalpy difference of propane is the sum of two negative quantities. The average error in the partial enthalpy difference of propane should be the sum of the overall average errors of the mixture enthalpy difference and the partial derivative $(\delta\triangle H/\delta y_1)_{T,P}$, or between 4 and 5%. The deviation of the calculated partial enthalpy difference of propane from the final smoothed values was calculated by

$$\% \text{ deviation} = \frac{\Delta\bar{H}_{smoothed} - \Delta\bar{H}_{calculated}}{\Delta\bar{H}_{smoothed}} \, 100 \qquad (43)$$

The partial enthalpy difference of propane was calculated at 488 different combinations of temperature, pressure and composition. There were 181 negative deviations, 26 points had no deviation and 281 had positive deviations from the smoothed values. The average negative deviation was 2.21% and the average positive deviation was 2.68%. The difference between the deviation calculated by equation 43 and the predicted deviation is undoubtedly due to the smoothing of the mixture enthalpy difference before the partial derivative $(\delta\Delta H/\delta y_1)_{T,P}$ was taken.

The consistency of the smoothed partial enthalpies was checked using equation 33. The smoothed partial enthalpy differences were plotted against mole fraction methane with a temperature parameter for each pressure as shown in Figures 11 and 12. Equation 33 was rearranged to the following form

$$\frac{\left(\dfrac{\delta\Delta\bar{H}_1}{\delta y_1}\right)_{T,P}}{-\left(\dfrac{\delta\Delta\bar{H}_2}{\delta y_1}\right)_{T,P}} = \frac{1-y_1}{y_1} \qquad (44)$$

and was applied to these curves at 0.50 mole fraction methane. The slope of the tangent to the methane and propane partial enthalpy difference curves was calculated by numerical differentiation. This calculation was performed for several temperatures at each of the nine pressures used in this work.

At 0.50 mole fraction the ratio of the partial derivatives would
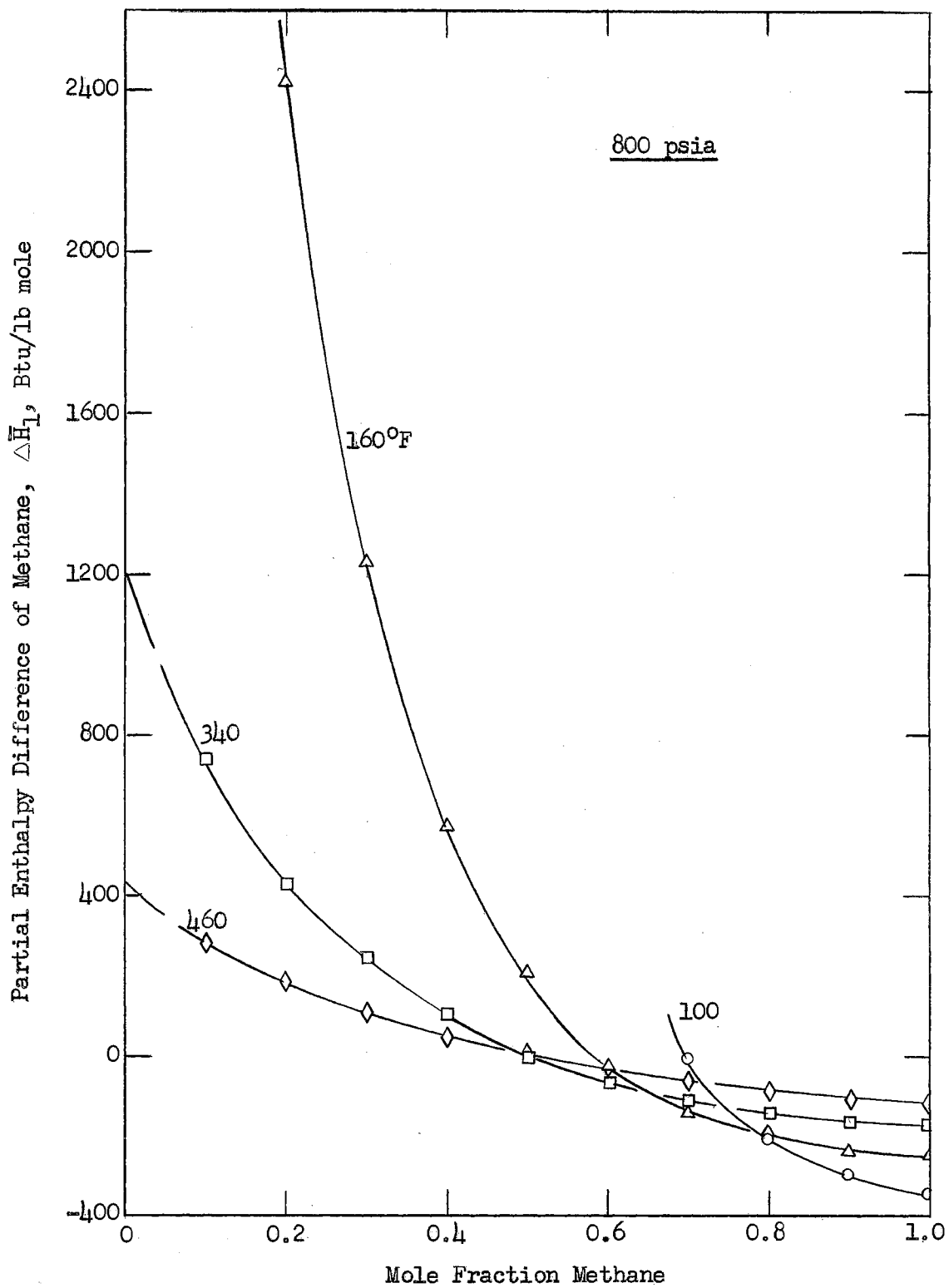
Figure 11

Partial Enthalpy Difference of Methane as a Function of Composition
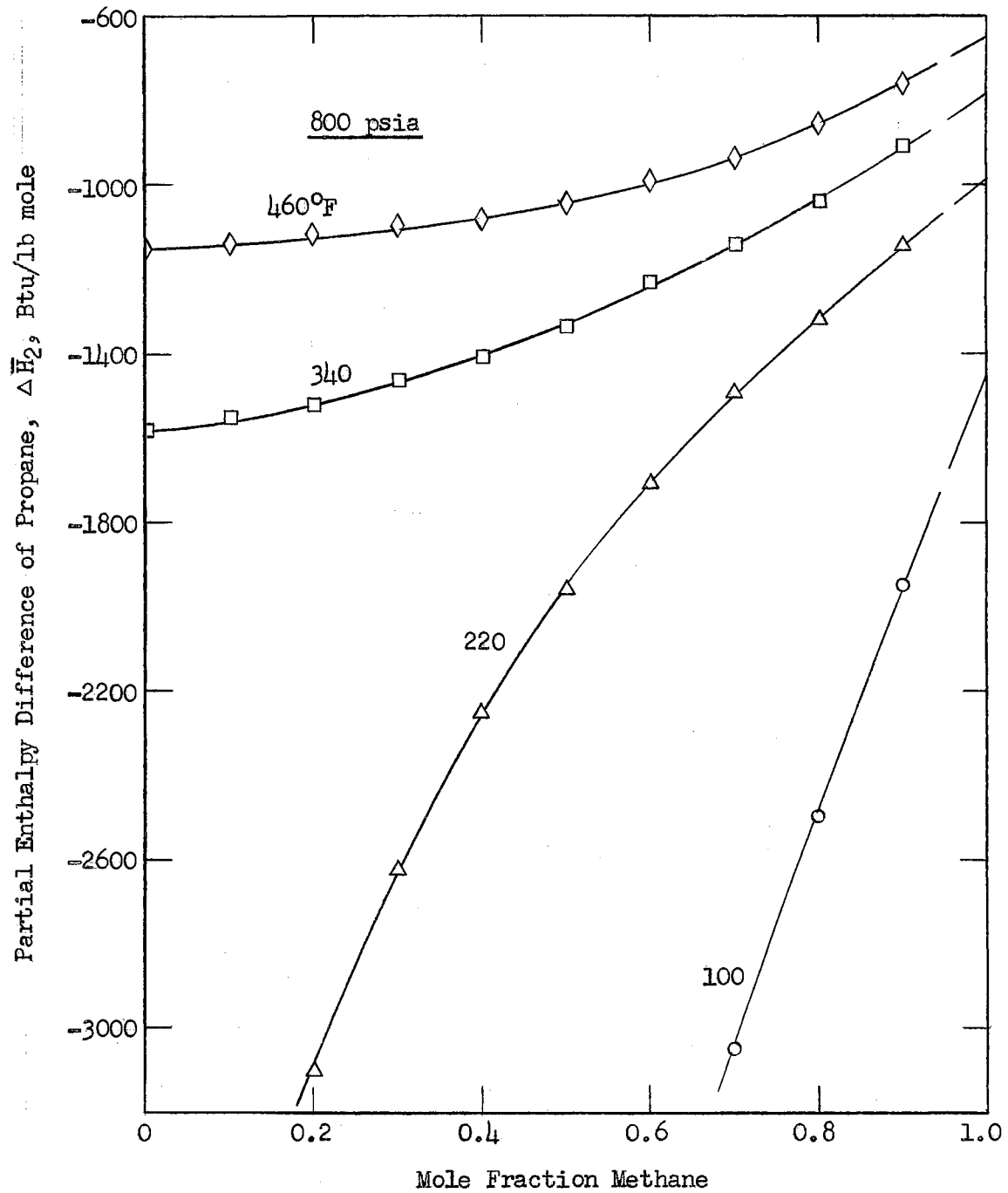
Figure 12

Partial Enthalpy Difference of Propane as a Function of Composition

be unity for consistent partial enthalpies. The average ratio of the 24 points tested was 1.03. This test is very critical for the partial enthalpy difference of methane. In this composition region the partial enthalpy difference of methane is a small difference between two relatively large numbers.

Results

The final smoothed values of the mixture enthalpy difference and the partial enthalpy differences of methane and propane are tabulated in Table I. To obtain the absolute value of the mixture enthalpy above the base temperature at a given temperature, pressure and composition, the ideal gas enthalpy of the mixture at the given temperature must be added to the mixture enthalpy difference.

$$H = (H^P - H^O)_{T,y} + (H^O_T - H^O_{T_b})_y \qquad (45)$$

where T_b is the base temperature for the ideal gas enthalpies.

The absolute value of the partial enthalpy of a component above the base temperature at a given condition (temperature, pressure and composition) may be obtained by adding the ideal gas enthalpy of the component at the given temperature to the partial enthalpy difference.

$$\overline{H}_i = (\overline{H}^P_i - H^O_i)_{T,y} + (H^O_T - H^O_{T_b})_{i,y} \qquad (46)$$

A consistent compilation of ideal gas enthalpies for hydrocarbons is given by Rossini (14). The data in Table I used with the compilations of Rossini give absolute values of mixture enthalpy and partial enthalpies that may be used in both chemical and physical equilibrium

calculations.

The comparison of the partial enthalpy differences calculated in this work with the partial enthalpy differences calculated from experimental Joule-Thomson coefficients and calculated heat capacities is shown in Table II. Table III is a comparison of the enthalpy difference for pure methane that was used in this work and the enthalpy difference calculated from Joule-Thomson coefficients and heat capacities (1). Table III is added only for convenience in comparing the two methods of obtaining enthalpy data.

TABLE I

1 of 7

ENTHALPY DIFFERENCES FOR METHANE - PROPANE BINARY

(Btu/lb mole)

100°F

y_1^*	ΔH	$\Delta \bar{H}_1$	$\Delta \bar{H}_2$	ΔH	$\Delta \bar{H}_1$	$\Delta \bar{H}_2$	ΔH	$\Delta \bar{H}_1$	$\Delta \bar{H}_2$
	——— 200 psia ———			——— 400 psia ———			——— 600 psia ———		
0.10	-770	450	-906						
0.20	-645	356	-895						
0.30	-527	262	-865						
0.40	-419	169	-811						
0.50	-328	86	-715	-685	280	-1843			
0.60	-252	6	-636	-548	33	-1460	-886	133	-2366
0.70	-193	-33	-554	-418	-52	-1258	-656	-36	-2061
0.80	-144	-52	-471	-300	-104	-1062	-471	-153	-1782
0.90	-107	-73	-401	-216	-145	-845	-342	-217	-1385
	——— 800 psia ———			——— 1000 psia ———			——— 1250 psia ———		
0.70	-918	-3	-3052	-1188	40	-4055			
0.80	-652	-203	-2496	-834	-273	-3146	-1054	-378	-3858
0.90	-467	-297	-1947	-596	-378	-2497	-757	-494	-3135
	——— 1500 psia ———			——— 1750 psia ———			——— 2000 psia ———		
0.80	-1267	-462	-4428	-1464	-534	-5180	-1642	-686	-5580
0.90	-925	-614	-3720	-1090	-736	-4278	-1243	-836	-4910

* Component 1 is Methane

TABLE I (Continued)   2 of 7

160°F

y_1	ΔH	$\Delta \bar{H}_1$	$\Delta \bar{H}_2$	ΔH	$\Delta \bar{H}_1$	$\Delta \bar{H}_2$	ΔH	$\Delta \bar{H}_1$	$\Delta \bar{H}_2$
	——— 200 psia ———			——— 400 psia ———			——— 600 psia ———		
0.10	-521	196	-599	-1356	1535	-1677			
0.20	-451	143	-595	-1072	913	-1568			
0.30	-383	99	-583	-856	507	-1444	-1454	1412	-2716
0.40	-320	66	-560	-680	267	-1293	-1112	717	-2262
0.50	-263	24	-534	-540	100	-1173	-847	253	-2157
0.60	-211	-17	-503	-430	-15	-1047	-658	14	-1678
0.70	-166	-40	-455	-335	-72	-932	-512	-95	-1457
0.80	-126	-56	-392	-254	-112	-803	-392	-162	-1248
0.90	-94	-66	-335	-189	-137	-684	-295	-207	-1068
	——— 800 psia ———			——— 1000 psia ———			——— 1250 psia ———		
0.40	-1642	2131	-4158	-2277	5157	-5790	-3015	4046	-7565
0.50	-1183	553	-2919	-1519	983	-4073	-2084	1606	-5776
0.60	-900	77	-2380	-1137	194	-3163	-1482	363	-4235
0.70	-693	-122	-2007	-879	-157	-2557	-1120	-196	-3277
0.80	-528	-220	-1735	-671	-283	-2214	-844	-353	-2776
0.90	-396	-271	-1433	-501	-337	-1878	-626	-426	-2317
	——— 1500 psia ———			——— 1750 psia ———			——— 2000 psia ———		
0.40	-3495	3515	-8660	-3875	3117	-8790	-4060	2773	-8350
0.50	-2553	1612	-6776	-2838	1438	-7156	-3064	1158	-7286
0.60	-1832	386	-5188	-2100	344	-5742	-2320	253	-6250
0.70	-1356	-224	-4006	-1572	-240	-4719	-1766	-95	-5264
0.80	-1020	-413	-3264	-1174	-475	-3754	-1323	-546	-4226
0.90	-746	-507	-2755	-855	-587	-3193	-970	-660	-3580

TABLE I (Continued)   3 of 7

220°F

y_1	ΔH	$\Delta \bar{H}_1$	$\Delta \bar{H}_2$	ΔH	$\Delta \bar{H}_1$	$\Delta \bar{H}_2$	ΔH	$\Delta \bar{H}_1$	$\Delta \bar{H}_2$
	——— 200 psia ———			——— 400 psia ———			——— 600 psia ———		
0.10	-409	143	-470	-948	600	-1153	-1691	2400	-2146
0.20	-353	101	-465	-786	433	-1106	-1312	1142	-1938
0.30	-299	66	-456	-641	285	-1037	-1027	674	-1785
0.40	-249	38	-447	-516	128	-954	-808	322	-1580
0.50	-204	4	-424	-413	28	-871	-642	114	-1400
0.60	-164	-25	-402	-330	-38	-806	-507	-36	-1253
0.70	-131	-42	-370	-264	-75	-742	-400	-105	-1108
0.80	-104	-54	-325	-208	-104	-655	-311	-152	-958
0.90	-81	-60	-281	-162	-121	-580	-240	-178	-863
	——— 800 psia ———			——— 1000 psia ———			——— 1250 psia ———		
0.20	-1937	2425	-3100	-2710	4466	-4504	-3630		
0.30	-1463	1234	-2623	-1937	2077	-3657	-2667	5067	-5982
0.40	-1123	574	-2253	-1437	917	-3006	-1854	1505	-4084
0.50	-874	211	-1958	-1108	302	-2525	-1416	423	-3207
0.60	-683	-22	-1710	-865	18	-2187	-1098	52	-2776
0.70	-537	-133	-1494	-673	-163	-1915	-850	-197	-2423
0.80	-417	-200	-1318	-521	-252	-1667	-653	-312	-2105
0.90	-321	-237	-1141	-398	-290	-1446	-496	-361	-1784
	——— 1500 psia ———			——— 1750 psia ———			——— 2000 psia ———		
0.20	-4176			-4436			-4628		
0.30	-3300	5528	-7082	-3474	4409	-7090	-3675	3965	-6949
0.40	-2240	1633	-4894	-2573	1629	-5372	-2817	1293	-5555
0.50	-1706	492	-3844	-1975	586	-4440	-2226	486	-4917
0.60	-1322	53	-3363	-1526	76	-3894	-1734	72	-4411
0.70	-1033	-220	-2926	-1174	-237	-3396	-1333	-208	-3866
0.80	-792	-364	-2527	-890	-414	-2910	-1012	-440	-3316
0.90	-600	-426	-2146	-673	-481	-2492	-763	-537	-2800

TABLE I (Continued)   4 of 7

280°F

y_1	ΔH	$\Delta \bar{H}_1$	$\Delta \bar{H}_2$	ΔH	$\Delta \bar{H}_1$	$\Delta \bar{H}_2$	ΔH	$\Delta \bar{H}_1$	$\Delta \bar{H}_2$
	——— 200 psia ———			——— 400 psia ———			——— 600 psia ———		
0.10	-340	108	-393	-736	369	-865	-1210	935	-1451
0.20	-293	75	-390	-625	244	-843	-1000	524	-1406
0.30	-251	48	-384	-529	148	-817	-831	296	-1332
0.40	-213	25	-375	-443	67	-776	-681	145	-1234
0.50	-178	-8	-356	-365	-7	-731	-550	24	-1141
0.60	-147	-27	-330	-300	-44	-684	-440	-54	-1047
0.70	-119	-38	-306	-240	-70	-638	-352	-98	-954
0.80	-94	-48	-275	-187	-91	-571	-277	-134	-849
0.90	-71	-54	-244	-141	-101	-509	-211	-148	-752
	——— 800 psia ———			——— 1000 psia ———			——— 1250 psia ———		
0.10	-1768	1790	-2157	-2394	3014	-2975	-3117	4401	-3952
0.20	-1420	1026	-2012	-1879	1646	-2715	-2407	2295	-3573
0.30	-1140	513	-1826	-1483	935	-2454	-1883	1312	-3227
0.40	-923	250	-1687	-1173	431	-2253	-1482	665	-2840
0.50	-750	68	-1567	-937	113	-2000	-1182	167	-2528
0.60	-601	-58	-1403	-744	-50	-1778	-938	-38	-2254
0.70	-475	-123	-1283	-591	-153	-1617	-740	-184	-2019
0.80	-369	-174	-1147	-462	-214	-1445	-576	-263	-1807
0.90	-278	-197	-1006	-349	-244	-1256	-432	-302	-1556
	——— 1500 psia ———			——— 1750 psia ———			——— 2000 psia ———		
0.10	-3641	4760	-4612	-3941	4713	-5062	-4130	4196	-5140
0.20	-2912	2723	-4306	-3263	2885	-4803	-3490	2583	-4955
0.30	-2275	1552	-3915	-2612	1635	-4433	-2874	1497	-4637
0.40	-1772	743	-3418	-2061	835	-3941	-2283	737	-4242
0.50	-1390	227	-3003	-1626	258	-3432	-1807	260	-3860
0.60	-1100	-38	-2684	-1274	-34	-3100	-1433	-14	-3509
0.70	-872	-204	-2408	-980	-214	-2770	-1127	-228	-3109
0.80	-677	-303	-2170	-745	-349	-2490	-872	-366	-2814
0.90	-511	-354	-1893	-557	-401	-2178	-651	-447	-2458

TABLE I (Continued) 5 of 7

340°F

y_1	ΔH	$\Delta \bar{H}_1$	$\Delta \bar{H}_2$	ΔH	$\Delta \bar{H}_1$	$\Delta \bar{H}_2$	ΔH	$\Delta \bar{H}_1$	$\Delta \bar{H}_2$
	——— 200 psia ———			——— 400 psia ———			——— 600 psia ———		
0.10	-297	80	-340	-622	240	-718	-967	434	-1123
0.20	-258	54	-336	-538	144	-704	-824	257	-1097
0.30	-223	34	-329	-461	83	-687	-700	142	-1058
0.40	-192	15	-321	-392	36	-664	-593	58	-1021
0.50	-162	-10	-308	-328	-18	-638	-492	-13	-974
0.60	-134	-24	-289	-269	-45	-607	-400	-56	-916
0.70	-108	-33	-271	-215	-60	-569	-319	-86	-857
0.80	-83	-40	-251	-166	-74	-515	-246	-108	-768
0.90	-62	-45	-222	-123	-83	-457	-183	-123	-681
	——— 800 psia ———			——— 1000 psia ———			——— 1250 psia ———		
0.10	-1325	738	-1554	-1738	1187	-2045	-2254	1875	-2643
0.20	-1112	430	-1521	-1437	742	-1966	-1838	1005	-2522
0.30	-943	244	-1463	-1194	393	-1864	-1507	583	-2413
0.40	-797	105	-1405	-996	186	-1768	-1241	280	-2264
0.50	-660	-3	-1334	-814	43	-1652	-1010	64	-2100
0.60	-535	-63	-1227	-655	-67	-1537	-808	-71	-1905
0.70	-424	-111	-1139	-522	-134	-1422	-642	-159	-1765
0.80	-324	-139	-1035	-403	-173	-1288	-495	-212	-1606
0.90	-239	-163	-903	-299	-201	-1130	-367	-252	-1400
	——— 1500 psia ———			——— 1750 psia ———			——— 2000 psia ———		
0.10	-2667	2160	-3150	-3046	2185	-3586	-3341	2192	-3934
0.20	-2180	1238	-3035	-2507	1344	-3470	-2773	1384	-3813
0.30	-1813	700	-2899	-2090	788	-3323	-2302	813	-3637
0.40	-1487	345	-2706	-1726	414	-3110	-1903	400	-3485
0.50	-1205	108	-2525	-1397	118	-2844	-1543	130	-3204
0.60	-967	-72	-2294	-1105	-69	-2623	-1227	-66	-2970
0.70	-757	-180	-2103	-864	-196	-2426	-960	-207	-2729
0.80	-575	-246	-1923	-657	-278	-2202	-730	-307	-2476
0.90	-421	-284	-1705	-483	-324	-1956	-542	-370	-2198

TABLE I (Continued)   6 of 7

400°F

y_1	ΔH	$\Delta \bar{H}_1$	$\Delta \bar{H}_2$	ΔH	$\Delta \bar{H}_1$	$\Delta \bar{H}_2$	ΔH	$\Delta \bar{H}_1$	$\Delta \bar{H}_2$
	——— 200 psia ———			——— 400 psia ———			——— 600 psia ———		
0.10	-266	57	-299	-541	159	-626	-818	235	-954
0.20	-232	39	-296	-468	90	-614	-705	144	-936
0.30	-200	23	-291	-401	55	-601	-605	88	-914
0.40	-169	9	-285	-342	21	-588	-516	32	-880
0.50	-142	-7	-274	-288	-16	-569	-433	-14	-855
0.60	-117	-18	-264	-235	-36	-546	-352	-43	-823
0.70	-93	-26	-250	-187	-46	-519	-278	-66	-774
0.80	-71	-32	-234	-143	-59	-472	-213	-87	-706
0.90	-52	-35	-209	-104	-67	-418	-155	-100	-623
	——— 800 psia ———			——— 1000 psia ———			——— 1250 psia ———		
0.10	-1115	400	-1296	-1401	650	-1646	-1768	1020	-2110
0.20	-950	231	-1275	-1188	330	-1600	-1486	480	-2065
0.30	-810	126	-1254	-1013	183	-1553	-1265	280	-1986
0.40	-686	56	-1220	-857	78	-1492	-1063	112	-1914
0.50	-571	-12	-1171	-714	17	-1435	-886	26	-1817
0.60	-466	-50	-1097	-579	-59	-1364	-722	-62	-1683
0.70	-368	-86	-1028	-454	-104	-1270	-570	-124	-1584
0.80	-280	-113	-939	-344	-139	-1158	-432	-172	-1448
0.90	-203	-133	-823	-250	-165	-1020	-313	-206	-1274
	——— 1500 psia ———			——— 1750 psia ———			——— 2000 psia ———		
0.10	-2132	1253	-2495	-2443	1400	-2934	-2705	1366	-3246
0.20	-1780	710	-2443	-2042	820	-2863	-2266	852	-3155
0.30	-1496	364	-2377	-1721	445	-2740	-1917	480	-3054
0.40	-1257	179	-2288	-1437	227	-2614	-1616	211	-2950
0.50	-1043	52	-2180	-1186	53	-2460	-1343	53	-2765
0.60	-847	-65	-2015	-962	-75	-2307	-1087	-82	-2602
0.70	-666	-143	-1872	-758	-160	-2162	-852	-181	-2422
0.80	-504	-202	-1722	-576	-230	-1983	-641	-260	-2206
0.90	-365	-240	-1536	-416	-274	-1758	-465	-305	-1973

TABLE I (Continued) 7 of 7

460°F

y_1	$\triangle H$	$\triangle \bar{H}_1$	$\triangle \bar{H}_2$	$\triangle H$	$\triangle \bar{H}_1$	$\triangle \bar{H}_2$	$\triangle H$	$\triangle \bar{H}_1$	$\triangle \bar{H}_2$
	--------- 200 psia ---------			--------- 400 psia ---------			--------- 600 psia ---------		
0.10	-250	35	-281	-498	103	-560	-741	183	-847
0.20	-218	25	-278	-434	70	-549	-639	122	-834
0.30	-187	14	-274	-375	45	-538	-547	77	-825
0.40	-159	6	-269	-318	20	-529	-462	33	-806
0.50	-132	-2	-263	-263	0	-513	-383	4	-786
0.60	-107	-10	-252	-212	-16	-498	-311	-22	-750
0.70	-83	-18	-238	-165	-31	-477	-245	-46	-702
0.80	-63	-22	-223	-123	-47	-438	-185	-70	-651
0.90	-45	-25	-202	-88	-55	-384	-132	-85	-572
	--------- 800 psia ---------			--------- 1000 psia ---------			--------- 1250 psia ---------		
0.10	-988	282	-1137	-1242	413	-1426	-1555	586	-1778
0.20	-843	186	-1115	-1070	262	-1402	-1326	360	-1744
0.30	-719	110	-1096	-921	148	-1366	-1132	205	-1694
0.40	-611	48	-1077	-777	64	-1328	-955	94	-1646
0.50	-511	10	-1040	-643	16	-1289	-786	26	-1590
0.60	-415	-27	-993	-516	-32	-1226	-636	-36	-1517
0.70	-326	-59	-933	-400	-73	-1150	-498	-92	-1437
0.80	-244	-88	-854	-297	-109	-1056	-377	-133	-1312
0.90	-174	-110	-755	-212	-136	-937	-267	-171	-1154
	--------- 1500 psia ---------			--------- 1750 psia ---------			--------- 2000 psia ---------		
0.10	-1840	783	-2123	-2107	950	-2442	-2345	884	-2718
0.20	-1575	470	-2070	-1800	572	-2398	-2007	538	-2643
0.30	-1342	260	-2016	-1535	286	-2317	-1718	299	-2580
0.40	-1130	126	-1950	-1295	135	-2226	-1453	96	-2497
0.50	-932	34	-1888	-1070	29	-2160	-1203	5	-2411
0.60	-752	-42	-1800	-862	-55	-2064	-967	-80	-2306
0.70	-587	-112	-1680	-677	-132	-1941	-754	-153	-2156
0.80	-441	-158	-1550	-512	-185	-1792	-563	-213	-1970
0.90	-314	-197	-1371	-365	-227	-1571	-401	-251	-1747

TABLE II   1 of 2

COMPARISON OF PARTIAL ENTHALPIES CALCULATED IN THIS WORK

AND BY BUDENHOLZER, ET AL (1)

$\Delta \overline{H}$ of Methane, Btu/lb mole

P, psia	100°F		160°F		220°F		280°F	
	This Work	Ref. (1)	This Work	Ref. (1)	This Work	Ref. (1)	This Work	Ref. (1)
	————————— 0.647 Mole Fraction Methane ————————————							
200	-15	-34	-29	-35	-33	-39	-33	-37
400	-17	-40	-43	-48	-55	-69	-58	-59
600			-53	-47	-72	-88	-80	-101
800			-35	-35	-75	-95	-97	-127
1000			-15	-13	-72	-90	-98	-143
1250					-78	-77	-108	-152
1500					-127	-64	-150	-148
	————————— 0.805 Mole Fraction Methane ————————————							
200	-63	-74	-57	-61	-53	-51	-49	-47
400	-106	-151	-112	-125	-109	-106	-93	-95
600	-155	-233	-174	-191	-151	-162	-137	-143
800	-212	-319	-245	-262	-206	-217	-179	-189
1000	-275	-419	-285	-334	-250	-270	-213	-234
1250			-355	-432	-315	-334	-262	-287
1500			-417	-536	-368	-393	-306	-335
	————————— 0.917 Mole Fraction Methane ————————————							
200	-78	-79	-66	-66	-60	-55	-52	-47
400	-146	-162	-133	-133	-124	-111	-101	-95
600	-223	-247	-211	-204	-178	-170	-152	-143
800	-313	-335	-279	-273	-240	-228	-199	-193
1000	-380	-425	-347	-345	-287	-284	-242	-239
1250	-522	-542	-435	-435	-346	-353	-300	-297
1500	-632	-666	-513	-525	-430	-420	-344	-353

TABLE II (Continued)

$\Delta\bar{H}$ of Propane, Btu/lb mole

P, psia	100°F This Work	100°F Ref. (1)	160°F This Work	160°F Ref. (1)	220°F This Work	220°F Ref. (1)	280°F This Work	280°F Ref. (1)
			0.647 Mole Fraction Methane					
200	-616	-569	-482	-463	-360	-357	-315	-287
400	-1340	-1252	-1001	-1001	-740	-754	-641	-587
600			-1578	-1587	-1181	-1186	-974	-908
800			-2180	-2200	-1603	-1654	-1350	-1244
1000			-2715	-2831	-2053	-2134	-1722	-1592
1250					-2626	-2729	-2190	-2050
1500					-3136	-3272	-2534	-2522
			0.805 Mole Fraction Methane					
200	-468	-463	-404	-379	-295	-318	-271	-260
400	-1141	-979	-833	-785	-606	-653	-550	-525
600	-1786	-1530	-1244	-1208	-992	-992	-825	-798
800	-2416	-2103	-1709	-1632	-1268	-1340	-1131	-1072
1000	-3162	-2668	-2147	-2046	-1623	-1684	-1448	-1354
1250	-3603	-3312	-2790	-2527	-2077	-2103	-1813	-1698
1500			-3410	-2946	-2475	-2491	-2130	-2028
			0.917 Mole Fraction Methane					
200	-369	-450	-337	-366	-248	-304	-238	-265
400	-860	-944	-713	-750	-511	-626	-486	-529
600	-1410	-1482	-1033	-1155	-780	-952	-723	-803
800	-1856	-2064	-1423	-1570	-1043	-1283	-980	-1075
1000	-2456	-2690	-1846	-1989	-1340	-1605	-1268	-1341
1250	-2812	-3506	-2320	-2505	-1705	-1997	-1560	-1662
1500	-3545	-4348	-2807	-2994	-2025	-2377	-1896	-1953

TABLE III

COMPARISON OF METHANE ENTHALPY DIFFERENCES FROM SAGE

AND LACEY (15) AND BUDENHOLZER, ET AL (1)

Btu/lb mole

P, psia	Ref. (15)	Ref. (1)	Ref. (15)	Ref. (1)
	--------- 100°F ---------		--------- 160°F ---------	
200	-87.1	-81.6	-73.5	-68.8
400	-174.6	-163.2	-146.8	-137.6
600	-262.6	-251.2	-219.5	-206.4
800	-350.3	-337.6	-291.3	-276.8
1000	-437.7	-422.4	-362.1	-340.8
1250	-546.2	-529.6	-448.4	-424.0
1500	-652.9	-632.0	-531.8	-502.4
	--------- 220°F ---------		--------- 280°F ---------	
200	-62.0	-54.4	-52.2	-46.4
400	-124.9	-112.0	-103.8	-94.4
600	-185.2	-169.6	-154.7	-142.2
800	-245.4	-227.2	-204.4	-190.4
1000	-304.4	-281.6	-253.0	-238.4
1250	-376.0	-348.8	-311.7	-296.0
1500	-445.0	-412.8	-368.2	-353.6

Note: Reference (15) values were used in this work.

CHAPTER III

GENERAL CORRELATIONS

Data Used in Correlations

The data used in the correlations of the mixture enthalpy differ-
ence of methane binaries and the partial enthalpy of methane in various
binaries were obtained from Sage and Lacey (15) and from Table I. Sage
and Lacey tabulate partial enthalpy values for both components of the
methane – ethane, methane – n-butane and methane – n-pentane binaries in
the superheated vapor region. For use in this work the ideal gas en-
thalpy of the component had to be subtracted from the tabulated values
of Sage and Lacey to obtain the partial enthalpy difference $\Delta \bar{H}_i$. The
partial enthalpy difference values obtained from Sage and Lacey and used
in this work are shown in Table XIV, Appendix C.

For the methane – ethane binary, the partial enthalpy of methane is
tabulated at 0.50, 0.60, 0.70, 0.80 and 0.90 mole fraction methane for
the temperature range 70 to 250°F and the pressure range 200 to 3000
psia. The partial enthalpy of ethane is tabulated for 0.10, 0.20, 0.30,
0.40, 0.50 and 0.60 mole fraction methane for the same temperature and
pressure ranges. Thus the mixture enthalpy can be calculated at only
two compositions, 0.50 and 0.60 mole fraction methane. The maximum
uncertainty of this data was estimated by Sage and Lacey to be about
30 Btu/lb mole.

The partial enthalpies of methane and n-butane were tabulated at

0.85, 0.90 and 0.95 mole fraction methane for the temperature range 100

to 250°F and the pressure range 200 to 3000 psia. Sage and Lacey state

that the uncertainty of the partial enthalpy of methane should be less

than 20 Btu/lb mole. Also the uncertainty should be less than 35

Btu/lb mole for the partial enthalpy of n-butane.

The partial enthalpies of methane and n-pentane were tabulated by

Sage and Lacey at 0.96 and 0.98 mole fraction methane for the tempera-

tures 100, 160 and 220°F and for the pressure range 200 to 3000 psia.

The volumetric data for this binary were less accurate than the volu-

metric data for the methane - ethane and methane - n-butane binaries.

No uncertainty was given for the methane and n-pentane partial enthalpy

values. However, the uncertainty of the partial enthalpies will un-

doubtedly be greater than that given for the methane - ethane and

methane - n-butane binaries.

The range and accuracy of the methane - propane mixture enthalpy

and partial enthalpy differences have already been discussed. The

methane - propane binary is the only system used that covers the com-

plete composition range, from pure methane to pure propane.

In the methane - ethane binary system Sage and Lacey did not tabu-

late partial enthalpies of a component when that component was present

in low mole fractions. They state that the greatest uncertainty in the

partial enthalpy is at small mole fractions of the component in question.

In this work the difficulty of poor accuracy in the partial enthalpy of

a component at low mole fractions was overcome by using the dimension-

less smoothing plots based on equations 38 through 41.

The pure component data of methane, ethane, propane and n-butane

were available from Sage and Lacey (15). These data were used in the

general correlations to assure that the mixture data and the pure component data were consistent. Also the partial enthalpy of methane should be consistent with the enthalpy of pure methane.

Correlation of Mixture Enthalpy

Pitzer, et al (12) extended the principle of corresponding states by introducing a third parameter, the acentric factor ω. The acentric factor of a component is defined as

$$\omega = - \log (P^O/P_c) - 1.000 \quad \text{at } T_r = 0.70 \tag{47}$$

where P^O is the vapor pressure of the component.

P_c is the critical temperature of the component.

T_r is the reduced temperature of the component, T/T_c.

For a pure fluid the acentric factor measures the deviation of the intermolecular potential function from that of the spherical molecules of the simple fluids, argon, krypton and xenon.

Pitzer, et al found that the compressibility factor of pure fluids could be represented by an equation linear in the acentric factor.

$$z = z^{(0)}(P_r, T_r) + \omega z^{(1)}(P_r, T_r) \tag{48}$$

where $z^{(0)}$ and $z^{(1)}$ are universal functions of the reduced temperature and pressure.

Curl and Pitzer (3) used the compressibility factor correlation to determine the enthalpy of pure fluids by

$$\frac{H^O - H}{RT_c} = \left(\frac{H^O - H}{RT_c}\right)^{(0)} + \omega \left(\frac{H^O - H}{RT_c}\right)^{(1)} \tag{49}$$

The functions $\left(\dfrac{H^0 - H}{RT_c}\right)^{(0)}$ and $\left(\dfrac{H^0 - H}{RT_c}\right)^{(1)}$ were calculated from values of $z^{(0)}$ and $z^{(1)}$, respectively, by the appropriate form of the thermo-dynamic equation

$$\left(\frac{H^0 - H}{RT_c}\right) = T_r^2 \int_0^{P_r} \frac{1}{P_r}\left(\frac{\delta z}{\delta T_r}\right)_P dP_r \tag{50}$$

The method used for correlating the superheated vapor enthalpies is an extension of the method developed by Curl and Pitzer. The mixture enthalpy difference was correlated by using a pseudo acentric factor ω_{pm}, a pseudo reduced temperature $T_{pr} = T/T_{pc}$ and a pseudo reduced pressure $P_{pr} = P/P_{pc}$. The pseudo critical temperature and pressure were calculated by Kay's Rule (9). The pseudo acentric factor was cal-culated for the binary by a mole fraction average of the pure component acentric factors.

$$\omega_{pm} = y_1\omega_1 + y_2\omega_2 \tag{51}$$

The pure component acentric factors used in this work were calculated using the data of Rossini (14). These values are shown in Table IV.

TABLE IV

PURE COMPONENT ACENTRIC FACTORS

Component	Acentric Factor
Methane	0.0102
Ethane	0.0985
Propane	0.1523
n-Butane	0.2009
n-Pentane	0.2518

The mixture enthalpy difference from the ideal gas was correlated by the equation

$$\Delta H = \Delta H^{(0)} + \omega_{pm} \Delta H^{(1)} \tag{52}$$

In using this correlation method, the mixture enthalpy difference was plotted against ω_{pm} with a P_{pr} parameter at a constant T_{pr} as shown in Figure 13. Straight lines were drawn through the data points, which included both mixture and pure component data. The value of ΔH for a given P_{pr} at the intercept of the $\omega_{pm} = 0$ axis is the value of $\Delta H^{(0)}$, and the slope of the given P_{pr} line gives the value of $\Delta H^{(1)}$ for a given T_{pr} and P_{pr}. The values of $\Delta H^{(0)}$ and $\Delta H^{(1)}$ were each plotted against T_{pr} with a P_{pr} parameter so that evenly spaced values of T_{pr} could be obtained. The final correlation of $\Delta H^{(0)}$ and $\Delta H^{(1)}$ plotted against P_{pr} with a T_{pr} parameter is shown in Figures 14 and 15. The values of $\Delta H^{(0)}$ and $\Delta H^{(1)}$ as a function of T_{pr} and P_{pr} are given in Table V.

TABLE V

VALUES OF $\Delta H^{(0)}$ AND $\Delta H^{(1)}$ AS FUNCTIONS OF T_{pr} AND P_{pr}

Btu/lb mole

P_{pr}	$\Delta H^{(0)}$	$\Delta H^{(1)}$	$\Delta H^{(0)}$	$\Delta H^{(1)}$	$\Delta H^{(0)}$	$\Delta H^{(1)}$	$\Delta H^{(0)}$	$\Delta H^{(1)}$
	$T_{pr} = 1.10$		$T_{pr} = 1.15$		$T_{pr} = 1.20$		$T_{pr} = 1.30$	
0.5	-380	-2420	-320	-2220	-270	-2080	-205	-1900
1.0	-850	-5670	-685	-5060	-575	-4590	-435	-3980
1.5	-1425	-9490	-1125	-8300	-925	-7430	-690	-6130
2.0	-2080	-11900	-1625	-10800	-1310	-9910	-950	-8170
2.5	-2875	-13460	-2175	-12440	-1715	-11510	-1225	-9920
3.0			-2890	-13740	-2150	-12770	-1515	-11090
3.5					-2650	-13840	-1835	-11970
	$T_{pr} = 1.40$		$T_{pr} = 1.60$		$T_{pr} = 1.80$		$T_{pr} = 2.00$	
0.5	-165	-1770	-125	-1540	-105	-1450	-90	-1380
1.0	-350	-3610	-250	-3090	-210	-2820	-185	-2710
1.5	-550	-5420	-380	-4580	-315	-4120	-260	-3960
2.0	-745	-7110	-510	-5940	-410	-5360	-330	-5100
2.5	-955	-8590	-650	-7140	-505	-6450	-395	-6100
3.0	-1175	-9740	-800	-8070	-610	-7320	-475	-6870
3.5	-1410	-10600	-965	-8720	-725	-7910	-580	-7320
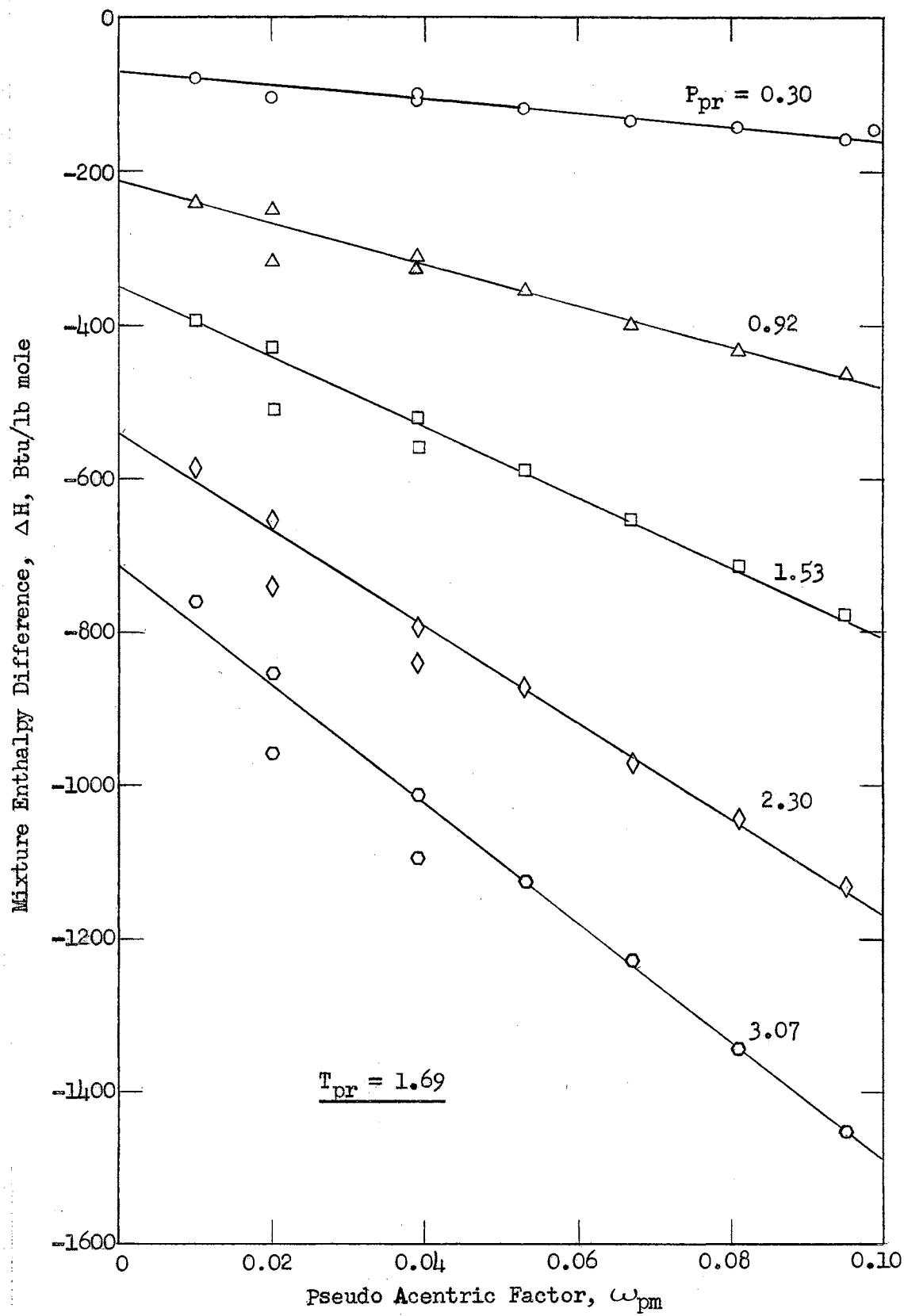
Figure 13

Mixture Enthalpy Difference of Methane Binaries
as a Function of the Pseudo Acentric Factor
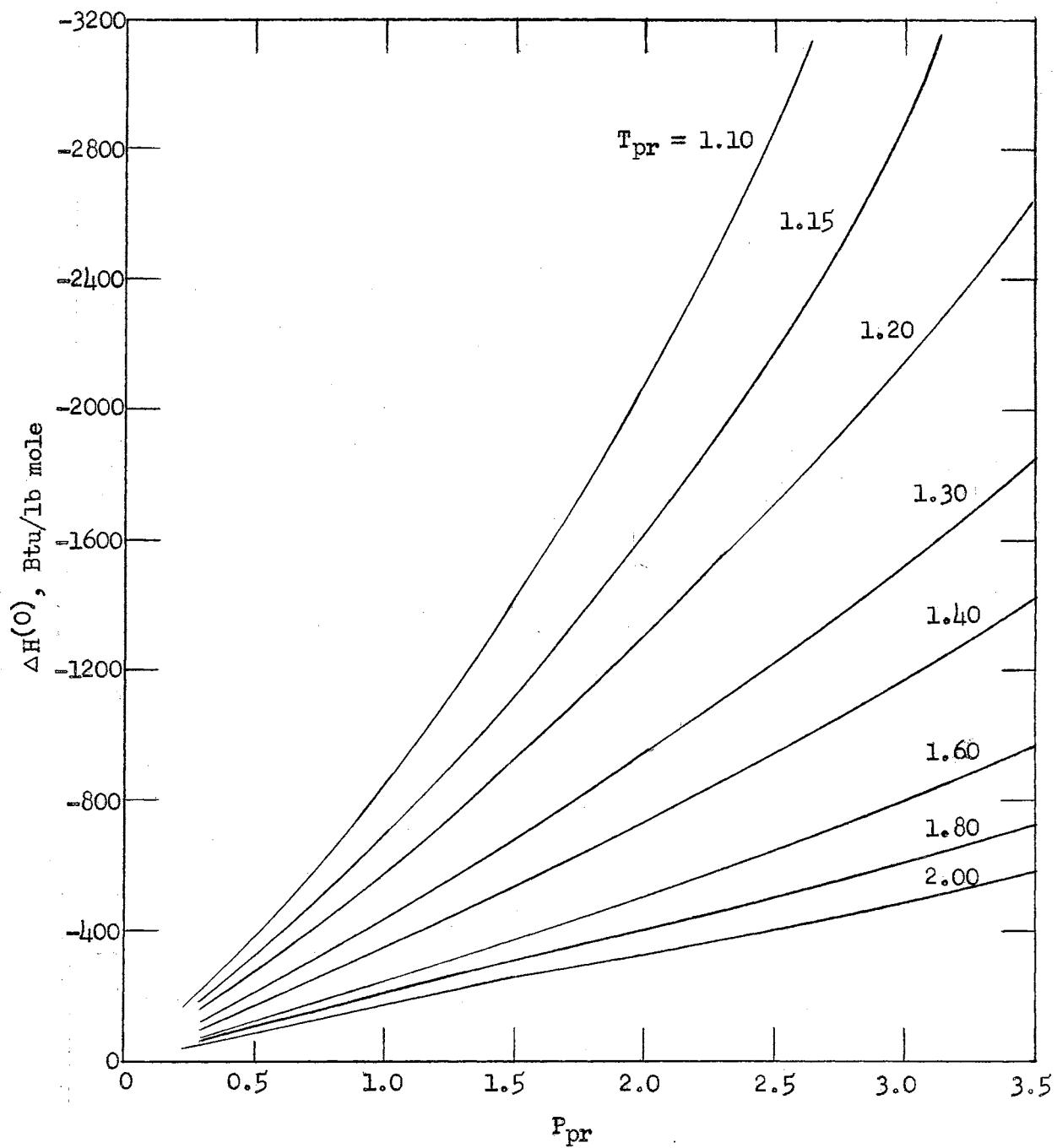
Figure 14

$\Delta H^{(0)}$ as a Function of T_{pr} and P_{pr}
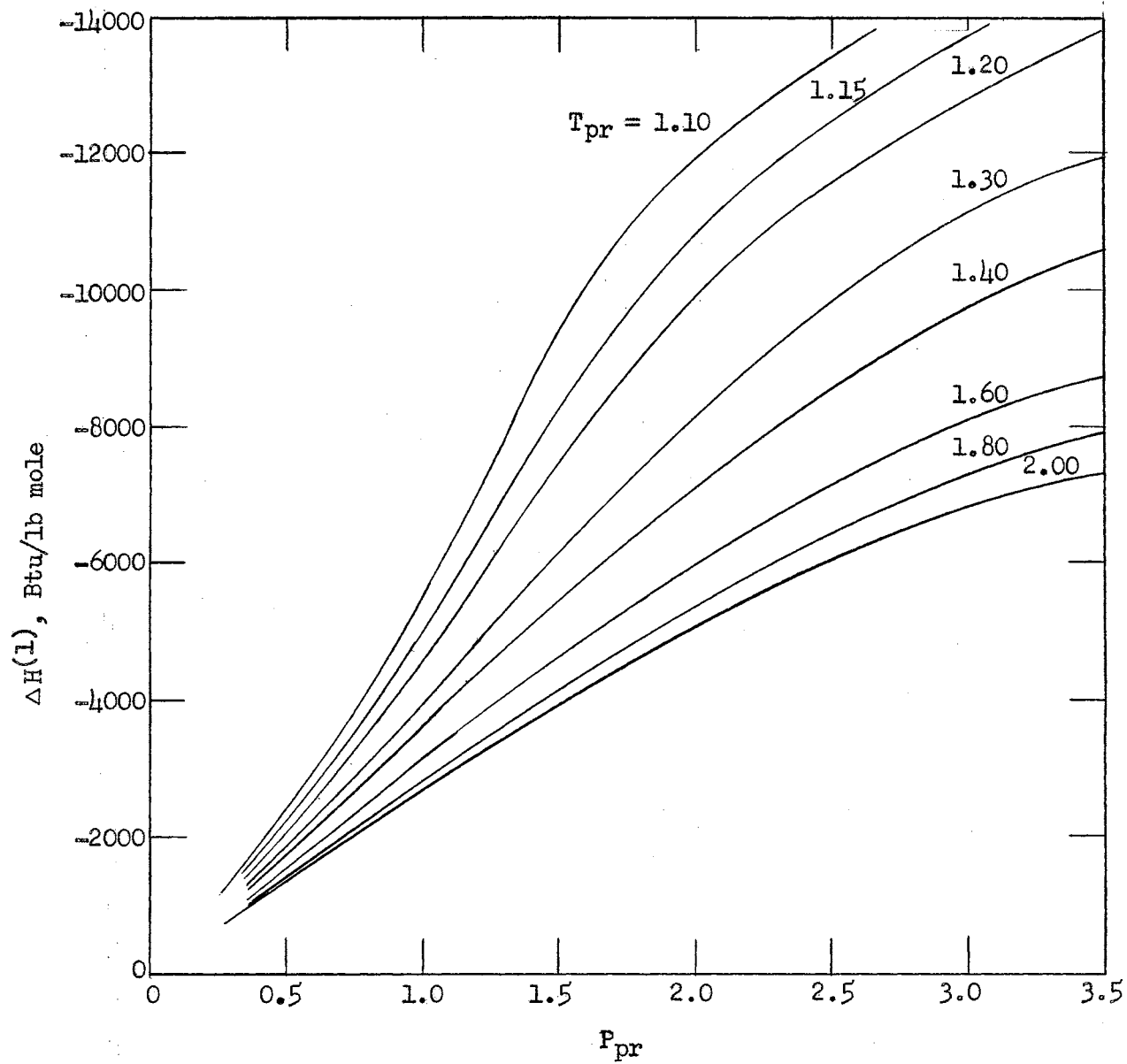
Figure 15

$\Delta H^{(1)}$ as a Function of T_{pr} and P_{pr}

Figures 14 and 15 and the values of $\Delta H^{(0)}$ and $\Delta H^{(1)}$ in Table 5 should not be used for an ω_{pm} above 0.15. No mixture enthalpy data were available at an ω_{pm} above 0.15, nor do Sage and Lacey give any enthalpy values for n-pentane above $T_r = 1.10$. The enthalpy values given for n-butane at 430°F were employed in the correlating plot at the lowest reduced temperature used. However, due to the lack of mixture enthalpy data and enthalpy data for n-butane at higher reduced temperatures the correlation is not recommended above $\omega_{pm} = 0.15$.

The accuracy of the general correlation was tested by comparing the mixture enthalpy difference obtained from the correlation with calculated data that were not used in making the correlation. The comparisons are shown in Table VI.

An attempt was made to correlate the mixture enthalpy difference using an equation of the form

$$\frac{\Delta H}{RT_{pc}} = \left(\frac{\Delta H}{RT_{pc}}\right)^{(0)} + \omega_{pm}\left(\frac{\Delta H}{RT_{pc}}\right)^{(1)} \tag{53}$$

However, the initial plots of $\Delta H/RT_{pc}$ against ω_{pm} for a given T_{pr} and P_{pr} gave a greater scatter of points than did the plots of ΔH against ω_{pm}.

Correlation of Partial Enthalpy of Methane

The partial enthalpy difference of methane was correlated by using the pseudo acentric factor, pseudo reduced temperature and pseudo reduced pressure. The equation used to correlate the partial enthalpy difference was

$$\Delta \bar{H} = \Delta \bar{H}^{(0)} + \omega_{pm}\Delta \bar{H}^{(1)} \tag{54}$$

TABLE VI

COMPARISON OF MIXTURE ENTHALPY DIFFERENCE CORRELATION

WITH CALCULATED VALUES

Btu/lb mole

P, psia	$\triangle H_{correl}$	$\triangle H_{calc}$
--- Methane - Ethane Binary ---		
$y_1^* = 0.50$, T = 250°F		
200	-119	-106
800	-447	-434
1500	-770	-812
2250	-1358	-1213
--- Methane - n-Butane Binary ---		
$y_1 = 0.90$, T = 130°F		
400	-223	-219
800	-461	-464
1250	-732	-739
1750	-1039	-1025
--- Methane - n-Pentane Binary -		
$y_1 = 0.96$, T = 100°F		
400	-204	-250
800	-423	-501
1250	-664	-775
2000	-1081	-1142

* Component 1 is Methane

P, psia	$\triangle H_{correl}$	$\triangle H_{calc}$
--- Methane - Propane Binary ---		
$y_1 = 0.20$, T = 340°F		
200	-267	-258
600	-850	-824
1000	-1440	-1437
1500	-2219	-2180
2000	-2879	-2773
$y_1 = 0.60$, T = 400°F		
200	-120	-117
600	-364	-352
1000	-603	-579
1500	-864	-847
2000	-1100	-1087
$y_1 = 0.50$, T = 220°F		
200	-194	-204
600	-645	-642
1000	-1124	-1108
1500	-1710	-1706
2000	-2242	-2226
$y_1 = 0.90$, T = 280°F		
200	-74	-71
600	-230	-211
1000	-362	-349
1500	-513	-511
2000	-664	-651

The partial enthalpy of methane was plotted against ω_{pm} with a P_{pr} parameter at a constant T_{pr} as shown in Figure 16. Straight lines were drawn through the data points which included pure component methane data. The values of $\Delta\bar{H}^{(0)}$ and $\Delta\bar{H}^{(1)}$ were obtained from the intercept and slope of the P_{pr} lines, respectively. These quantities were each plotted against T_{pr} with a P_{pr} parameter so that evenly spaced values of T_{pr} could be obtained. The final correlation of $\Delta\bar{H}^{(0)}$ and $\Delta\bar{H}^{(1)}$ plotted against P_{pr} with a T_{pr} parameter is shown in Figures 17 and 18. The values of $\Delta\bar{H}^{(0)}$ and $\Delta\bar{H}^{(1)}$ as a function of T_{pr} and P_{pr} are given in Table VII. These values of $\Delta\bar{H}^{(0)}$ and $\Delta\bar{H}^{(1)}$ should not be used above $\omega_{pm} = 0.12$.

The accuracy of the correlation was checked by comparing the partial enthalpy difference obtained from the correlation with calculated data that were not used in making the correlation. The comparisons are shown in Table VIII.

An attempt was made to correlate the partial enthalpy difference of methane by using the pseudo acentric factor and the pure component reduced temperature and pressure. No correlation could be developed by this method.

An attempt was also made to correlate the partial enthalpy differences of the solvents: ethane, propane, n-butane and n-pentane. The equation that was used in this attempt was

$$\left(\frac{\Delta\bar{H}}{RT_c}\right)_i = \left(\frac{\Delta\bar{H}}{RT_c}\right)_i^{(0)} + \omega_{pm}\left(\frac{\Delta\bar{H}}{RT_c}\right)_i^{(1)} \tag{55}$$

The pseudo critical temperatures and pressures were the parameters. However, the partial enthalpy difference of the solvents did not correlate by this method.
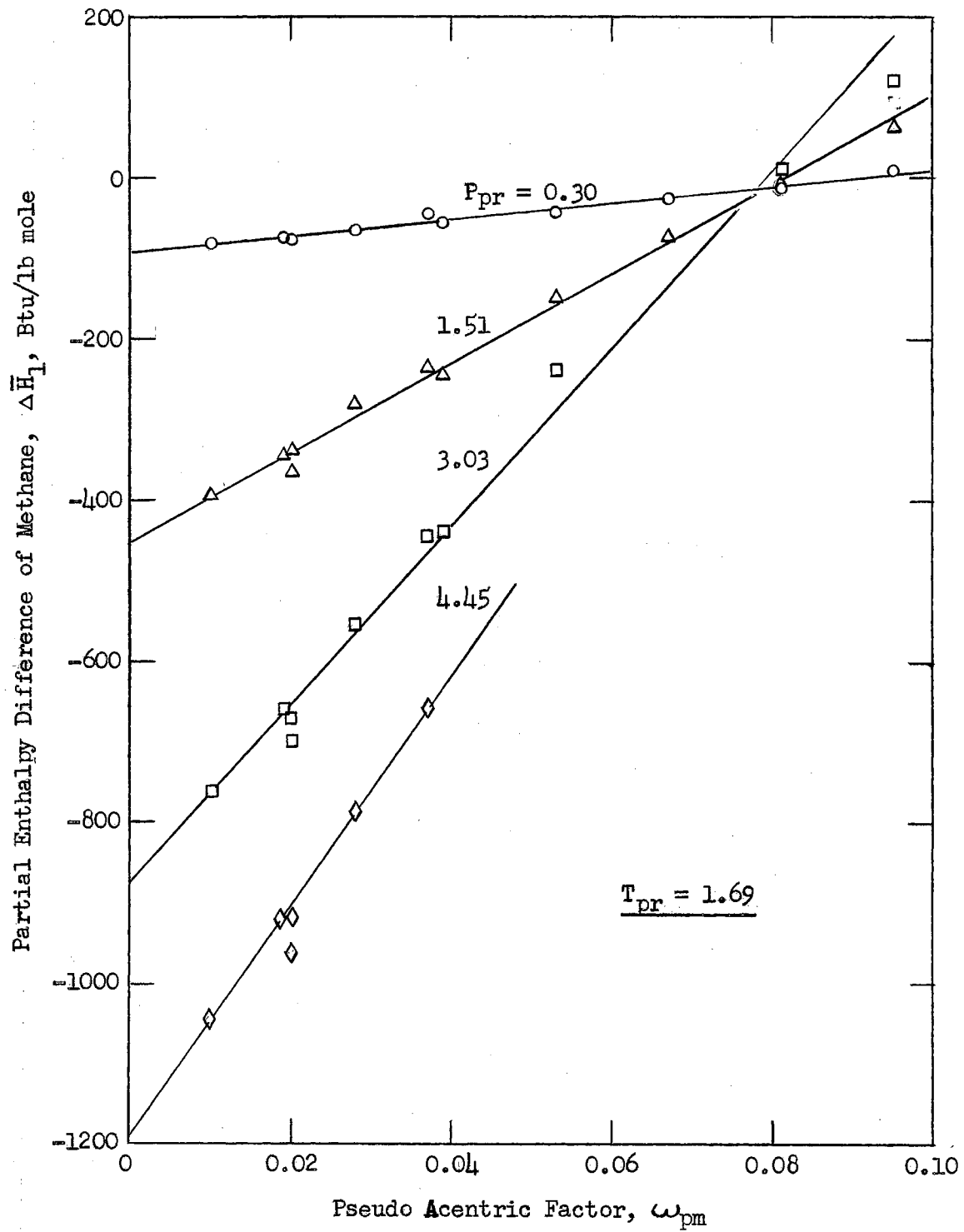
Figure 16

Partial Enthalpy Difference of Methane as a
Function of the Pseudo Acentric Factor
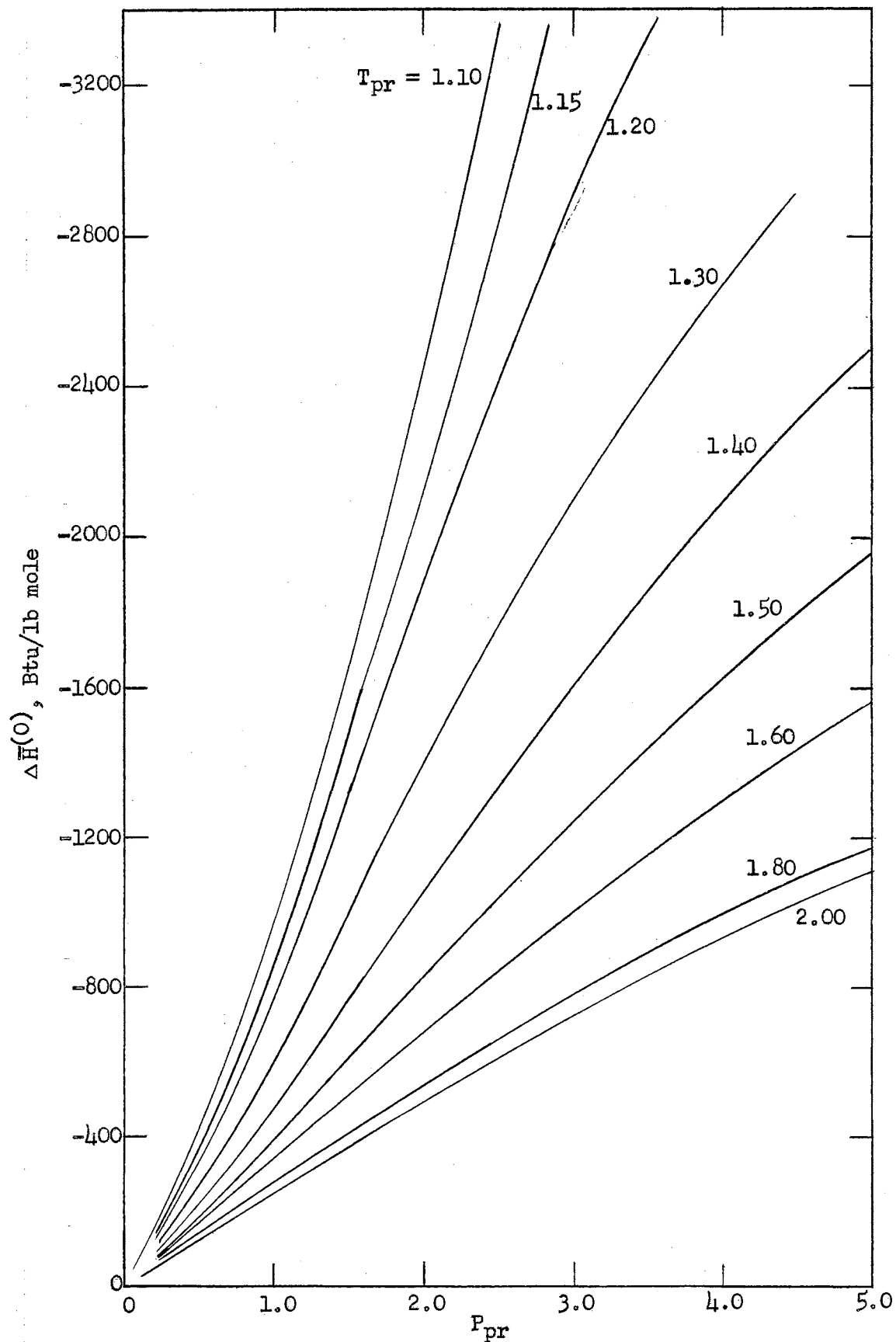
Figure 17

$\triangle \overline{H}^{(0)}$ as a Function of T_{pr} and P_{pr}
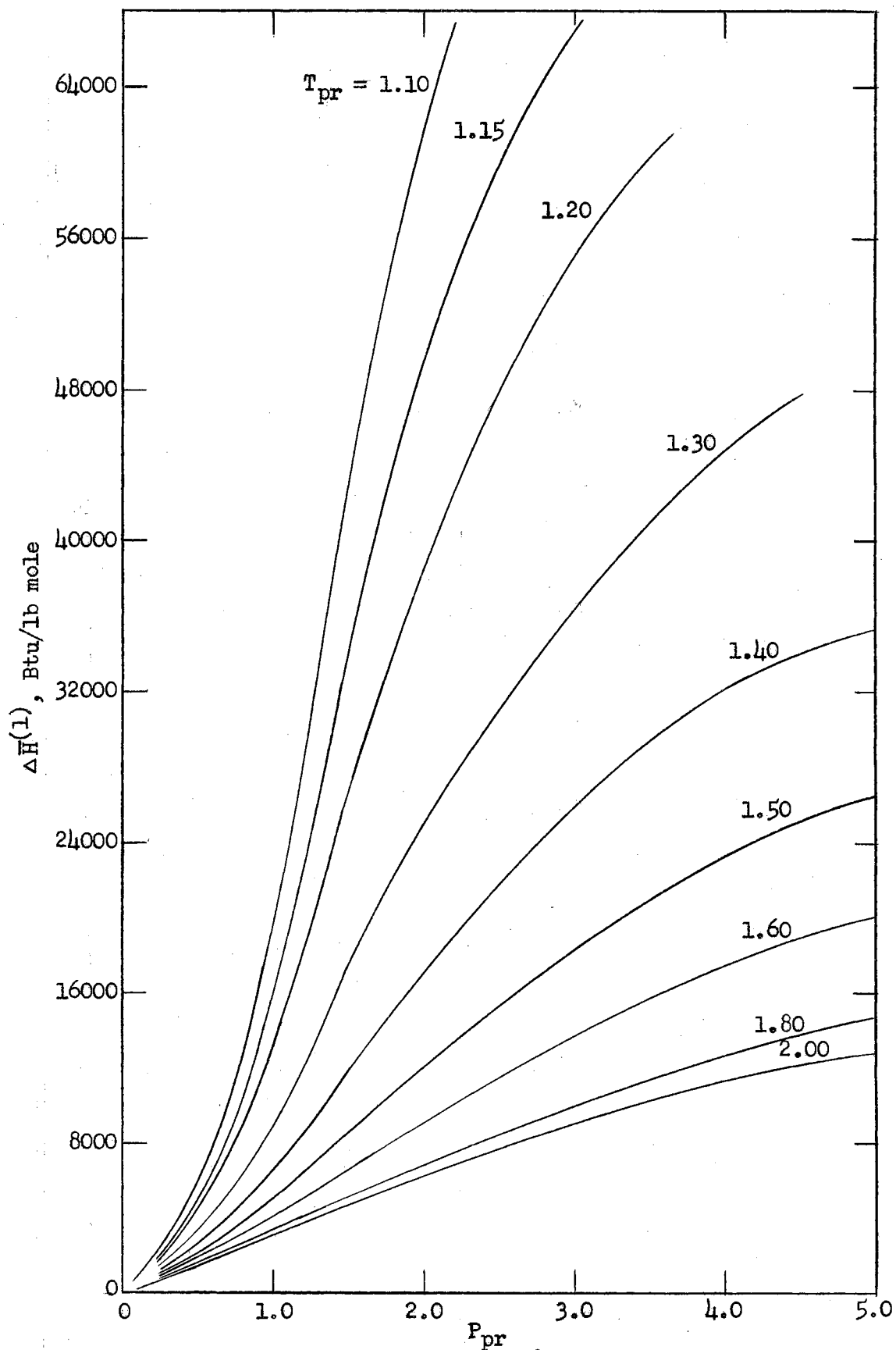
Figure 18

$\Delta \overline{H}^{(1)}$ as a Function of T_{pr} and P_{pr}

TABLE VII

VALUES OF $\Delta\bar{H}^{(0)}$ AND $\Delta\bar{H}^{(1)}$ AS FUNCTIONS OF T_{pr} AND P_{pr}

Btu/lb mole

P_{pr}	$\Delta\bar{H}^{(0)}$	$\Delta\bar{H}^{(1)}$	$\Delta\bar{H}^{(0)}$	$\Delta\bar{H}^{(1)}$	$\Delta\bar{H}^{(0)}$	$\Delta\bar{H}^{(1)}$
	$T_{pr} = 1.10$		$T_{pr} = 1.15$		$T_{pr} = 1.20$	
0.5	-435	6050	-380	5200	-335	4650
1.0	-985	20000	-875	16300	-765	13300
1.5	-1670	43200	-1490	34300	-1320	26950
2.0	-2465	61600	-2135	49500	-1890	39100
2.5	-3340	73800	-2835	59900	-2425	47900
3.0			-3620	67050	-2910	55100
3.5					-3335	60350
	$T_{pr} = 1.30$		$T_{pr} = 1.40$		$T_{pr} = 1.50$	
0.5	-275	3500	-220	2700	-190	2250
1.0	-605	9050	-480	6600	-395	5150
1.5	-1005	17600	-770	11850	-615	8700
2.0	-1400	25200	-1060	17150	-830	12150
2.5	-1770	31250	-1335	21850	-1045	15400
3.0	-2105	36600	-1605	26000	-1250	18400
3.5	-2400	41250	-1860	29550	-1445	19000
4.0	-2675	45000	-2100	32300	-1630	23550
4.5			-2315	34200	-1805	25200
5.0			-2505	35650	-1960	26550
	$T_{pr} = 1.60$		$T_{pr} = 1.80$		$T_{pr} = 2.00$	
0.5	-170	1950	-135	1650	-120	1500
1.0	-345	4150	-270	3600	-245	3050
1.5	-515	6700	-410	5150	-370	4750
2.0	-680	9200	-540	6850	-495	6300
2.5	-840	11550	-665	8500	-610	7800
3.0	-1000	13750	-785	10050	-725	9200
3.5	-1155	15850	-895	11550	-835	10450
4.0	-1300	17700	-1000	12850	-935	11500
4.5	-1435	19100	-1090	13900	-1025	12300
5.0	-1560	18150	-1170	14800	-1105	12850

TABLE VIII

COMPARISON OF PARTIAL ENTHALPY DIFFERENCE CORRELATION

WITH CALCULATED VALUES

Btu/lb mole

P, psia	$\Delta \bar{H}_{correl}$	$\Delta \bar{H}_{calc}$	P, psia	$\Delta \bar{H}_{correl}$	$\Delta \bar{H}_{calc}$
--- Methane – Ethane Binary ---			--- Methane – Propane Binary --		
$y_1^* = 0.70$, T = 190°F			$y_1 = 0.60$, T = 400°F		
200	-55	-56	200	-33	-18
800	-221	-214	600	-37	-43
1500	-373	-386	1000	-66	-59
2250	-538	-553	1500	-87	-65
3000	-714	-730	2000	-118	-82
$y_1 = 0.90$, T = 250°F			$y_1 = 0.90$, T = 280°F		
200	-58	-47	200	-48	-54
800	-229	-206	600	-152	-148
1500	-421	-376	1000	-258	-244
2250	-613	-547	1500	-389	-354
3000	-789	-699	2000	-513	-447
--- Methane – n-Butane Binary ---			-- Methane – n-Pentane Binary -		
$y_1 = 0.90$, T = 130°F			$y_1 = 0.96$, T = 100°F		
400	-126	-120	400	-168	-182
800	-286	-260	800	-335	-367
1250	-523	-430	1250	-519	-582
1750	-735	-620	2000	-820	-878
2500	-1025	-860	3000	-1203	-1173

* Component 1 is Methane

CHAPTER IV

ENTHALPIES VIA THE REDLICH - KWONG EQUATION OF STATE

Method of Using the Equation

The Redlich-Kwong equation of state (13) is an empirical, two constant equation of the form

$$P = \frac{RT}{V - b} - \frac{a}{T^{0.5}V(V + b)} \qquad (56)$$

where $a = 0.4278 \ R^2 T_c^{2.5}/P_c$ for a component.

   $b = 0.0867 \ RT_c/P_c$ for a component.

For use in numerical calculations the following were defined,

$$A_i^2 = a_i/RT^{2.5} \qquad \text{and} \qquad B_i = b_i/RT$$

For applying this equation of state to gaseous mixtures the combination rules for the constants are defined.

$$A = \sum_i y_i A_i \qquad \text{and} \qquad B = \sum_i y_i B_i$$

The Redlich-Kwong equation of state was used to derive an expression for the effect of pressure on the gas phase enthalpy, and this expression was programmed for use on the IBM 650 digital computer (7). In this work the derived expression for the effect of pressure on the gas phase enthalpy was rearranged into a more convenient form for hand

calculations as shown in Appendix D. The rearranged form for the effect of pressure on the partial enthalpy of component i is

$$-\frac{\Delta \overline{H}_i}{RT} = \left[\frac{\Delta H}{RT}\right] + M\left(\frac{A_i}{A} - 1\right) + N\left(\frac{B_i}{B} - 1\right) \qquad (57)$$

This equation can be easily evaluated since A_i, B_i, A and B can be calculated from the critical constants of the components, composition of the mixture and the temperature of the system. Once these parameters have been calculated, $\left[\Delta H/RT\right]$, M and N can be obtained from Figures 19, 20 and 21, respectively. Equation 57 has been programmed for use on the IBM 650 computer. The values of $\left[\Delta H/RT\right]$, M and N tabulated in Table XV, Appendix E, as functions of BP and A^2/B were calculated using the IBM 650 digital computer.

The effect of pressure on the mixture enthalpy can also be calculated by using equation 57. When calculating the mixture enthalpy difference both terms in parentheses in equation 57 become zero and $-\Delta H/RT = \left[\Delta H/RT\right]$. This is the reason that the value obtained from Figure 19 was given the symbol $\left[\Delta H/RT\right]$. A sample calculation using equation 57 with Figures 19, 20 and 21 is shown in Appendix F.

Comparison of Redlich-Kwong Enthalpies with Other Enthalpies

The mixture and partial enthalpy differences from an ideal gas calculated by the Redlich-Kwong equation of state are compared in Table IX with the mixture and partial enthalpy differences calculated by using PVTx data and graphical methods. The methane - propane binary enthalpy differences calculated in this work and the methane - n-butane and methane - n-pentane binary enthalpy differences obtained from Sage and Lacey (15) were used for the comparisons. A per cent
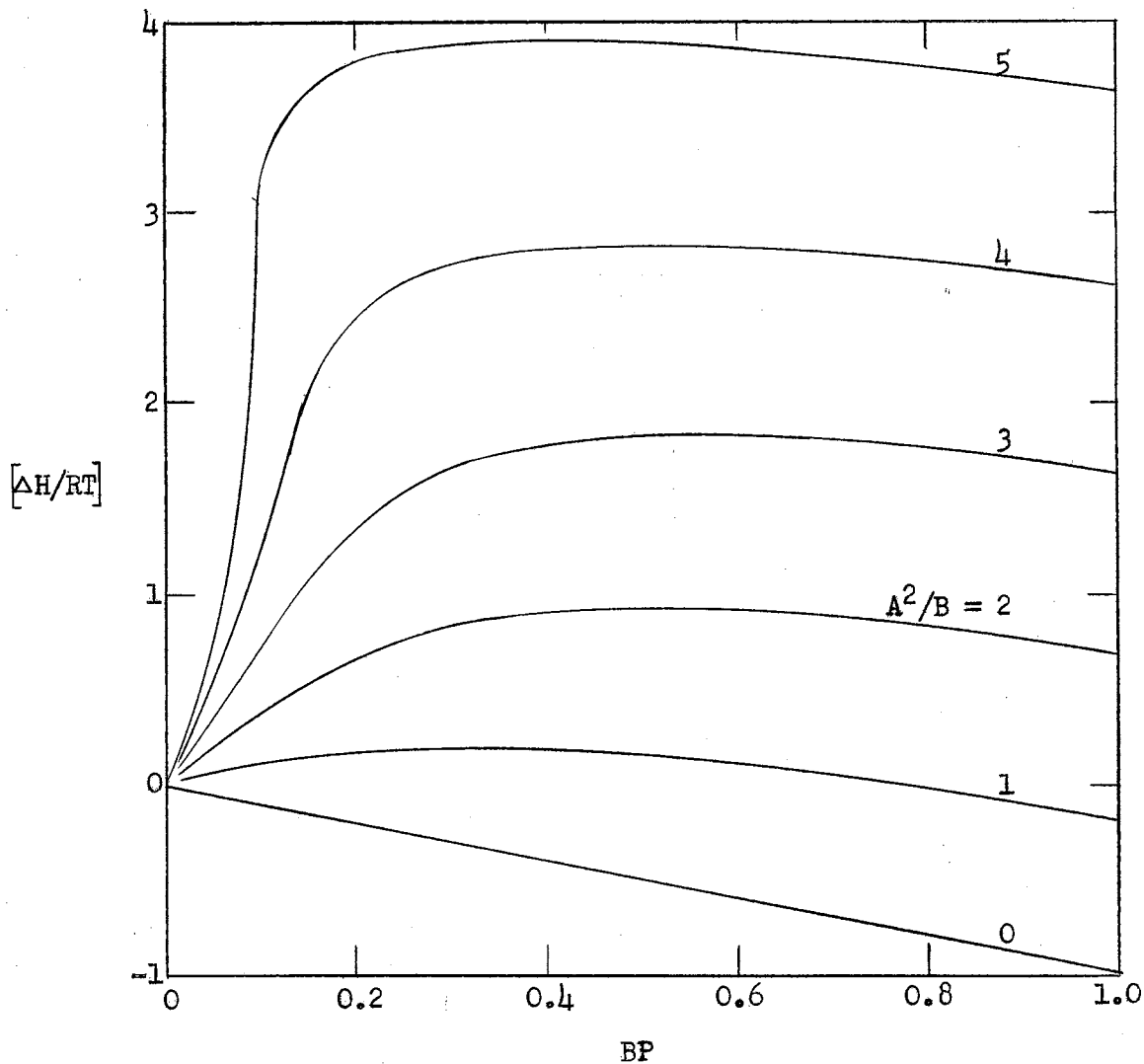
Figure 19

$[\Delta H/RT]$ as a Function of A^2/B and BP
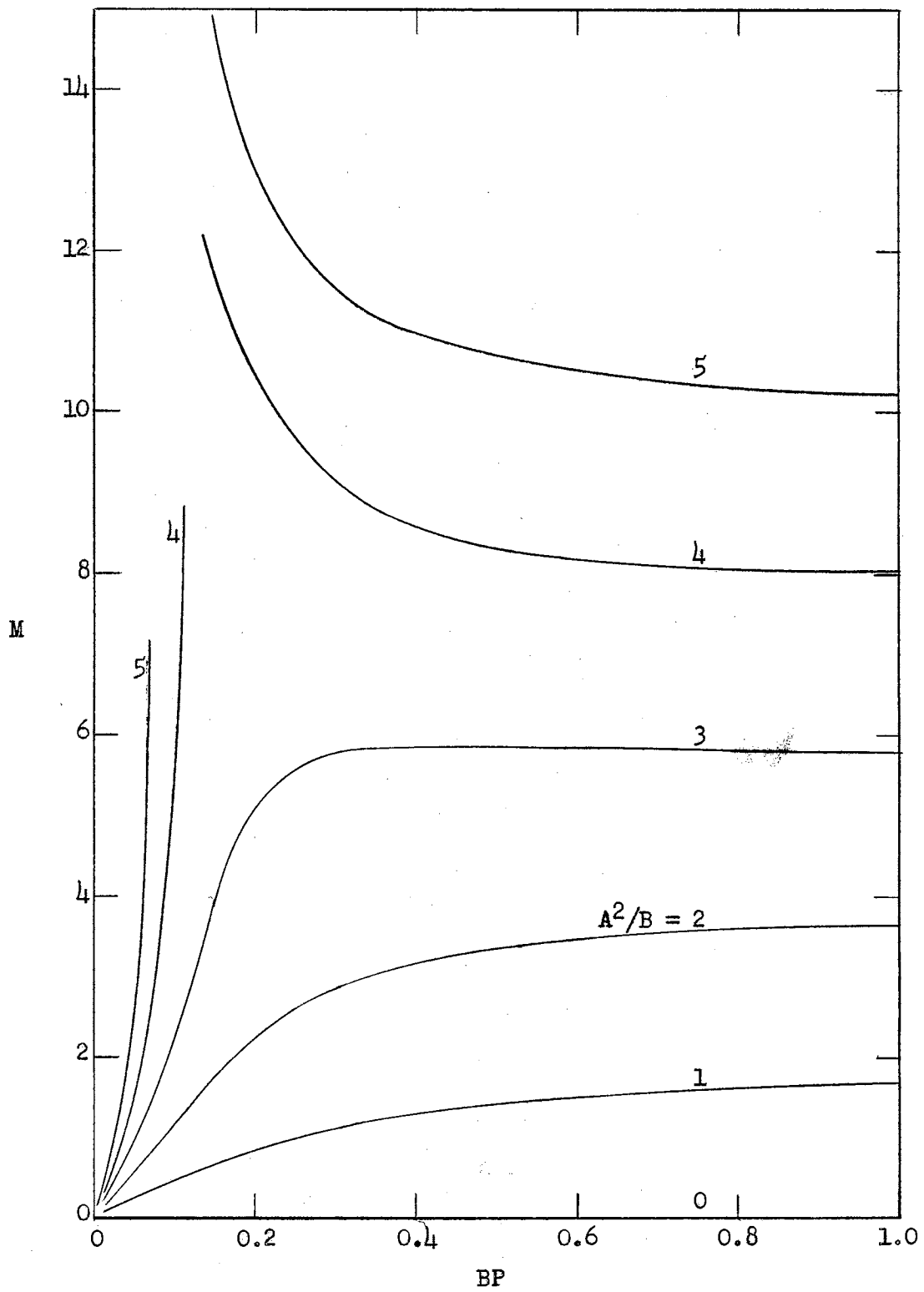
Figure 20

M as a Function of A^2/B and BP
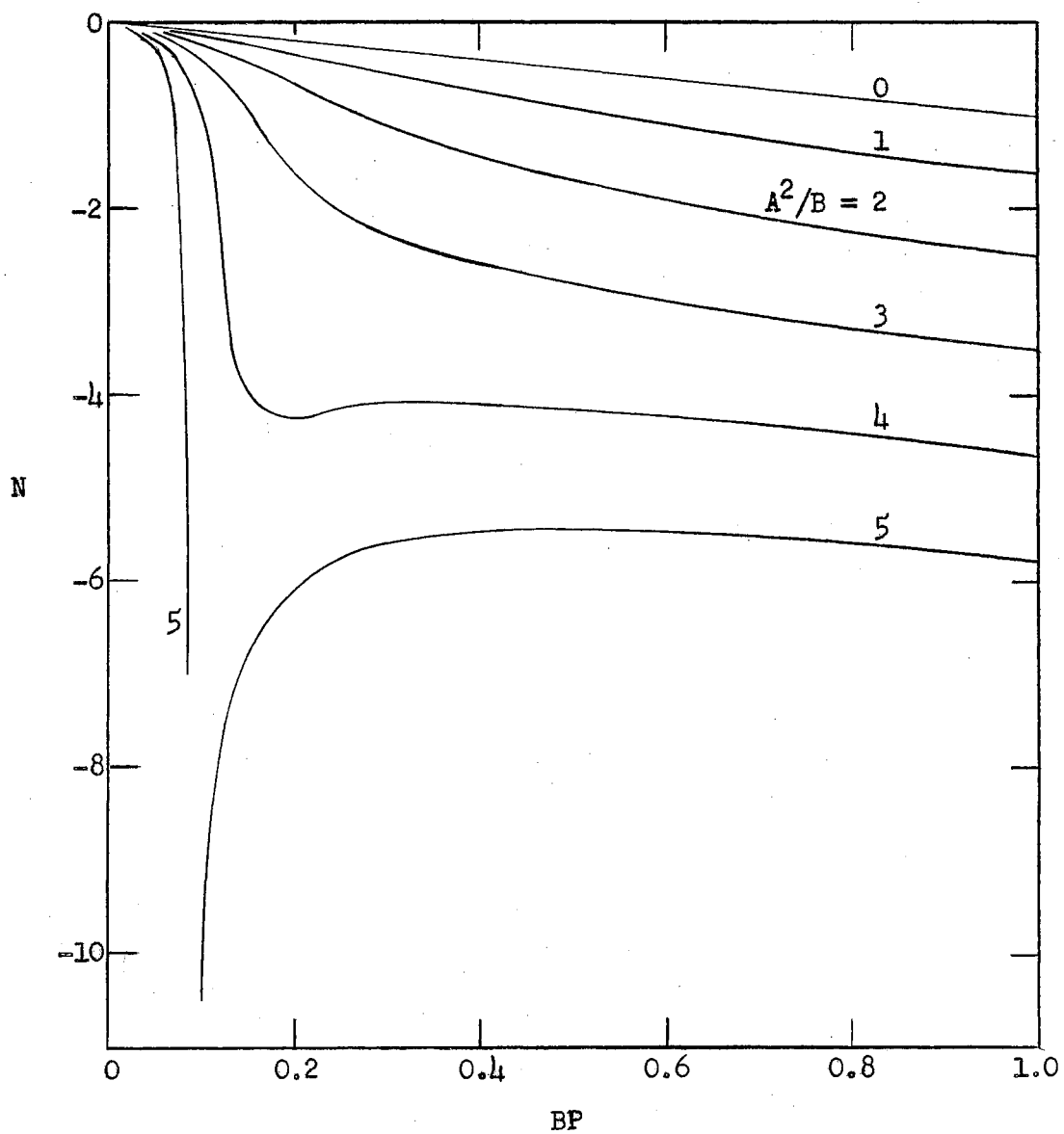
Figure 21

N as a Function of A^2/B and BP

COMPARISON OF REDLICH-KWONG ENTHALPIES WITH ENTHALPIES FROM PVTx DATA

Btu/lb mole

y_1^*	ΔH PVTx	ΔH R-K	$\Delta \bar{H}_1$ PVTx	$\Delta \bar{H}_1$ R-K	$\Delta \bar{H}_2$ PVTx	$\Delta \bar{H}_2$ R-K
——————————————— Methane – Propane Binary ———————————————						
100°F and 200 psia						
0.20	-645	-496	356	166	-895	-661
0.40	-419	-351	169	29	-811	-604
0.60	-252	-239	-6	**	-638	**
0.80	-144	-153	-52	-77	-471	-454
220°F and 200 psia						
0.20	-353	-334	109	74	-468	-436
0.40	-249	-242	38	9	-444	-408
0.60	-164	-167	-21	-32	-378	-368
0.80	-104	-106	-54	-53	-299	-318
340°F and 200 psia						
0.20	-258	-246	54	48	-336	-319
0.40	-192	-179	8	5	-321	-301
0.60	-134	-123	-25	-23	-298	-274
0.80	-83	-78	-40	-38	-258	-237
460°F and 200 psia						
0.20	-218	-190	25	37	-278	-246
0.40	-159	-138	6	6	-271	-233
0.60	-107	-94	-10	-16	-252	-212
0.80	-63	-59	-24	-28	-219	-184
160°F and 400 psia						
0.20	-1072	-910	913	529	-1568	-1270
0.40	-680	-616	240	112	-1293	-1101
0.60	-430	-409	-15	-55	-1063	-939
0.80	-254	-256	-115	-125	-826	-779
280°F and 400 psia						
0.20	-625	-596	250	196	-854	-791
0.40	-433	-423	70	36	-781	-729
0.60	-300	-287	-44	-47	-684	-648
0.80	-187	-181	-91	-88	-555	-552
400°F and 400 psia						
0.20	-468	-438	90	107	-608	-574
0.40	-342	-314	21	20	-577	-537
0.60	-235	-214	-36	-34	-544	-483
0.80	-143	-134	-59	-63	-476	-416

* Component 1 is Methane
** No Computer value available

TABLE IX (Continued)

y_1	ΔH PVTx	ΔH R-K	$\Delta \bar{H}_1$ PVTx	$\Delta \bar{H}_1$ R-K	$\Delta \bar{H}_2$ PVTx	$\Delta \bar{H}_2$ R-K
Methane – Propane Binary						
220°F and 800 psia						
0.20	-1937	-1784	2425	2198	-3060	-2780
0.40	-1123	-1100	574	380	-2204	-2087
0.60	-683	-701	1	-52	-1710	-1675
0.80	-417	-428	-200	-199	-1288	-1342
340°F and 800 psia						
0.20	-1112	-1074	445	478	-1533	-1462
0.40	-797	-741	105	114	-1405	-1311
0.60	-535	-493	-53	-62	-1227	-1139
0.80	-324	-305	-139	-143	-1051	-953
460°F and 800 psia						
0.20	-843	-778	186	245	-1130	-1033
0.40	-611	-549	46	59	-1077	-955
0.60	-415	-369	-27	-49	-993	-848
0.80	-244	-227	-88	-104	-854	-721
280°F and 1500 psia						
0.20	-2912	-2697	2723	2018	-4306	-3877
0.40	-1772	-1720	827	622	-3509	-3281
0.60	-1100	-1083	-11	-49	-2702	-2633
0.80	-677	-651	-308	-292	-2179	-2084
400°F and 1500 psia						
0.20	-1780	-1716	660	838	-2366	-2355
0.40	-1257	-1170	140	223	-2173	-2099
0.60	-847	-769	-76	-77	-1987	-1805
0.80	-504	-469	-202	-212	-1694	-1497
220°F and 2000 psia						
0.40	-2817	-2715	1293	604	-5555	-4927
0.60	-1734	-1718	50	-12	-4411	-4277
0.80	-1012	-1012	-440	-437	-3299	-3308
340°F and 2000 psia						
0.20	-2773	-2626	1384	1142	-3813	-3589
0.40	-1903	-1787	415	402	-3514	-3246
0.60	-1227	-1159	-61	-92	-2982	-2759
0.80	-730	-703	-307	-316	-2462	-2248
460°F and 2000 psia						
0.20	-2007	-1848	538	707	-2643	-2487
0.40	-1453	-1284	96	202	-2485	-2274
0.60	-967	-848	-80	-88	-2306	-1988
0.80	-563	-516	-213	-228	-2017	-1664

TABLE IX (Continued) 3 of 4

y_1	ΔH PVTx	ΔH R-K	$\Delta \bar{H}_1$ PVTx	$\Delta \bar{H}_1$ R-K	$\Delta \bar{H}_2$ PVTx	$\Delta \bar{H}_2$ R-K
----	----	---- Methane	- n-Butane	Binary ----	----	----
			160°F and 600 psia			
0.85	-378	-402	-83	-175	-2050	-1688
0.95	-250	-268	-203	-210	-1200	-1384
			160°F and 1000 psia			
0.85	-649	-680	-183	-270	-3290	-2998
0.95	-430	-445	-343	-344	-2130	-2360
			160°F and 1500 psia			
0.85	-970	-1015	-343	-375	-4520	-4641
0.95	-652	-653	-413	-501	-3340	-3549
			160°F and 2000 psia			
0.85	-1250	-1302	-519	-492	-5390	-5891
0.95	-855	-839	-673	-643	-4380	-4577
			220°F and 200 psia			
0.85	-101	-110	-10	-52	-610	-441
0.95	-72	-75	-60	-59	-290	-378
			220°F and 600 psia			
0.85	-329	-333	-60	-148	-1850	-1379
0.95	-212	-223	-170	-174	-990	-1149
			220°F and 1000 psia			
0.85	-559	-553	-120	-233	-3050	-2367
0.95	-368	-365	-290	-283	-1840	-1924
			220°F and 1500 psia			
0.85	-842	-815	-220	-328	-4360	-3570
0.95	-555	-533	-430	-411	-2910	-2848
			220°F and 2000 psia			
0.85	-1097	-1045	-340	-421	-5390	-4580
0.95	-727	-682	-560	-525	-3890	-3665
			220°F and 2500 psia			
0.85	-1308	-1234	-460	-518	-6110	-5292
0.95	-859	-811	-660	-626	-4640	-4329
			100°F and 600 psia			
0.90	-360	-409	-186	-240	-1930	-1927
0.95	-311	-330	-234	-257	-1770	-1718
			100°F and 1000 psia			
0.95	-522	-555	-416	-425	-2540	-3030

TABLE IX   (Continued)   4 of 4

70

P, psia	ΔH PVTx	ΔH R-K	$\Delta \bar{H}_1$ PVTx	$\Delta \bar{H}_1$ R-K	$\Delta \bar{H}_2$ PVTx	$\Delta \bar{H}_2$ R-K
----------	----------	----------	Methane - n-Butane Binary	----------	----------	----------
			100°F and $y_1 = 0.95$			
1500	-773	-827	-616	-624	-3760	-4681
2000	-1004	-1065	-806	-805	-4770	-6013
2500	-1209	-1253	-976	-960	-5630	-6824
			250°F and $y_1 = 0.90$			
600	-216	-251	-110	-151	-1170	-1158
1000	-383	-413	-200	-243	-2030	-1943
1500	-590	-603	-310	-350	-3110	-2882
2000	-781	-773	-420	-447	-4030	-3704
----------	----------	----------	Methane - n-Pentane Binary	----------	----------	----------
			100°F and $y_1 = 0.96$			
200	-123	-109	-89	-86	-940	-670
600	-362	-333	-262	-257	-2765	-2154
1000	-624	-559	-463	-424	-4500	-3796
1500	-912	-832	-689	-623	-6255	-5847
2000	-1143	-1071	-878	-804	-7505	-7464
2500	-1337	-1258	-1042	-960	-8405	-8404
			160°F and $y_1 = 0.96$			
200	-107	-90	-74	-71	-870	-557
600	-318	-270	-226	-209	-2545	-1732
1000	-515	-448	-365	-343	-4115	-2952
1500	-745	-657	-532	-500	-5840	-4428
2000	-957	-844	-697	-642	-7180	-5686
2500	-1126	-1000	-835	-766	-8100	-6609
3000	-1274	-1124	-961	-871	-8775	-7198
			220°F and $y_1 = 0.96$			
600	-243	-224	-163	-174	-2174	-1437
1000	-399	-368	-271	-283	-3473	-2404
1500	-583	-536	-399	-410	-4998	-3552
2000	-751	-686	-524	-525	-6207	-4554
2500	-900	-815	-642	-626	-7098	-5356
3000	-1024	-922	-744	-713	-7751	-5944

deviation was calculated for each mixture enthalpy difference in Table IX by assuming the enthalpy differences calculated from the PVTx data are correct. The error was calculated by equation 58 for 108 comparisons.

$$\% \text{ error} = \frac{\Delta H_{PVTx} - \Delta H_{R-K}}{\Delta H_{PVTx}} 100 \tag{58}$$

Of the 108 compared values, 81 were positive deviations, 1 had no deviation and 26 were negative deviations. The average positive deviation was 7.42% and the average negative deviation was 5.22%.

The comparisons in Table IX show that the pressure correction to the ideal gas enthalpy (enthalpy difference) of the mixture calculated by the Redlich-Kwong equation is usually smaller than the correction calculated from PVTx data (the correction is a negative quantity). The partial enthalpy differences calculated by the Redlich-Kwong equation also do not agree with the partial enthalpy differences calculated from PVTx data. The pressure correction to the partial enthalpy of the heavy component (the correction is a negative quantity) calculated by the Redlich-Kwong equation is generally smaller than the correction calculated from PVTx data. For high mole fractions of methane the partial enthalpy difference values of methane should compare better than at low mole fractions of methane. This composition effect on the partial enthalpy difference of methane is shown by the methane - propane binary comparison in Table IX. At low mole fractions of methane the effect of temperature at constant pressure on the methane partial enthalpy difference is greater for the Redlich-Kwong equation values than for the values calculated from PVTx data. This temperature effect can also be seen by observing the methane - propane binary comparison in Table IX.

Mixture enthalpy differences for saturated vapor calculated by using the Redlich-Kwong equation were compared with the values of Weber, et al (19,20) and values obtained from Edmister's generalized correlation (6) in Table X. Weber's values were calculated by the Benedict-Webb-Rubin equation of state. Edmister's correlation was extended to mixtures by the pseudocritical concept. The Redlich-Kwong values do not agree very well with the values calculated by the other two methods.

Table XI is a comparison of the mixture enthalpy differences for superheated vapor calculated by the Redlich-Kwong equation, Benedict-Webb-Rubin equation (10), Edmister's general correlation and the correlation developed in this work (Figures 14 and 15). The correlation developed in this work was applied only to methane binaries at conditions where the pseudo reduced temperature was equal to or greater than 1.10. These comparisons show that the Benedict-Webb-Rubin equation agrees better with the correlation developed in this work than the Redlich-Kwong equation and Edmister's correlation, both of which agree about equally.

A comparison of the partial enthalpy difference for superheated vapor calculated by the Redlich-Kwong equation and the Benedict-Webb-Rubin equation (10) is shown in Table XII. The partial enthalpies of some normal paraffins have been calculated as being present in the binary mixture in infinite dilution. Partial enthalpy differences calculated by the Benedict-Webb-Rubin equation were available only for methane, ethane and propane no matter what the components of the binary system were. The partial enthalpy values calculated by the Redlich-Kwong equation are presented for the normal paraffins through n-heptane except at -100 and -50°F.

TABLE X

COMPARISON OF SATURATED VAPOR ENTHALPIES

Btu/lb mole

T, °F	y_1^*	ΔH^* R-K	ΔH^{**} BWR	ΔH^{**} EC	T, °F	y_1	ΔH R-K	ΔH BWR	ΔH EC
Methane – Ethane Binary at 200 psia					Methane – n-Butane Binary at 200 psia				
-6.2	0	-5100	-687	-736	202.7	0	-6400	-1043	-1270
-51.2	0.526	-325	-394	-413	159.5	0.393	-553	-834	-784
-85.5	0.764	-272	-319	-330	122.5	0.640	-512	-645	-615
-112.0	0.882	-259	-317	-323	93.0	0.784	-466	-598	-566
-143.9	0.959	-278	-342	-380	69.0	0.866	-446	-554	-564
-161.2	0.983	-540	-375	-440	34.0	0.949	-451	-608	-624
-178.5	1.0	-3200	-370	-505	10.0	0.984	-4475	-618	-680
					-6.2	1.0	-5100	-687	-736
Ethane – n-Heptane Binary at 100 psia					Ethane – n-Heptane Binary at 600 psia				
358	0	-2600	-1214	-2140	484	0.20	-4930	-6750	-7750
334	0.20	-560	-890	-1320	471	0.30	-3340	-4696	-5090
305.5	0.40	-388	-595	-837	450	0.40	-2135	-3095	-4020
272.5	0.60	-291	-420	-557	400	0.60	-1623	-1896	-2580
223	0.80	-242	-276	-390	328	0.80	-1040	-1246	-1910
132	0.96	-159	-170	-344	198	0.96	-915	-1025	-1840
55.5	0.995	-179	-225	-450	75.8	1.0	-1940	-1926	-4260

* Component 1 is the light component of the binary.

* R-K values are calculated by the Redlich-Kwong equation.

** BWR values are from Weber, et al (19,20).

** EC values are from Edmister's Generalized Correlation (6).

TABLE XI

COMPARISON OF MIXTURE ENTHALPY DIFFERENCES IN SUPERHEATED VAPOR

Btu/lb mole

T, °F	P, psia	y_1	$\triangle H$ R-K	$\triangle H$ BWR	$\triangle H$ EC	$\triangle H^*$ CTW
--- Methane - Ethane Binary ---					
-100	181.5	0.8561	-229	-254	-274	
-100	130.2	0.7420	-190	-225	-246	
-100	85.6	0.6778	-140	-169	-197	
-100	51.8	0.3994	-110	-151	-171	
-50	717.8	0.8561	-906	-948	-935	-1052
-50	421.0	0.7420	-559	-616	-607	
-50	150.3	0.3994	-275	-343	-374	
0	902.5	0.8561	-838	-855	-843	-882
0	949.9	0.7420	-1173	-1222	-1166	-1242
0	450.1	0.6278	-552	-601	-693	
50	950.1	0.3994	-1858	-1977	-1813	
50	148.9	0.3545	-330	-441	-211	
50	499.5	0.1710	-1148	-1137	-1122	
100	783.7	0.3994	-938	-958	-949	-997
100	900.3	0.1710	-1793	-1740	-1811	
100	491.6	0.1710	-736	-798	-782	
--- Methane - Propane Binary ---					
-100	603.0	0.9819	-845	-883	-914	
-100	396.9	0.9819	-466	-489	-513	
-50	56.0	0.7728	-76	-95	-84	
0	334.0	0.9122	-280	-310	-288	-292
0	170.0	0.7728	-198	-228	-208	-244
50	879.1	0.9122	-637	-647	-617	-639
50	464.4	0.7728	-479	-526	-471	-491
100	1000.0	0.7728	-893	-892	-850	-885
100	790.4	0.6333	-1044	-1173	-988	-1171
100	522.5	0.6333	-623	-710	-619	-653
100	351.4	0.3545	-739	-895	-794	
100	216.9	0.0757	-675	-906	-956	
--- Ethane - Propane Binary ---					
-100	17.0	0.9102	-56	-89	-89	
-50	57.8	0.9102	-160	-222	-252	
-50	16.0	0.1943	-67	-115	-106	
0	45.2	0.1943	-164	-253	-148	
50	110.2	0.1943	-361	-531	-277	
100	658.1	0.9102	-1816	-2052	-2162	
100	374.2	0.5523	-1024	-1266	-1354	

* CTW values are from the correlation developed in this work. All other symbols are the same as in Table X.

The comparison of the partial enthalpy differences calculated by the Redlich-Kwong equation and Benedict-Webb-Rubin equation can be made for both components of the methane - ethane, methane - propane and ethane - propane binaries. For these binaries the pressure correction to the partial enthalpy of the heavy component (the correction is a negative quantity) calculated by the Redlich-Kwong equation is smaller than the correction calculated by the Benedict-Webb-Rubin equation. When the composition of methane is high in the methane binaries, the two equations agree quite well.

TABLE XII

COMPARISON OF REDLICH-KWONG AND BENEDICT-WEBB-RUBIN (10)

PARTIAL ENTHALPIES FOR SUPERHEATED VAPOR

Btu/lb mole

Comp*	y_i	$\Delta \bar{H}_{R-K}$	$\Delta \bar{H}_{BWR}$	y_i	$\Delta \bar{H}_{R-K}$	$\Delta \bar{H}_{BWR}$
			-100°F			
		603.0 psia			9.1 psia	
C_1	0.9819	-753.5	-766.9	0.8831	-7.9	-6.3
C_2		-3546.5	-4119.		-24.9	-36.1
C_3	0.0181	-5785.8	-7179.		-39.0	-65.3
nC_4		-7959.		0.1169	-52.8	
		396.9 psia			130.2 psia	
C_1	0.9819	-432.9	-444.	0.7420	-117.2	-109.4
C_2		-1431.4	-1774.	0.2580	-398.5	-556.3
C_3	0.0181	-2247.3	-2951.		-631.1	-994.8
nC_4		-3041.9			-858.2	
		798.6 psia			84.6 psia	
C_1	0.9865	-1248.8	-1071.	0.6278	-70.5	-58.7
C_2		-18592.	-26700	0.3722	-257.0	-355.2
C_3		-31358.	-46600		-411.6	-679.8
nC_4	0.0135	-43520.			-562.6	
		14.4 psia			51.8 psia	
C_1	0.9348	-13.1	-12.8	0.3994	-34.3	-14.1
C_2		-37.7	-52.0	0.6006	-160.8	-242.3
C_3		-58.2	-90.8		-265.9	-470.2
nC_4	0.0652	-78.2			-368.5	
		181.5 psia			17.0 psia	
C_1	0.8561	-174.7	-173.5		-2.8	18.7
C_2	0.1439	-551.6	-736.1	0.9102	-51.9	-79.6
C_3		-862.7	-1333.5	0.0898	-92.8	-179.0
nC_4		-1166.2			-132.8	

* Comp. refers to the normal paraffin components: C_1 = methane, C_2 = ethane, C_3 = propane, nC_4 = n-butane, etc.

TABLE XII (Continued)   2 of 10

Comp.	y_i	$\triangle\bar{H}_{R-K}$	$\triangle\bar{H}_{BWR}$	y_i	$\triangle\bar{H}_{R-K}$	$\triangle\bar{H}_{BWR}$
			-50°F			
		1065.3 psia			56.0 psia	
C_1	0.9891	-1037.7	-1039.	0.7728	-36.6	-27.9
C_2		-4727.2	-5159.5		-132.6	-177.2
C_3		-7602.	-7095.	0.2272	-212.1	-323.7
nC_4		-10375.			-289.8	
nC_5	0.0109	-12993.			-365.4	
		1469.6 psia			150.3 psia	
C_1	0.9891	-1505.8	-1542.	0.3994	-67.3	-21.3
C_2		-6338.	-6896.	0.6006	-412.9	-557.6
C_3		-9932.	-11190.		-698.4	-1131.
nC_4		-13364.			-977.0	
nC_5	0.0109	-16525.			-1247.6	
		717.8 psia			57.8 psia	
C_1	0.8561	-555.6	-531.1		0.7	55.8
C_2	0.1439	-2991.3	-3429.	0.9102	-149.2	-197.8
C_3		-4936.8	-3442.	0.0898	-273.6	-464.4
nC_4		-6823.			-395.2	
nC_5		-8626.			-513.5	
		48.2 psia			15.8 psia	
C_1	0.9348	-35.4	-33.9		12.1	52.6
C_2		-104.1	-130.8	0.1943	-35.0	-39.8
C_3		-161.0	-225.0	0.8057	-74.2	-133.0
nC_4	0.0652	-216.5			-112.6	
nC_5		-270.5			-150.0	
		421.1 psia			3.0 psia	
C_1	0.7420	-288.7	-254.1		5.6	21.0
C_2	0.2580	-1338.0	-1656.		-4.7	-1.3
C_3		-2193.3	-2972.	0.4157	-13.3	-34.2
nC_4		-3026.0		0.5843	-21.7	
nC_5		-3829.7			-29.9	

TABLE XII (Continued) 3 of 10

Comp.	y_i	$\Delta \bar{H}_{R-K}$	$\Delta \bar{H}_{BWR}$	y_i	$\Delta \bar{H}_{R-K}$	$\Delta \bar{H}_{BWR}$
				$0^{\circ}F$		
		450.0 psia			45.2 psia	
C_1	0.9865	-290.2	-282.		39.1	129.3
C_2		-857.8	-940.3	0.1943	-82.8	-82.6
C_3		-1320.8	-1545.	0.8057	-184.1	-294.5
nC_4	0.0135	-1771.6			-283.0	
nC_5		-2206.9			-379.4	
nC_6		-2626.6			-472.8	
nC_7		-3032.3			-563.7	
		1299.7 psia			20.3 psia	
C_1	0.9906	-907.2	-902.		39.3	125.1
C_2		-3295.7	-3560.5		-24.3	0
C_3		-5167.0	-5845.	0.4157	-77.3	-119.7
nC_4		-6974.		0.5843	-129.1	
nC_5		-8685.			-179.7	
nC_6	0.0094	-10310			-228.7	
nC_7		-11850			-276.4	
		334.0 psia			3.0 psia	
C_1	0.9122	-206.4	-214.		10.7	31.8
C_2		-665.6	-836.3		-1.0	10.2
C_3	0.0878	-1041.6	-1306.		-9.9	-11.5
nC_4		-1407.9		0.5601	-18.5	
nC_5		-1762.3		0.4399	-26.9	
nC_6		-2104.5			-35.1	
nC_7		-2435.1			-43.1	
		902.5 psia			900.9 psia	
C_1	0.8561	-572.5	-552.	0.9891	-610.9	-602.
C_2	0.1439	-2416.6	-2658.		-2027.9	-2210.
C_3		-3887.2	-4517.		-3163.4	-3639.
nC_4		-5312.4			-4265.1	
nC_5		-6677.		0.0109	-5319.8	
nC_6		-7976.			-6330.	
nC_7		-9219.			-7298.	
		3355.4 psia			450.1 psia	
C_1	0.9596	-1725.8	-1740.	0.6278	-212.8	-170.0
C_2		-4898.0	-5321.	0.3722	-1125.4	-1328.5
C_3		-7116.	-8122.		-1868.7	-2424.
nC_4		-9205.			-2592.2	
nC_5		-11059.			-3290.3	
nC_6		-12734.			-3692.9	
nC_7	0.0404	-14213.			-4611.3	

Comp.	y_i	$\Delta\bar{H}_{R-K}$	$\Delta\bar{H}_{BWR}$	y_i	$\Delta\bar{H}_{R-K}$	$\Delta\bar{H}_{BWR}$

——————————————————— 0°F ———————————————————

		949.9 psia			170.0 psia	
C_1	0.7420	-383.0	-337.	0.7728	-88.7	-65.7
C_2	0.2580	-3442.8	-3769.		-352.3	-431.7
C_3		-5846.5	-6768.5	0.2272	-569.5	-781.0
nC_4		-8169.			-781.5	
nC_5		-10370.			-987.1	
nC_6		-12465.			-1186.1	
nC_7		-14451.			-1378.7	

——————————————————— 50°F ———————————————————

		2751.4 psia			9.9 psia	
C_1	0.9544	-1263.7	-1286.		28.5	71.9
C_2		-4292.5	-4679.		-1.9	14.2
C_3		-6497.	-7401.5		-27.2	-30.4
nC_4		-8591.		0.5601	-51.9	
nC_5		-10496.		0.4399	-76.0	
nC_6	0.0456	-12251.			-99.4	
nC_7		-13846.			-122.2	

		1562.6 psia			110.2 psia	
C_1	0.8831	-594.0	-545		127.2	352.
C_2		-3918.8	-4201.	0.1943	-165.6	-159.9
C_3		-6441.	-7172.	0.8057	-407.8	-620.8
nC_4	0.1169	-8861.			-644.3	
nC_5		-11113.			-874.2	
nC_6		-13227.			-1096.8	
nC_7		-15196.			-1312.8	

		3595.5 psia			37.6 psia	
C_1	0.9275	-1450.9	-1420.		69.2	180.
C_2		-4374.2	-4782.		-35.6	19.2
C_3		-6416	-7519.	0.4157	-122.7	-174.2
nC_4		-8339.		0.5843	-207.9	
nC_5		-10044.			-290.8	
nC_6		-11583.			-371.2	
nC_7	0.0725	-12944.			-449.4	

		464.4 psia			879.1 psia	
C_1	0.7728	-182.5	-136.3	0.9122	-447.7	-423.
C_2		-902.0	-871.0		-1641.2	-1776.
C_3	0.2272	-1487.9	-1851.0	0.0878	-2598.8	-2972.
nC_4		-2058.2			-3528.2	
nC_5		-2609.4			-4418.5	
nC_6		-3138.6			-5272.0	
nC_7		-3649.7			-6089.	

Comp.	y_i	$\Delta \bar{H}_{R-K}$	$\Delta \bar{H}_{BWR}$	y_i	$\Delta \bar{H}_{R-K}$	$\Delta \bar{H}_{BWR}$

---------------------------------- 50°F ----------------------------------

		950.1 psia			499.4 psia	
C_1	0.3994	2143.3	1990.	0.1710	-442.6	682.
C_2		-4518.7	-4615.	0.8290	-1293.0	-1512.
C_3	0.6006	-9575.	-9724.5		-2692.5	-3493.
nC_4		-14424.			-4052.9	
nC_5		-18940.			-5357.2	
nC_6		-23179.			-6611.	
nC_7		-27127.			-7814.	

		65.3 psia			148.9 psia	
C_1	0.6245	-7.0	25.1	0.3545	43.1	158.
C_2		-115.8	-135.2		-273.8	-314.3
C_3		-205.9	-291.3	0.6455	-535.4	-769.9
nC_4	0.3755	-293.8			-790.7	
nC_5		-379.3			-1038.6	
nC_6		-462.1			-1278.5	
nC_7		-542.5			-1511.0	

---------------------------------- 100°F ----------------------------------

		321.1 psia			86.7 psia	
C_1	0.9544	-135.2	-122.5	0.4176	43.6	119.1
C_2		-433.8	-468.0		-120.9	-114.9
C_3		-677.6	-783.0		-257.1	-345.8
nC_4		-915.1		0.5824	-390.1	
nC_5		-1144.4			-519.3	
nC_6	0.0456	-1365.6			-644.5	
nC_7		-1579.1			-766.0	

		1396.0 psia			374.2 psia	
C_1	0.9469	-567.8	-540.5		852.8	1479.
C_2		-2154.6	-2311.	0.5523	-523.8	-492.
C_3		-3404.0	-3829.	0.4477	-1640.7	-2220.
nC_4		-4611.8			-2726.9	
nC_5	0.0531	-5758.1			-3773.0	
nC_6		-6850.			-4779.7	
nC_7		-7886.			-5748.5	

		2480.0 psia			216.9 psia	
C_1	0.8625	-805.3	-680.	0.0757	390.9	779.
C_2		-3859.2	-4153.		-242.0	-157.1
C_3		-6072.	-6860.	0.9243	-761.8	-1044.
nC_4		-8172.			-1268.6	
nC_5	0.1375	-10077.			-1759.5	
nC_6		-11828.			-2233.8	
nC_7		-13415.			-2692.7	

TABLE XII (Continued)   6 of 10

Comp.	y_i	$\Delta\bar{H}_{R-K}$	$\Delta\bar{H}_{BWR}$	y_i	$\Delta\bar{H}_{R-K}$	$\Delta\bar{H}_{BWR}$
			100°F			
		790.4 psia			900.3 psia	
C_1	0.6333	95.7	235.5	0.1710	2286.0	2415.
C_2		-1633.8	-1758.5	0.8290	-2634.9	-2597.
C_3	0.3667	-3013.3	-3605.		-6422.	-7040.5
nC_4		-4350.2			-10066.	
nC_5		-5627.2			-13484.	
nC_6		-6849.			-16710.	
nC_7		-8016.			-19738.	
		3699.0 psia			466.5 psia	
C_1	0.8314	-1242.1	-859.	0.8314	-154.6	-117.2
C_2		-3973.6	-4175.		-733.8	-810.4
C_3		-5845.7	-6645.		-1205.4	-1446.
nC_4		-7599.		0.1686	-1664.3	
nC_5		-9134.			-2106.9	
nC_6		-10506.			-2533.4	
nC_7	0.1686	-11697.			-2944.4	
		351.4 psia			17.7 psia	
C_1	0.3545	268.8	522.		61.5	208.5
C_2		-591.2	-638.3		8.8	96.5
C_3	0.6455	-1292.7	-1673.5		-33.5	35.5
nC_4		-1975.7		0.1035	-77.9	
nC_5		-2635.2		0.8965	-119.7	
nC_6		-3271.0			-160.3	
nC_7		-3884.1			-199.7	
		658.1 psia			25.0 psia	
C_1		5809.7	6710.		69.3	176.6
C_2	0.9102	-1318.6	-1455.5		-0.3	60.5
C_3	0.0898	-6859.	-8097		-55.8	-55.3
nC_4		-12200.		0.5601	-114.8	
nC_5		-17236.		0.4399	-170.0	
nC_6		-22008.			-223.4	
nC_7		-26510.			-275.4	
		88.8 psia			149.3 psia	
C_1	0.9544	-37.4	-34.0	0.6245	-4.5	23.7
C_2		-115.3	-124.4		-232.9	-285.5
C_3		-176.4	-207.9		-413.1	-577.6
nC_4		-241.4		0.3755	-604.8	
nC_5		-301.8			-783.0	
nC_6	0.0456	-360.0			-955.3	
nC_7		-416.3			-1122.1	

TABLE XII (Continued)　　　　7 of 10

Comp.	y_i	$\Delta \bar{H}_{R-K}$	$\Delta \bar{H}_{BWR}$	y_i	$\Delta \bar{H}_{R-K}$	$\Delta \bar{H}_{BWR}$
			100°F			
		3502.0 psia			491.6 psia	
C_1	0.9596	-1177.8	-1306.	0.1710	80.4	169.
C_2		-3765.0	-4115.5	0.8290	-904.9	-997.1
C_3		-5546.1	-7140.		-1669.4	-2061.0
nC_4		-7413.			-2481.7	
nC_5		-9024.			-3230.2	
nC_6		-10503			-3950.6	
nC_7	0.0404	-11841.			-4642.9	
		299.7 psia			200.3 psia	
C_1	0.8314	-104.2	-79.9		27.3	89.8
C_2		-448.8	-494.8	0.9734	-318.7	-352.3
C_3		-718.1	-879.5		-591.0	-771.7
nC_4	0.1686	-1004.4			-880.8	
nC_5		-1269.6			-1149.9	
nC_6		-1535.5		0.0266	-1410.1	
nC_7		-1772.5			-1661.5	
		1000.0 psia			49.8 psia	
C_1	0.7728	-280.2	-135.1		31.9	91.7
C_2		-1813.9	-1849.	0.6990	-64.6	-53.1
C_3	0.2272	-2979.4	-3468.5		-141.1	-195.2
nC_4		-4214.9			-222.7	
nC_5		-5341.9		0.3010	-298.6	
nC_6		-6419.			-372.4	
nC_7		-7445.			-443.8	
		80.0 psia			124.6 psia	
C_1	0.7782	-18.7	-2.0		118.7	254.6
C_2		-119.7	-143.4	0.5743	-158.9	-141.9
C_3		-199.5	-278.3		-378.3	-524.3
nC_4		-284.4		0.4257	-611.9	
nC_5	0.2218	-363.3			-829.3	
nC_6		-439.7			-1039.8	
nC_7		-513.7			-1243.6	
		522.6 psia			136.3 psia	
C_1	0.6333	-66.9	35.7		236.6	525.0
C_2		-920.7	-1026.		-128.6	-36.8
C_3	0.3667	-1583.2	-1999.0	0.8167	-417.2	-578.5
nC_4		-2287.1		0.1833	-724.4	
nC_5		-2936.0			-1010.2	
nC_6		-3560.4			-1286.8	
nC_7		-4160.9			-1554.5	

TABLE XII (Continued) 8 of 10

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Comp.	y_i	$\Delta\bar{H}_{R-K}$	$\Delta\bar{H}_{BWR}$	y_i	$\Delta\bar{H}_{R-K}$	$\Delta\bar{H}_{BWR}$
			100°F			
		783.7 psia			73.0 psia	
C_1	0.3994	-21.9	51.5		137.2	313.8
C_2	0.6006	-1547.2	-1629.		-51.8	14.4
C_3		-2712.9	-3190.0	0.4157	-201.7	-303.3
nC_4		-3949.6		0.5843	-361.5	
nC_5		-5081.0			-510.3	
nC_6		-6165.			-654.5	
nC_7		-7199.			-794.4	
			200°F			
		3524.0 psia			128.0 psia	
C_1	0.7673	-728.3	-405.7		483.7	998.6
C_2		-3233.2	-3423.		114.2	442.6
C_3		-4967.6	-5611.		-190.9	-98.1
nC_4		-6597.		0.5601	-488.6	
nC_5		-8033.		0.4399	-777.6	
nC_6		-9324.			-1057.4	
nC_7	0.2327	-10456.			-1328.6	
		1200.2 psia			43.9 psia	
C_1		1796.7	1222.		176.0	439.8
C_2	0.9776	-1774.1	-2250.		56.9	252.7
C_3		-4486.9	-5008.5		-42.0	68.5
nC_4		-7090.			-138.6	
nC_5		-9514.		0.6062	-232.6	
nC_6		-11791.		0.3938	-323.9	
nC_7	0.0224	-13914.			-412.5	
		799.2 psia			16.8 psia	
C_1		2886.8	3431.		88.2	215.
C_2	0.8327	-590.1	-393.1		39.3	137.2
C_3		-3296.7	-3736.		-1.4	60.0
nC_4		-5907.0			-41.3	
nC_5	0.1673	-8370.			-80.1	
nC_6		-10705.		0.5456	-117.8	
nC_7		-12910.		0.4544	-154.4	
		610.6 psia			867.2 psia	
C_1		4629.3	5782.	0.6245	319.1	488.1
C_2	0.5743	680.7	-301.9		-1188.1	-1229.
C_3		-2419.1	-2844.		-2386.9	-2717.
nC_4	0.4257	-5413.7		0.3755	-3548.1	
nC_5		-8252.			-4655.8	
nC_6		-10951.			-5714.3	
nC_7		-13510.			-6724.	

TABLE XII (Continued)   9 of 10

Comp.	y_i	$\Delta\bar{H}_{R-K}$	$\Delta\bar{H}_{BWR}$	y_i	$\Delta\bar{H}_{R-K}$	$\Delta\bar{H}_{BWR}$

---------------------------------- 200°F ----------------------------------

		199.4 psia			888.5 psia	
C_1		269.1	457.		4668.1	3960.
C_2		-135.7	-65.4	0.8327	-429.5	-837.4
C_3	0.9458	-470.3	-556.9		-4310.0	-4747.
nC_4		-795.6			-8034.	
nC_5		-1110.9		0.1673	-11508	
nC_6		-1415.7			-14772	
nC_7	0.0542	-1710.6			-17819.	
		457.3 psia			457.5 psia	
C_1		3584.7	5454.	0.8097	-38.4	65.4
C_2		879.9	1719.		-554.4	-578.9
C_3	0.8167	-1279.5	-1477.		-974.0	-1161.
nC_4	0.1833	-3372.7			-1382.3	
nC_5		-5373.1			-1775.9	
nC_6		-7287.		0.1903	-2155.0	
nC_7		-9116.			-2520.2	
		349.9 psia				
C_1		3083.2	7122.			
C_2		1052.6	3238.			
C_3	0.4157	-584.7	-20.3			
nC_4	0.5843	-2175.1				
nC_5		-3702.2				
nC_6		-5168.7				
nC_7		-6576.				

---------------------------------- 300°F ----------------------------------

		1899.0 psia			309.9 psia	
C_1	0.8314	-55.3	108.9		1098.5	1715.
C_2		-1744.0	-1768.		274.9	665.5
C_3		-3040.7	-2912.5	0.6304	-396.2	-246.6
nC_4		-4287.5			-1049.3	
nC_5		-5455.8			-1679.6	
nC_6		-6557.		0.3696	-2287.0	
nC_7	0.1686	-7590.			-2872.6	
		2003.4 psia			235.4 psia	
C_1	0.6650	620.2	982.2		911.3	1602.
C_2		-1937.5	-1829.		268.8	784.3
C_3		-3817.7	-4002.		-247.8	32.7
nC_4		-5608.6		0.8377	-723.0	
nC_5		-7247.			-1205.0	
nC_6	0.3350	-8764.			-1670.2	
nC_7		-10151.		0.1623	-2119.8	

Comp.	y_i	$\Delta\bar{H}_{R-K}$	$\Delta\bar{H}_{BWR}$	y_i	$\Delta\bar{H}_{R-K}$	$\Delta\bar{H}_{BWR}$
				300°F		
		1405.2 psia			153.1 psia	
C_1	0.5252	1832.4	1986.		837.2	1648.
C_2		-1147.3	-1124.		384.5	990.8
C_3		-3373.4	-3562.5		11.7	372.7
nC_4		-5501.1			-351.9	
nC_5	0.4748	-7466.		0.6062	-704.5	
nC_6		-9297.		0.3938	-1045.4	
nC_7		-10988.			-1375.6	
		1247.0 psia			801.7 psia	
C_1		3086.4	3288.	0.5926	1158.0	1687.
C_2	0.7994	-542.7	-421.5		-489.2	-248.0
C_3		-3227.7	-3465.		-1793.9	-1908.
nC_4		-5788.7			-3056.7	
nC_5		-8140.			-4258.8	
nC_6		-10323.		0.4074	-5405.9	
nC_7	0.2006	-12328.			-6498.	
		220.0 psia			800.5 psia	
C_1		238.3	404.4		1655.1	2032.
C_2	0.7103	-107.0	-16.2	0.7616	-294.4	-143.3
C_3		-390.4	-407.4		-1832.3	-1970.
nC_4		-666.7			-3319.6	
nC_5		-934.1			-4732.5	
nC_6		-1192.6		0.2384	-6079.	
nC_7	0.2897	-1442.4			-7358.	
		550.3 psia			456.8 psia	
C_1		1485.1	2057.5	0.7032	194.6	378.5
C_2	0.6557	62.3	367.5		-388.2	-337.5
C_3		-1078.6	-1113.		-861.6	-982.2
nC_4		-2185.5			-1322.0	
nC_5		-3245.6			-1765.7	
nC_6	0.3443	-4261.5			-2192.7	
nC_7		-5234.2		0.2968	-2603.9	
		159.6 psia			452.6 psia	
C_1		235.1	418.5		1631.9	2248.
C_2	0.6212	-36.7	76.1		323.3	672.
C_3		-260.5	-246.0	0.8272	-731.3	-410.6
nC_4		-478.8			-1755.5	
nC_5		-690.5			-2738.7	
nC_6	0.3788	-895.2			-3682.7	
nC_7		-1093.4		0.1728	-4588.4	

CHAPTER V

CONCLUSIONS AND RECOMMENDATIONS

The comparison of the partial enthalpy differences of methane and propane calculated from PVTx data in this work and calculated from Joule-Thomson coefficient and heat capacity data (1) is shown in Table II. Most of the comparisons of the partial enthalpy differences calculated by the two methods compare within the error given for these values (20 to 25 Btu/lb mole). The partial enthalpy differences of propane calculated by the two methods do not compare within the given error in the high pressure range for the low temperatures. At the higher temperatures the comparison for propane is better. The comparison of the pure methane enthalpy differences (Table III) between the values calculated by the two methods are not within the error given for the values. The results of the comparisons in Tables II and III show that the enthalpy differences calculated from PVTx data and Joule-Thomson coefficient and heat capacity data are not always consistent.

For process or design calculations the mixture enthalpy difference correlation for methane binaries developed in this work is preferred over the partial enthalpy difference correlation for methane. The mixture enthalpy difference correlation can be used for both pure components and binary mixtures containing methane and another normal paraffin. This correlation should not be used for a pure component or mixture that has an acentric factor or pseudo acentric factor greater

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than 0.15. The partial enthalpy difference correlation for methane should not be used for a pseudo acentric factor greater than 0.12.

More mixture and partial enthalpy difference data are needed for methane binaries in order to check the proposed correlation methods. The data that would place a stringent requirement on the proposed correlation methods are data for the complete composition range of a system where the acentric factors of the components are widely separated. Data for the methane – n-pentane system would be an example of such a system. If the proposed correlation methods prove to be adequate, the correlations can be extended to higher values of the pseudo acentric factor, pseudo reduced temperature and pseudo reduced pressure as well as lower values of the pseudo reduced temperature.

The primary advantage of using the Redlich-Kwong equation of state to calculate the mixture and partial enthalpy differences of superheated vapor is that it affords a quick and easy way to obtain values by hand calculations. The calculations can be made by using the critical constants and compositions of the components in the mixture and the temperature and pressure of the system in conjunction with Figures 19, 20 and 21. However, the comparisons of the mixture enthalpy differences shown in Tables IX and XI and the partial enthalpy differences shown in Tables IX and XII indicate that the Benedict-Webb-Rubin equation values compare better with the values calculated from PVTx data than do the Redlich-Kwong equation values. The mixture enthalpy difference values calculated from PVTx data and the correlation obtained from these values are recommended over either equation of state. When no enthalpy difference values or correlations are available for mixtures, estimation methods can be used. Equations of state can be used or pure component

correlations can be extended to mixtures (3,6) in order to obtain an estimate of the enthalpy difference. These estimation methods must be used with caution.

A SELECTED BIBLIOGRAPHY

1. Budenholzer, R. A., et al, "Phase Equilibrium in Hydrocarbon Systems: Joule-Thomson Coefficients in the Methane - Propane System", Ind. Engr. Chem. 34, No. 7, 878 (1942).

2. Canjar, L. N. and W. C. Edmister, "Hydrocarbon Partial Enthalpies: I - Values for Methane, Ethene, Ethane, Propene, Propane and n-Butane", Chem. Engr. Prog. Sym. Series 49, No. 7, 119 (1953).

3. Curl, R. F. and K. S. Pitzer, "Volumetric and Thermodynamic Properties of Fluids - Enthalpy, Free Energy and Entropy", Ind. Engr. Chem. 50, No. 2, 265 (1958).

4. Deming, W. E. and L. E. Shupe, "Some Physical Properties of Compressed Gases. I - Nitrogen", Phys. Rev. 37, 638 (1931).

5. Dodge, B. F., Chemical Engineering Thermodynamics, McGraw-Hill Book Co., Inc., New York (1944), p. 15.

6. Edmister, W. C., "Applications of Thermodynamics to Hydrocarbon Processing. Part XVI - Effects of Pressure on Enthalpy and Entropy", Pet. Ref. 28, No. 2, 137 (1949).

7. Erbar, J. H. and R. E. Thompson, "Calculation of Gas Phase Fugacity Coefficients and Generalized Enthalpy Difference from the Redlich-Kwong Equation of State on the IBM 650 Computer", Interoffice Report, School of Chemical Engineering, Oklahoma State University (1959).

8. Hobson, H. and J. H. Weber, "Saturated Liquid Phase Enthalpies for the System n-Butane - n-Heptane at Elevated Pressures", Chem. Engr. Data Series 2, No. 1,7 (1957).

9. Kay, W. B., "Density of Hydrocarbon Gases and Vapors", Ind. Engr. Chem. 28, 1014 (1936).

10. Papadopoulos, A., "Partial Molal Enthalpies of the Lighter Hydrocarbons in Solution with Other Hydrocarbons", M. S. Thesis, University of Delaware (1952).

11. Papadopoulos, A., R. L. Pigford and L. Friend, "Partial Molal Enthalpies of the Lighter Hydrocarbons in Solution with Other Hydrocarbons", Chem. Engr. Prog. Sym. Series 49, No. 7, 119 (1953).

12. Pitzer, K. S., et al "The Volumetric and Thermodynamic Properties of Fluids. II – Compressibility Factor, Vapor Pressure, and Entropy of Vaporization", J. Am. Chem. Soc. 77, 3433 (1955).

13. Redlich, O. and J. N. S. Kwong, "On the Thermodynamics of Solutions. V – An Equation of State. Fugacities of Gaseous Solutions", Chem. Rev. 44, 233 (1949).

14. Rossini, F. D., Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds, Carnegie Institute of Technology, Pittsburgh (1953).

15. Sage, B. H. and W. N. Lacey, Thermodynamic Properties of the Lighter Paraffin Hydrocarbons and Nitrogen, Monograph on API Research Project 37, API New York (1950).

16. Sage B. H. and W. N. Lacey, "Phase Equilibria in Hydrocarbon Systems: The Methane – Ethane System in the Gaseous Region", Ind. Engr. Chem. 31, No. 12, 1497 (1939).

17. Sage, B. H., R. A. Budenholzer and W. N. Lacey, "Phase Equilibria in Hydrocarbon Systems: Methane – n-Butane System in the Gaseous and Liquid Regions", Ind. Engr. Chem. 32, No. 9, 1262 (1940).

18. Salvadori M. G. and M. L. Baron, Numerical Methods in Engineering, Prentice-Hall, Inc., Englewood Cliffs, N. J. (1959).

19. Stiehl, J. S., M. Hobson and J. H. Weber, "Differential Heats of Condensation and Enthalpies of Saturated Liquid Hydrocarbon Mixtures", A. I. Ch. E. Journal 2, No. 3, 389 (1956).

20. Weber, J. H., "Saturated Liquid Phase Enthalpies at High Pressures, Ethane – n-Heptane System", Chem. Engr. Data Series 4, No. 4, 301 (1959).

APPENDIX A

NOMENCLATURE

a,A = parameters for the Redlich-Kwong equation of state

b,B = parameters for the Redlich-Kwong equation of state

G = Gibbs free energy, energy/mole

H = enthalpy, energy/mole

H' = enthalpy, energy

$\bar{H}$ = partial enthalpy of a component, energy/mole

$\triangle H$ = mixture enthalpy difference from an ideal gas or the effect of pressure on the mixture enthalpy, energy/mole

$\triangle\bar{H}$ = partial enthalpy difference of a component from an ideal gas or the effect of pressure on the partial enthalpy of a component, energy/mole

h = distance between equally spaced temperatures in equations 34, 35 and 36

$[\triangle H/RT]$ = parameter for the Redlich-Kwong equation of state

j,k,L = parameters for the Redlich-Kwong equation of state

M,N = parameters for the Redlich-Kwong equation of state

n = number of moles

P = absolute pressure

P^O = vapor pressure of a component

Q = heat put into a system, energy/mole

R = universal gas constant

S   = entropy, energy/degree-mole

T   = absolute temperature

U   = internal energy, energy/mole

V   = volume/mole

W   = work done on a system, energy/mole

x   = general term indicating composition

y   = mole fraction of a component in the vapor

z   = compressibility factor

$\propto$ = residual volume, volume/mole

Θ = dimensionless parameter defined by equation 16

d   = increase or decrease of an extensive property

$\emptyset$ = gas phase fugacity coefficient of a component

ω = acentric factor

Superscripts

P   = value at the system pressure

0   = value in the ideal gas state

(0)   = universal function of reduced temperature and pressure at $\omega = 0$

(1)   = universal function of reduced temperature and pressure that is dependent on the acentric factor

Subscripts

1,2   = refers to component 1 (light component) and component 2 (heavy component) in a binary system, respectively

c   = critical values

i   = value of component i

pc   = pseudo critical values

pr   = pseudo reduced values

r   = reduced values

T,P,n,y   = values being held constant

APPENDIX B

PVTx DATA FOR THE METHANE - PROPANE BINARY

TABLE XIII   1 of 3

COMPRESSIBILITY DATA FOR THE METHANE - PROPANE BINARY (15)

P, psia	100°F	160°F	220°F	280°F	340°F	400°F	460°F
───────────────── 0.10 Mole Fraction Methane ─────────────────							
200	0.7918	0.8629	0.9020	0.9271	0.9439	0.9567	0.9669
400		0.6705	0.7887	0.8498	0.8880	0.9143	0.9344
600			0.6483	0.7671	0.8321	0.8736	0.9040
800				0.6810	0.7779	0.8349	0.8754
1000				0.5976	0.7250	0.7990	0.8501
1250				0.5277	0.6678	0.7605	0.8228
1500				0.4975	0.6295	0.7301	0.7994
1750				0.5079	0.6128	0.7100	0.7839
2000				0.5314	0.6145	0.7021	0.7765
───────────────── 0.20 Mole Fraction Methane ─────────────────							
200	0.8279	0.8840	0.9159	0.9371	0.9518	0.9627	0.9717
400		0.7391	0.8237	0.8724	0.9044	0.9270	0.9440
600			0.7209	0.8059	0.8584	0.8929	0.9188
800			0.6105	0.7407	0.8151	0.8619	0.8959
1000			0.5002	0.6803	0.7752	0.8338	0.8760
1250			0.4291	0.6163	0.7300	0.8034	0.8548
1500			0.4339	0.5734	0.6960	0.7788	0.8376
1750			0.4610	0.5629	0.6747	0.7617	0.8248
2000			0.4970	0.5727	0.6695	0.7529	0.8166

TABLE XIII (Continued)   2 of 3

P, psia	100°F	160°F	220°F	280°F	340°F	400°F	460°F
			0.30 Mole Fraction Methane				
200	0.8590	0.9032	0.9288	0.9464	0.9592	0.9689	0.9763
400		0.7923	0.8542	0.8928	0.9198	0.9391	0.9539
600		0.6552	0.7763	0.8391	0.8820	0.9110	0.9332
800			0.6989	0.7880	0.8473	0.8862	0.9150
1000			0.6185	0.7416	0.8161	0.8639	0.8993
1250			0.5291	0.6911	0.7803	0.8402	0.8832
1500			0.5038	0.6528	0.7534	0.8224	0.8701
1750			0.5112	0.6308	0.7344	0.8092	0.8600
2000			0.5349	0,6294	0.7257	0.7997	0.8537
			0.40 Mole Fraction Methane				
200	0.8860	0.9207	0.9408	0.9553	0.9663	0.9746	0.9810
400		0.8348	0.8812	0.9111	0.9341	0.9506	0.9633
600		0.7400	0.8213	0.8686	0.9035	0.9278	0.9469
800		0.6358	0.7637	0.8287	0.8755	0.9082	0.9326
1000		0.5379	0.7092	0.7925	0.8511	0.8912	0.9204
1250		0.4652	0.6483	0.7543	0.8243	0.8728	0.9083
1500		0.4533	0.6071	0.7249	0.8038	0.8597	0.8991
1750		0.4715	0.5890	0.7046	0.7900	0.8497	0.8911
2000		0.5019	0.5928	0.6961	0.7800	0.8426	0.8875
			0.50 Mole Fraction Methane				
200	0.9086	0.9351	0.9520	0.9636	0.9729	0.9799	0.9850
400	0.8063	0.8692	0.9048	0.9281	0.9470	0.9608	0.9715
600		0.8019	0.8586	0.8947	0.9232	0.9430	0.9590
800		0.7313	0.8149	0.8640	0.9005	0.9277	0.9480
1000		0.6670	0.7744	0.8365	0.8821	0.9146	0.9390
1250		0.5880	0.7306	0.8078	0.8624	0.9004	0.9304
1500		0.5450	0.6970	0.7853	0.8469	0.8907	0.9242
1750		0.5373	0.6752	0.7692	0.8361	0.8835	0.9183
2000		0.5542	0.6663	0.7616	0.8289	0.8799	0.9165
			0.60 Mole Fraction Methane				
200	0.9283	0.9482	0.9622	0.9716	0.9790	0.9846	0.9899
400	0.8531	0.8984	0.9257	0.9441	0.9591	0.9702	0.9789
600	0.7692	0.8470	0.8901	0.9184	0.9410	0.9571	0.9700
800		0.7979	0.8573	0.8951	0.9238	0.9453	0.9620
1000		0.7502	0.8269	0.8748	0.9100	0.9353	0.9557
1250		0.6941	0.7944	0.8534	0.8956	0.9254	0.9498
1500		0.6519	0.7688	0.8364	0.8841	0.9181	0.9455
1750		0.6322	0.7500	0.8243	0.8766	0.9136	0.9423
2000		0.6297	0.7389	0.8186	0.8716	0.9120	0.9408

TABLE XIII (Continued)

P, psia	100°F	160°F	220°F	280°F	340°F	400°F	460°F
———————————————— 0.70 Mole Fraction Methane ————————————————
200	0.9448	0.9606	0.9714	0.9789	0.9847	0.9892	0.9925
400	0.8878	0.9222	0.9439	0.9590	0.9703	0.9791	0.9857
600	0.8279	0.8836	0.9172	0.9401	0.9572	0.9700	0.9796
800	0.7692	0.8473	0.8928	0.9229	0.9449	0.9614	0.9742
1000	0.7127	0.8126	0.8705	0.9078	0.9351	0.9542	0.9700
1250		0.7728	0.8470	0.8921	0.9249	0.9477	0.9661
1500		0.7408	0.8270	0.8802	0.9168	0.9430	0.9640
1750		0.7192	0.8113	0.8714	0.9113	0.9398	0.9631
2000		0.7089	0.8014	0.8652	0.9079	0.9395	0.9625
———————————————— 0.80 Mole Fraction Methane ————————————————
200	0.9588	0.9716	0.9792	0.9853	0.9896	0.9931	0.9966
400	0.9159	0.9421	0.9593	0.9716	0.9800	0.9870	0.9917
600	0.8718	0.9143	0.9402	0.9584	0.9713	0.9810	0.9880
800	0.8307	0.8875	0.9226	0.9468	0.9634	0.9759	0.9851
1000	0.7914	0.8627	0.9069	0.9364	0.9570	0.9713	0.9828
1250	0.7485	0.8361	0.8899	0.9257	0.9501	0.9677	0.9808
1500	0.7146	0.8131	0.8750	0.9169	0.9449	0.9650	0.9804
1750	0.6893	0.7965	0.8642	0.9104	0.9414	0.9632	0.9812
2000	0.6781	0.7862	0.8563	0.9065	0.9399	0.9640	0.9827
———————————————— 0.90 Mole Fraction Methane ————————————————
200	0.9700	0.9802	0.9858	0.9904	0.9938	0.9964	0.9980
400	0.9398	0.9589	0.9722	0.9816	0.9881	0.9931	0.9965
600	0.9086	0.9400	0.9594	0.9732	0.9828	0.9901	0.9951
800	0.8809	0.9220	0.9478	0.9659	0.9786	0.9877	0.9943
1000	0.8541	0.9048	0.9375	0.9595	0.9751	0.9858	0.9940
1250	0.8225	0.8866	0.9259	0.9533	0.9716	0.9845	0.9940
1500	0.7977	0.8733	0.9164	0.9481	0.9692	0.9844	0.9953
1750	0.7768	0.8626	0.9102	0.9450	0.9683	0.9849	0.9979
2000	0.7660	0.8550	0.9054	0.9430	0.9690	0.9868	1.0004

APPENDIX C

DATA FROM LITERATURE USED IN ENTHALPY DIFFERENCE CORRELATIONS

PARTIAL ENTHALPY DIFFERENCES FROM LITERATURE (15)

Btu/lb mole

P, psia	70°F	100°F	130°F	160°F	190°F	220°F	250°F

———————— Partial Enthalpy Difference of Methane in Ethane ————————

0.50 Mole Fraction Methane

P, psia	70°F	100°F	130°F	160°F	190°F	220°F	250°F
200	-62	-58	-58	-52	-42	-35	-35
400	-100	-101	-103	-94	-79	-70	-72
600	-63	-105	-119	-115	-114	-101	-104
800	-54	-107	-143	-142	-137	-133	-135
1000	8	-70	-128	-149	-154	-161	-155
1250	148	35	-120	-166	-174	-182	-186
1500	147	178	-102	-152	-189	-201	-216
1750	-41	329	-115	-182	-218	-244	-247
2000	-282	-151	-171	-225	-244	-281	-296
2250	-500	-176	-271	-285	-295	-324	-337
2500	-712	-204	-385	-349	-351	-376	-388
2750	-914	-462	-489	-430	-419	-436	-457
3000	-1109	-718	-574	-507	-482	-498	-526

0.60 Mole Fraction Methane

P, psia	70°F	100°F	130°F	160°F	190°F	220°F	250°F
200	-69	-74	-71	-58	-51	-39	-37
400	-128	-133	-128	-113	-100	-86	-84
600	-184	-193	-185	-162	-145	-128	-118
800	-221	-225	-226	-205	-187	-170	-156
1000	-231	-256	-270	-244	-225	-211	-193
1250	-242	-272	-296	-287	-273	-252	-237
1500	-352	-308	-328	-334	-319	-293	-284
1750	-558	-425	-381	-371	-363	-337	-327
2000	-779	-556	-455	-422	-409	-382	-375
2250	-947	-641	-531	-483	-457	-429	-422
2500	-1103	-789	-627	-554	-512	-482	-484
2750	-1213	-883	-700	-608	-577	-533	-546
3000	-1346	-929	-790	-674	-643	-600	-604

TABLE XIV (Continued)   2 of 7

P, psia	70°F	100°F	130°F	160°F	190°F	220°F	250°F

------------ Partial Enthalpy Difference of Methane in Ethane ------------

0.70 Mole Fraction Methane

P, psia	70°F	100°F	130°F	160°F	190°F	220°F	250°F
200	-80	-83	-79	-64	-56	-42	-40
400	-157	-153	-143	-124	-113	-98	-92
600	-231	-226	-221	-185	-163	-141	-131
800	-306	-288	-268	-242	-214	-188	-173
1000	-368	-352	-331	-294	-263	-236	-215
1250	-558	-430	-390	-362	-327	-290	-266
1500	-580	-523	-452	-428	-386	-340	-316
1750	-730	-641	-526	-487	-442	-392	-370
2000	-901	-741	-606	-552	-499	-444	-420
2250	-1059	-844	-687	-614	-553	-501	-474
2500	-1167	-972	-768	-685	-611	-554	-534
2750	-1277	-1057	-844	-738	-673	-603	-591
3000	-1379	-1148	-919	-798	-730	-657	-646

0.80 Mole Fraction Methane

P, psia	70°F	100°F	130°F	160°F	190°F	220°F	250°F
200	-89	-89	-81	-69	-62	-48	-45
400	-179	-163	-151	-132	-121	-102	-96
600	-260	-239	-232	-201	-175	-152	-143
800	-352	-319	-288	-262	-230	-202	-187
1000	-440	-397	-355	-322	-283	-259	-235
1250	-564	-506	-437	-402	-358	-318	-292
1500	-699	-614	-521	-477	-424	-379	-356
1750	-818	-723	-603	-552	-491	-436	-405
2000	-942	-836	-692	-622	-553	-495	-456
2250	-1061	-929	-775	-690	-611	-553	-513
2500	-1170	-1029	-848	-762	-673	-609	-566
2750	-1266	-1113	-923	-821	-731	-658	-619
3000	-1365	-1188	-996	-877	-787	-701	-676

0.90 Mole Fraction Methane

P, psia	70°F	100°F	130°F	160°F	190°F	220°F	250°F
200	-92	-91	-83	-73	-63	-52	-47
400	-190	-166	-159	-140	-130	-110	-105
600	-279	-253	-238	-213	-190	-169	-155
800	-379	-339	-307	-280	-248	-225	-206
1000	-479	-423	-375	-344	-305	-285	-257
1250	-616	-536	-468	-429	-335	-345	-317
1500	-751	-646	-564	-512	-459	-412	-376
1750	-869	-751	-648	-589	-524	-472	-436
2000	-982	-857	-738	-660	-596	-532	-487
2250	-1080	-951	-819	-734	-661	-598	-547
2500	-1182	-1035	-891	-800	-713	-651	-596
2750	-1271	-1117	-958	-867	-774	-700	-650
3000	-1358	-1183	-1030	-922	-833	-748	-699

TABLE XIV (Continued)   3 of 7

P, psia	70°F	100°F	130°F	160°F	190°F	220°F	250°F

———————— Partial Enthalpy Difference of Ethane in Methane ————————

0.50 Mole Fraction Methane

P, psia	70°F	100°F	130°F	160°F	190°F	220°F	250°F
200	-294	-269	-251	-216	-206	-243	-171
400	-652	-585	-537	-474	-422	-443	-352
600	-1160	-947	-872	-764	-671	-669	-539
800	-1842	-1415	-1266	-1067	-948	-903	-733
1000	-2554	-1995	-1674	-1414	-1238	-1148	-941
1250	-2474	-2779	-2190	-1860	-1613	-1454	-1202
1500	-4504	-3455	-2759	-2312	-1971	-1761	-1456
1750	-4865	-3929	-3263	-2754	-2302	-2043	-1706
2000	-4997	-4242	-3656	-3125	-2601	-2310	-1951
2250	-5030	-4392	-3879	-3412	-2824	-2551	-2159
2500	-4991	-4469	-4016	-3614	-3006	-2746	-2343
2750	-4884	-4490	-4129	-3737	-3172	-2891	-2509
3000	-4737	-4498	-4232	-3836	-3261	-3026	-2661

0.60 Mole Fraction Methane

P, psia	70°F	100°F	130°F	160°F	190°F	220°F	250°F
200	-286	-262	-241	-210	-196	-239	-166
400	-626	-564	-510	-454	-402	-428	-341
600	-1067	-879	-816	-720	-635	-639	-522
800	-1651	-1296	-1173	-994	-889	-856	-704
1000	-2255	-1810	-1526	-1310	-1152	-1083	-901
1250	-2996	-2425	-1989	-1705	-1494	-1373	-1152
1500	-3666	-2912	-2485	-2081	-1621	-1661	-1381
1750	-4167	-3304	-2916	-2508	-2130	-1934	-1616
2000	-4341	-3599	-3286	-2907	-2401	-2196	-1857
2250		-3730	-3551	-3185	-2636	-2424	-2049
2500	-4455	-3863	-3701	-3436	-2816	-2633	-2233
2750		-3954	-3884	-3554	-2992	-2768	-2420
3000	-4467	-4035	-3997	-3704	-3094	-2920	-2586

TABLE XIV (Continued)   4 of 7

P, psia	100°F	130°F	160°F	220°F	250°F

————————— Partial Enthalpy Difference of Methane in n-Butane —————————

0.85 Mole Fraction Methane

P, psia	100°F	130°F	160°F	220°F	250°F
200				-10	0
400	-86	-90	-40	-30	-20
600	-86	-150	-80	-60	-40
800		-210	-130	-90	-70
1000		-290	-180	-120	-100
1250		-390	-260	-160	-140
1500		-490	-340	-220	-190
1750		-590	-430	-270	-250
2000		-690	-516	-340	-290
2500		-880	-690	-460	-390
3000		-860	-860	-570	-490

0.90 Mole Fraction Methane

P, psia	100°F	130°F	160°F	220°F	250°F
200				-40	-50
400	-126	-120	-100	-80	-80
600	-186	-190	-160	-120	-110
800		-260	-220	-170	-160
1000		-340	-290	-220	-200
1250		-430	-370	-290	-250
1500		-530	-460	-350	-310
1750		-620	-540	-420	-360
2000		-710	-620	-480	-420
2500		-860	-760	-590	-520
3000		-1000	-870	-700	-620

0.95 Mole Fraction Methane

P, psia	100°F	130°F	160°F	220°F	250°F
200				-60	-60
400	-156	-150	-130	-110	-100
600	-236	-220	-200	-170	-150
800	-326	-300	-270	-230	-200
1000	-416	-370	-340	-290	-240
1250	-516	-470	-430	-360	-310
1500	-616	-560	-510	-430	-380
1750	-716	-650	-590	-490	-430
2000	-806	-730	-670	-560	-490
2500	-976	-890	-810	-660	-600
3000	-1006	-1020	-920	-770	-700

TABLE XIV (Continued) 5 of 7

P, psia	100°F	130°F	160°F	220°F	250°F

------------ Partial Enthalpy Difference of n-Butane in Methane -----------

0.85 Mole Fraction Methane

P, psia	100°F	130°F	160°F	220°F	250°F
200	-230	-710	-680	-610	-550
400	-1440	-1430	-1370	-1220	-1110
600		-2120	-2050	-1850	-1680
800		-2750	-2690	-2460	-2250
1000		-3340	-3290	-3050	-2810
1250		-3970	-3940	-3740	-3470
1500		-4500	-4520	-4360	-4080
1750		-4920	-4990	-4920	-4120
2000		-5260	-5390	-5390	-5110
2500		-5660	-5940	-6110	-5890
3000		-5750	-6230	-6550	-6390

0.90 Mole Fraction Methane

P, psia	100°F	130°F	160°F	220°F	250°F
200	-620	-550	-480	-390	-360
400	-1270	-1110	-990	-810	-760
600		-1710	-1500	-1260	-1170
800		-2300	-2020	-1710	-1600
1000		-2870	-2530	-2160	-2030
1250		-3720	-3130	-2720	-2560
1500		-4130	-3700	-3250	-3110
1750		-4670	-4200	-3740	-3590
2000		-5130	-4640	-4170	-4030
2500		-5860	-5320	-4900	-4730
3000		-6290	-5870	-5400	-5210

0.95 Mole Fraction Methane

P, psia	100°F	130°F	160°F	220°F	250°F
200	-470	-420	-360	-290	-270
400	-970	-830	-760	-620	-580
600	-1470	-1320	-1200	-990	-920
800	-1990	-1810	-1670	-1400	-1310
1000	-2540	-2330	-2130	-1840	-1710
1250	-3140	-2960	-2750	-2380	-2230
1500	-3760	-3550	-3340	-2910	-2730
1750	-4250	-4130	-3880	-3420	-3200
2000	-4770	-4730	-4380	-3890	-3660
2500	-5630	-5630	-5230	-4640	-4450
3000	-6310	-6260	-5830	-5180	-4870

TABLE XIV (Continued)   6 of 7

P, psia	100°F	160°F	220°F

_____ Partial Enthalpy Difference _____
of Methane in n-Pentane

0.96 Mole Fraction Methane

P, psia	100°F	160°F	220°F
200	-89	-75	-4
400	-182	-148	-111
600	-272	-226	-163
800	-367	-293	-216
1000	-463	-365	-271
1250	-582	-449	
1500	-689	-532	-399
1750	-789	-617	-462
2000	-878	-697	-524
2500	-1042	-835	-642
3000	-1173	-961	-744

_____ Partial Enthalpy Difference _____
of n-Pentane in Methane

0.96 Mole Fraction Methane

P, psia	100°F	160°F	220°F
200	-940	-870	-782
400	-1885	-1705	-1474
600	-2765	-2545	-2174
800	-3715	-3280	-2851
1000	-4500	-4115	-3473
1250	-5405	-5480	-4273
1500	-6255	-5840	-4998
1750	-6965	-6590	-5644
2000	-7505	-7180	-6207
2500	-8405	-8100	-7098
3000	-8885	-8775	-7751

TABLE XIV (Continued)

P, psia	100°F	160°F	220°F	280°F	340°F	400°F	460°F
———————————————— Enthalpy Difference of Methane ————————————————
200	-87.1	-73.5	-62.0	-52.2	-43.6	-36.4	-30.5
400	-174.6	-146.8	-124.9	-103.8	-86.6	-72.2	-60.5
600	-262.6	-219.5	-185.2	-154.7	-128.8	-107.3	-90.0
800	-350.3	-291.3	-245.4	-204.4	-170.0	-141.5	-118.7
1000	-437.7	-362.1	-304.4	-253.0	-210.2	-174.7	-146.6
1250	-546.2	-448.4	-376.0	-311.7	-258.8	-215.0	-181.0
1500	-652.9	-531.8	-445.0	-368.2	-305.3	-253.3	-213.2
1750	-756.0	-612.2	-510.7	-422.3	-349.9	-290.0	-244.2
2000	-852.9	-688.5	-573.5	-473.7	-392.4	-324.9	-273.5
———————————————— Enthalpy Difference of Propane ————————————————
200		-593.5	-466.1	-390.2	-340.4	-305.5	-283.6
400			-1115.6	-858.5	-712.2	-619.9	-570.2
600			-2149.6	-1436.2	-1122.7	-950.2	-858.6
800			-4722.1	-2191.1	-1584.4	-1299.0	-1148.3
1000			-5107.5	-3160.7	-2099.4	-1664.1	-1441.1
1250			-5290.0	-4055.8	-2755.5	-2131.1	-1805.3
1500			-5393.7	-4427.6	-3335.8	-2579.1	-2160.7
1750			-5456.3	-4648.0	-3732.7	-2972.0	-2493.6
2000			-5499.5	-4788.7	-3991.9	-3290.3	-2789.1

APPENDIX D

REARRANGEMENT OF REDLICH-KWONG EQUATION OF STATE FOR
HAND CALCULATIONS OF THE ENTHALPY DIFFERENCES

Erbar and Thompson (7) used the thermodynamic relationship

$$\left(\frac{\delta\ln\phi_i}{\delta T}\right)_{P,y} = - \frac{\Delta\bar{H}_i}{RT^2} \tag{59}$$

where ϕ_i is the gas phase fugacity coefficient of component i.

to calculate the partial enthalpy difference of component i from the
equation presented by Redlich and Kwong (13),

$$\ln\phi_i = (z - 1)\frac{B_i}{B} - \ln(z - BP) - \frac{A^2}{B}\left(\frac{2A_i}{A} - \frac{B_i}{B}\right)\ln\left(1 + \frac{BP}{z}\right) \tag{60}$$

The partial enthalpy difference equation derived by Erbar and Thompson
is shown below. This equation was programmed for use on the IBM 650
digital computer.

$$- \frac{\Delta\bar{H}_i}{RT^2} = \frac{B_i}{B}\left(\frac{\delta z}{\delta T}\right)_{P,y} - \frac{1}{(z - BP)}\left[\left(\frac{\delta z}{\delta T}\right)_{P,y} - P\left(\frac{\delta B}{\delta T}\right)_{P,y}\right]$$

$$- \left[\frac{2A_i}{A} - \frac{B_i}{B}\right]\left[\ln 1 + \frac{BP}{z}\right]\left[\frac{\delta(A^2/B)}{\delta T}_{P,y}\right]$$

$$- \frac{A^2}{B}\left[\frac{2A_i}{A} - \frac{B_i}{B}\right]\left[\frac{\frac{P}{z}\left(\frac{\delta B}{\delta T}\right)_{P,y} - \frac{BP}{z^2}\left(\frac{\delta z}{\delta T}\right)_{P,y}}{1 + \frac{BP}{z}}\right] \tag{61}$$

where
$$\left(\frac{\delta B}{\delta T}\right)_{P,y} = -\frac{B}{T} \tag{62}$$

$$\left[\frac{\delta(A^2/B)}{\delta T}\right]_{P,y} = -\frac{1.5A^2}{BT} \tag{63}$$

$$\left(\frac{\delta z}{\delta T}\right)_{P,y} = \left(\frac{\delta z}{\delta T}\right)_{V,y} - \left(\frac{\delta z}{\delta V}\right)_{T,y}\frac{\left(\frac{\delta P}{\delta T}\right)_{V,y}}{\left(\frac{\delta P}{\delta V}\right)_{T,y}} \tag{64}$$

and
$$\left(\frac{\delta z}{\delta T}\right)_{V,y} = \frac{1.5a}{RT^{2.5}(V + b)} \tag{65}$$

$$\left(\frac{\delta z}{\delta V}\right)_{T,y} = -\frac{b}{(V - b)^2} + \frac{a}{RT^{1.5}(V + b)^2} \tag{66}$$

$$\left(\frac{\delta P}{\delta T}\right)_{V,y} = \frac{R}{V - b} + \frac{0.5a}{T^{1.5}V(V + b)} \tag{67}$$

$$\left(\frac{\delta P}{\delta V}\right)_{T,y} = -\frac{RT}{(V - b)^2} + \frac{a}{T^{0.5}V^2(V + b)} + \frac{a}{T^{0.5}V(V + b)^2} \tag{68}$$

First change all the parameters into terms of A^2/B and B. This can be done since $a = A^2R^2T^{2.5}$ and $b = BRT$.

$$\left(\frac{\delta z}{\delta T}\right)_{V,y} = \frac{A^2}{B}\frac{1}{T}\frac{1.5}{(z/BP + 1)} \tag{69}$$

$$\left(\frac{\delta z}{\delta V}\right)_{T,y} = -\frac{1}{BRT(z/BP - 1)^2} + \frac{A^2}{B}\frac{1}{BRT(z/BP + 1)^2} \tag{70}$$

$$\left(\frac{\delta P}{\delta T}\right)_{V,y} = \frac{R}{BRT(z/BP - 1)} + \frac{A^2}{B}\frac{0.5R}{BRT(z/BP)(z/BP + 1)} \tag{71}$$

$$\left(\frac{\delta P}{\delta V}\right)_{T,y} = -\frac{RT}{(BRT)^2(z/BP - 1)^2} + \frac{A^2}{B}\frac{RT}{(BRT)^2(z/BP)^2(z/BP + 1)}$$

$$+ \frac{A^2}{B}\frac{RT}{(BRT)^2(z/BP)(z/BP + 1)^2} \tag{72}$$

Let $z/BP = j = 1/h$ and $A^2/B = k$. Using these definitions in equations 69, 70, 71 and 72 and substituting these equations into equation 64 gives upon simplification,

$$\left(\frac{\delta z}{\delta T}\right)_{P,y} = \frac{1}{T}\left(\frac{1.5k}{(j+1)}\right.$$

$$+ \frac{j\left[j(j+1)^3 + 0.5k(j+1)^2(j-1) - kj(j+1)(j-1)^2 - 0.5k^2(j-1)^3\right]}{(j-1)(j+1)\left[-j^2(j+1)^2 + k(j-1)^2(j+1) + kj(j-1)^2\right]}\left.\right) \tag{73}$$

or

$$\left(\frac{\delta z}{\delta T}\right)_{P,y} = \frac{1}{T}\left[\frac{1.5k}{(j+1)} + L\right] \tag{74}$$

where equation 74 defines L.

Equation 61 can be rearranged to the following form.

$$- \frac{\Delta \bar{H}_i}{RT^2} = \left[\left(\frac{B_i}{B} - 1\right) + 1 \left(\frac{\delta z}{\delta T}\right)_{P,y}\right] - \frac{1}{(z - BP)}\left[\left(\frac{\delta z}{\delta T}\right)_{P,y} - P\left(\frac{\delta B}{\delta T}\right)_{P,y}\right]$$

$$- \left[2\left(\frac{A_i}{A} - 1\right) - \left(\frac{B_i}{B} - 1\right) + 1\right]\left[\ln(1 + BP/z)\right]\left[\frac{\delta(A^2/B)}{\delta T}\right]_{P,y}$$

$$- \frac{A^2}{B}\left[2\left(\frac{A_i}{A} - 1\right) - \left(\frac{B_i}{B} - 1\right) + 1\right]\left[\frac{\frac{P}{z}\left(\frac{\delta B}{\delta T}\right)_{P,y} - \frac{BP}{z^2}\left(\frac{\delta z}{\delta T}\right)_{P,y}}{1 + BP/z}\right] \tag{75}$$

Collecting terms that are multiplied by $(A_i/A - 1)$ and $(B_i/B - 1)$ and substituting equations 62, 63 and 74 into equation 75 gives

$$- \frac{\Delta \bar{H}_i}{RT^2} = \frac{1}{T}\left[L - \frac{1}{(z - BP)}(L + BP) + 1.5k \ln(1 + h) - kh\left(\frac{1 + L/z}{1 + h}\right)\right]$$

$$+ \frac{1}{T}\left(\frac{A_i}{A} - 1\right)\left[3k \ln(1 + h) + 2kh\left(\frac{1 + L/z}{1 + h}\right)\right]$$

$$+ \frac{1}{T}\left(\frac{B_i}{B} - 1\right)\left[L - 1.5k \ln(1 + h) - kh\left(\frac{1 + L/z}{1 + h}\right)\right] \tag{76}$$

or

$$- \frac{\Delta \bar{H}_i}{RT} = \left[\frac{\Delta H}{RT}\right] + \left(\frac{A_i}{A} - 1\right)M + \left(\frac{B_i}{B} - 1\right)N \tag{77}$$

where equation 77 defines the quantities $\left[\Delta H/RT\right]$, M and N which are functions of A^2/B and BP. Equation 77 was programmed for the IBM 650 digital computer.

VALUES FOR GENERAL ENTHALPY PLOT BASED ON THE REDLICH-KWONG EQUATION

TABLE XV   1 of 2

VALUES OF $[\Delta H/RT]$, M AND N AS FUNCTIONS OF A^2/B AND BP

BP	$[\Delta H/RT]$	M	N	$[\Delta H/RT]$	M	N
	——— $A^2/B = 0.5$ *———			——— $A^2/B = 1.0$ ———		
0.02	0.004	0.049	-0.021	0.029	0.100	-0.022
0.04	0.007	0.095	-0.044	0.055	0.198	-0.048
0.06	0.008	0.140	-0.068	0.080	0.294	-0.078
0.08	0.008	0.181	-0.094	0.102	0.387	-0.111
0.10	0.007	0.220	-0.120	0.121	0.475	-0.146
0.15	-0.002	0.308	-0.190	0.159	0.678	-0.244
0.20	-0.017	0.383	-0.262	0.185	0.850	-0.349
0.25	-0.037	0.446	-0.335	0.198	0.993	-0.455
0.30	-0.062	0.500	-0.408	0.202	1.111	-0.559
0.40	-0.120	0.585	-0.549	0.186	1.288	-0.754
0.60	-0.264	0.697	-0.816	0.098	1.501	-1.096
0.80	-0.428	0.766	-1.065	-0.034	1.621	-1.390
1.00	-0.603	0.812	-1.302	-0.188	1.698	-1.657
	——— $A^2/B = 1.5$ ———			——— $A^2/B = 2.0$ ———		
0.02	0.054	0.152	-0.023	0.080	0.208	-0.024
0.04	0.106	0.309	-0.053	0.158	0.429	-0.059
0.06	0.155	0.467	-0.089	0.236	0.663	-0.104
0.08	0.202	0.624	-0.132	0.310	0.906	-0.160
0.10	0.245	0.778	-0.181	0.382	1.151	-0.228
0.15	0.338	1.138	-0.321	0.541	1.743	-0.438
0.20	0.410	1.443	-0.476	0.669	2.238	-0.675
0.25	0.462	1.688	-0.631	0.765	2.609	-0.904
0.30	0.496	1.879	-0.779	0.831	2.870	-1.107
0.40	0.526	2.143	-1.039	0.903	3.184	-1.434
0.60	0.487	2.422	-1.451	0.905	3.459	-1.890
0.80	0.382	2.564	-1.779	0.820	3.585	-2.230
1.00	0.245	2.651	-2.064	0.695	3.662	-2.521

* For $A^2/B = 0$; $[\Delta H/RT] = -BP$, M = 0 and N = - BP

TABLE XV (Continued)

BP	$[\Delta H/RT]$	M	N	$[\Delta H/RT]$	M	N
		$A^2/B = 2.5$			$A^2/B = 3.0$	
0.02	0.106	0.265	-0.026	0.133	0.325	-0.027
0.04	0.213	0.562	-0.065	0.271	0.709	-0.073
0.06	0.321	0.892	-0.122	0.414	1.164	-0.145
0.08	0.429	1.252	-0.198	0.562	1.699	-0.253
0.10	0.535	1.635	-0.297	0.712	2.312	-0.407
0.15	0.779	2.600	-0.629	1.071	3.964	-0.990
0.20	0.976	3.377	-1.009	1.355	5.113	-1.617
0.25	1.120	3.870	-1.341	1.545	5.589	-2.045
0.30	1.218	4.154	-1.601	1.665	5.745	-2.308
0.40	1.323	4.418	-1.961	1.786	5.798	-2.619
0.60	1.351	4.592	-2.409	1.822	5.785	-2.993
0.80	1.278	4.667	-2.736	1.753	5.787	-3.283
1.00	1.160	4.717	-3.018	1.638	5.800	-3.546
		$A^2/B = 3.5$			$A^2/B = 4.0$	
0.02	0.160	0.389	-0.029	0.188	0.455	-0.030
0.04	0.332	0.875	-0.082	0.396	1.065	-0.093
0.06	0.516	1.502	-0.176	0.630	1.941	-0.222
0.08	0.715	2.323	-0.339	0.899	3.313	-0.495
0.10	0.927	3.391	-0.610	1.214	5.605	-1.102
0.15	1.461	6.523	-1.813	2.049	11.704	-3.975
0.20	1.841	7.710	-2.729	2.451	10.510	-4.253
0.25	2.053	7.669	-3.055	2.630	9.589	-4.161
0.30	2.173	7.485	-3.196	2.726	9.084	-4.111
0.40	2.286	7.220	-3.358	2.813	8.576	-4.108
0.60	2.314	6.998	-3.614	2.820	8.197	-4.246
0.80	2.241	6.924	-3.856	2.741	8.062	-4.442
1.00	2.126	6.899	-4.094	2.622	8.004	-4.655
		$A^2/B = 4.5$			$A^2/B = 5.0$	
0.02	0.217	0.526	-0.032	0.247	0.600	-0.034
0.04	0.465	1.287	-0.107	0.540	1.553	-0.125
0.06	0.761	2.563	-0.292	0.920	3.576	-0.421
0.08	1.144	5.362	-0.869	1.605	17.724	-3.685
0.10	1.732	15.481	-3.904	3.354	22.674	-10.130
0.15	2.873	15.159	-6.376	3.659	14.595	-6.787
0.20	3.122	12.075	-5.406	3.780	12.818	-6.069
0.25	3.238	10.973	-5.070	3.843	11.992	-5.761
0.30	3.301	10.403	-4.919	3.878	11.510	-5.603
0.40	3.355	9.823	-4.817	3.902	10.972	-5.473
0.60	3.337	9.367	-4.873	3.860	10.504	-5.485
0.80	3.248	9.190	-5.030	3.761	10.305	-5.615
1.00	3.126	9.106	-5.220	3.634	10.203	-5.786

APPENDIX F

SAMPLE HAND CALCULATION OF ENTHALPY DIFFERENCES
USING THE REDLICH-KWONG EQUATION

The sample calculation will be performed for a methane – ethane binary system at $0°F$ ($459.7°R$) and 950 psia. The composition is 0.742 mole fraction methane (component 1) and 0.258 mole fraction ethane (component 2).

$$A_i^2 = 0.4278R/P_{c_i}T_{r_i}^{2.5} \quad \text{and} \quad B_i = 0.0867/P_{c_i}T_{r_i}$$

Component	A_i^2	A_i	B_i
Methane	0.000306	0.0175	0.0000961
Ethane	0.000945	0.0308	0.0001461

$A = 0.0210$, $A^2 = 0.000441$, $B = 0.0001090$, $A^2/B = 4.02$, $BP = 0.1036$

From Figures 19, 20 and 21,

$$[\Delta H/RT] = 1.29 \qquad M = 6.30 \qquad N = -1.30$$

$$-\frac{\Delta \bar{H}_1}{RT} = 1.29 + \left(\frac{0.0175}{0.0210} - 1\right)6.3 + \left(\frac{0.0000961}{0.0001090} - 1\right)(-1.30)$$

$$= 1.29 - 1.05 + 0.15 = 0.39, \qquad \Delta \bar{H}_1 = -356 \text{ Btu/lb mole}$$

$$-\frac{\Delta \bar{H}_2}{RT} = 1.29 + \left(\frac{0.0308}{0.0210} - 1\right)6.3 + \left(\frac{0.0001461}{0.0001090} - 1\right)(-1.30)$$

$$= 1.29 + 2.94 - 0.44 = 3.79, \qquad \Delta \bar{H}_2 = -3460 \text{ Btu/lb mole}$$

$$-\frac{\Delta H}{RT} = 1.29, \qquad \Delta H = -1178 \text{ Btu/lb mole}$$

The IBM 650 computer values are $\Delta \bar{H}_1 = -383$ Btu/lb mole, $\Delta \bar{H}_2 = -3443$ Btu/lb mole and $\Delta H = -1173$ Btu/lb mole.

VITA

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