Enthalpy of Hydrocarbon Mixtures

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A method of estimating enthalpies of mixtures of light hydrocarbons is presented. Enthalpies so obtained are consistent with equilibrium-vaporization constants that have been correlated with the composition characterization factor, the molal average boiling point (M.A.B.P.).

Values of the isothermal-pressure corrections to the enthalpy of ideal gas mixtures ($H° - H$) are presented on three plots with parameters of temperature, pressure, and molal-average boiling point. Pressures range from zero to 1,500 lb./sq. in. abs., temperatures from −200° to 500°F., and M.A.B.P. from −200° to 150°F.

Process-design engineers need a rapid and reliable method for estimating the enthalpies of complex hydrocarbon systems. Of the past work devoted to the general solution of this problem, undoubtedly the greatest contribution has been made by Benedict, Webb, Rubin, and Friend (*2*), who formulated an equation of state that could not only predict the pressure-volume-temperature relationships, but also describe the two-phase regions, of pure components and mixtures. They correlated fugacity coefficients for paraffins and olefins in hydrocarbon mixtures by use of this equation and suggested that enthalpy data may be calculated in the same way. More specific work followed the lead of Benedict and coworkers in the form of isothermal-pressure corrections to the partial-molal enthalpies of hydrocarbons in the ideal gas state. Two independent investigations carried on at the same time started with the original work of Benedict and coworkers but proceeded along different lines. Papadopoulos, Pigford, and Friend (*11*), using the same mixtures, densities, and temperatures that were used in the original work on fugacity coefficients, differentiated the Benedict-Webb-Rubin equation of state and calculated the isothermal-pressure corrections to the ideal gas partial-molal enthalpy. However the analytical equation which resulted from the differentiation of the B.W.R. equation of state was so complicated that the investigators finally presented partial-molal enthalpies only for methane, ethane, and propane in solution with other hydrocarbons.

At the same time Canjar and Edmister (*4*), starting with the fugacity coefficients which had already been calculated by Benedict and coworkers, differentiated these numerically and arrived at isothermal-pressure correction to the ideal-gas-state partial-molal quantities. They extended the study to methane, ethene, ethane, propene, propane, and *n*-butane but did not cover the pressure range covered by Papadopoulos et al. (*11*).

Being limited in scope, neither of these papers presented enthalpy data in a convenient form for process-design engineers. Consequently there existed a need for a method of estimating enthalpy data for hydrocarbon mixtures which was not only easy to use but comprehensive.

THE M.A.B.P. CONCEPT

The very heart of all the work discussed above is the molal-average-boiling-point (M.A.B.P.) concept, which is described by Equation (1).

$$\text{M.A.P.B} = \sum x_i B_i \qquad (1)$$

Benedict and coworkers (*2*) demonstrated that the fugacity coefficients calculated from their equation of state could be correlated by the simple composition-characterization factor, the M.A.B.P. Specifically, they found that at a given temperature and pressure the fugacity coefficient of a pure paraffin or olefin was a function only of the M.A.B.P. of the mixture regardless of what components made up the mixture or how they were distributed. Of course this is only approximately true and holds only for mixtures of the lighter hydrocarbons.

Papadopoulos et al. (*11*) demonstrated the same thing to be true of isothermal-pressure corrections to ideal-gas-state partial-molal enthalpies. Canjar and Edmister (*4*), on the other hand, assumed that if the M.A.B.P. correlation held for the fugacity coefficients then it must also be valid for the partial-molal-enthalpy-pressure corrections which were derived thermodynamically from them. It is obvious that if the M.A.B.P. successfully correlates the fugacity coefficients and isothermal-pressure corrections to the ideal gas partial-molal enthalpies at a given temperature and pressure, then the pressure-volume-temperature and all the derived thermodynamic properties of the mixtures must also be a function of the M.A.B.P. at a given temperature and pressure.

A much more convenient way to present enthalpy data therefore is not in the form of partial-molal quantities but as isothermal-pressure corrections to the total enthalpy of the ideal gas mixture.

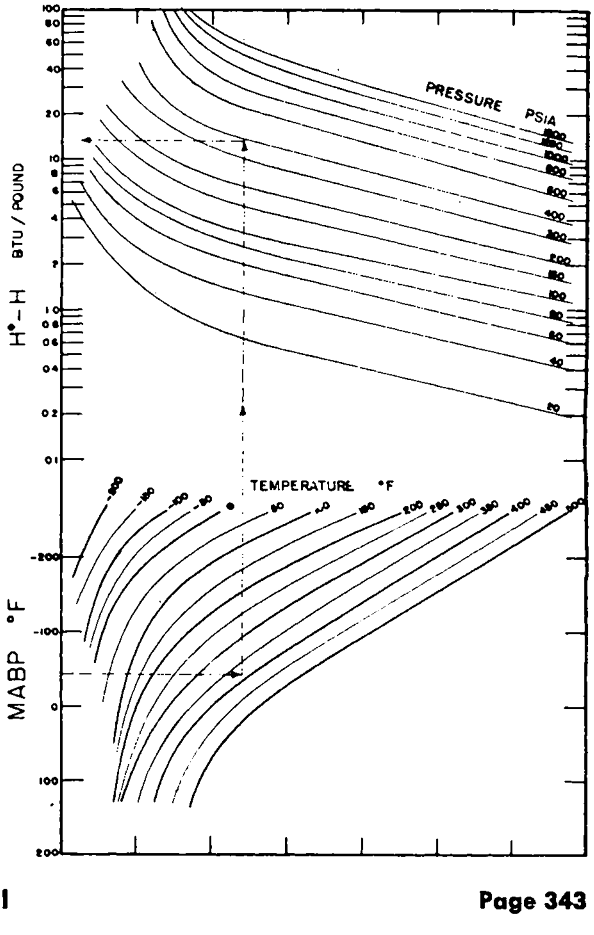

Fig. 1. Pressure correction to enthalpies of hydrocarbon mixtures in ideal gas state, vapor phase.

A direct method for computing these pressure corrections would be to use the equation for enthalpy derived from the B.W.R. equation of state. There are, however, two major disadvantages to this approach. The equation presents the enthalpy of the mixture as a function of temperature and density which involves considerable plotting and cross plotting in order to obtain the more convenient variables temperature and pressure. Second, the B.W.R. equation is inaccurate in the high-density, low-temperature regions unless suitable corrections are made, and consequently it is not convenient for the calculation of enthalpies in the liquid phase.

It is also obvious upon examination of the M.A.B.P. concept that when a mixture has the same M.A.B.P. as the normal boiling point of some pure hydrocarbon, pressure-volume-temperature as well as the derived thermodynamic relationships for the mixture are identical with those of the pure compound. This is borne out by the work done previously on fugacity coefficients and partial-molal enthalpies. Since this is true, a plot of isothermal-pressure corrections to the total enthalpy of an ideal gas mixture vs. the M.A.B.P. of the mixture at constant temperature and pressure coincides with a plot of isothermal-pressure corrections to the total enthalpy of pure compounds in the ideal gas state vs. the normal boiling points of the pure compounds. Or, in other words, such a correlation of isothermal-pressure corrections to the enthalpy of an ideal gas mixture will also hold for the limiting case of a mixture consisting of one component.

It follows then that to find such a correlation it is sufficient to plot the isothermal-pressure corrections to the ideal-gas-state enthalpy of pure components, which are already known to a high degree of accuracy, vs. their normal boiling points. This has been done with the normal paraffins by means of the data of the following investigators: Matthews and Hurd (*9*) for methane; Barkelew, Valentine, and Hurd (*1*) for ethane; Hoover (*8*) for propane; Prengle, Greenhaus, and York (*12*) for normal butane below 40 atm. pressure and Sage and Lacey (*14*) for the liquid region and higher pressures; and Brydon, Walen, and Canjar (*3*) for normal pentane. In addition to these a set of unpublished thermodynamic charts prepared by the Kamerlingh-Onnes laboratory at Leiden were also used particularly in the liquid region where other investigators failed to estimate thermodynamic properties. Plots of all these data vs. the normal boiling points of the pure compounds at constant pressure and temperature formed the basis for this work.

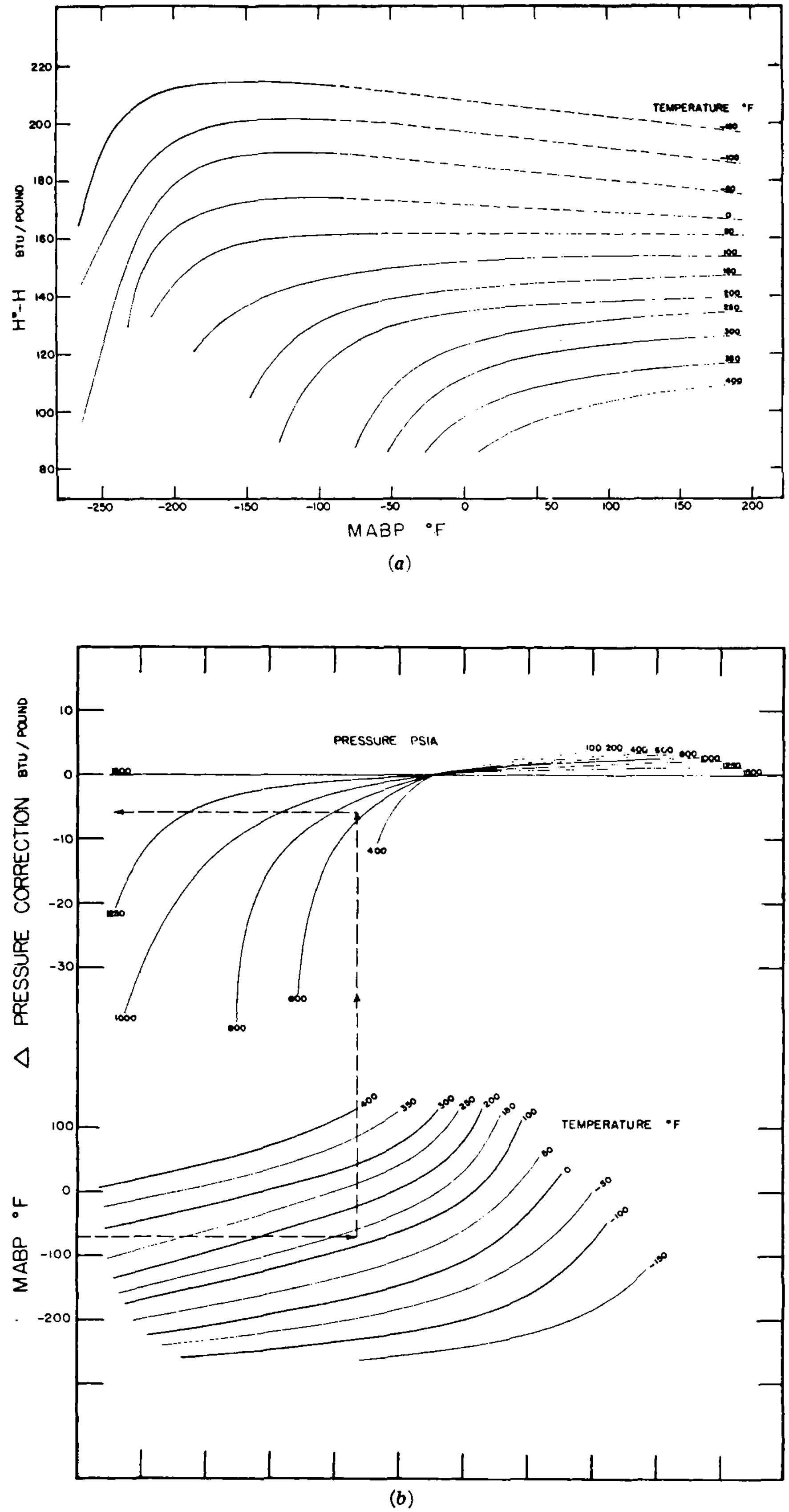

Fig. 2.(*a*) Pressure correction of 1,500 lb./sq. in. abs. to enthalpies of hydrocarbon mixtures in ideal gas state, liquid phase; (*b*) pressure correction to *a*.

DEVELOPMENT OF THERMODYNAMIC PLOTS

The major criticism of the previous works on hydrocarbon-mixture enthalpies is the inconvenient form of presentation. In order to apply the reported values to process-design calculations a considerable amount of interpolation is necessary. To avoid this it is necessary either to present an enormous number of charts and tables reporting enthalpy data at many closely spaced intervals of pressure, temperature, and M.A.B.P. or to consolidate all the data on one or two charts in such a way that interpolation may be readily accomplished in any of the variables mentioned above. DePriester (*5*) was successful in consolidating all the data reported by Benedict and coworkers in their many plots of equilibrium vaporization constants, known more commonly as the Kellogg charts, on two plots for each of the hydrocarbons discussed. The success of DePriester with fugacity coefficients prompted a similar attempt in this work.

Figures 1 and 2* represent the consolidation of all the isothermal-pressure corrections to the enthalpy of the light normal paraffins in the ideal gas state taken from the authors mentioned above. Figure 1 deals exclusively with the vapor phase. Figure 2*a* is a plot of the liquid-phase–pressure corrections for systems at 1,500 lb./sq. in. abs. only. Inclusion of the other isobars complicated the plot to such an extent that it was deemed desirable to prepare an auxiliary plot, Figure 2*b*. If a system is in the liquid region at a pressure other than 1,500 lb./sq. in. abs., its isothermal-pressure correction to the ideal gas enthalpy is first determined for 1,500 lb./sq. in. abs. from Figure 2*a* and then corrected to the desired pressure by the algebraic addition of the delta correction plotted in Figure 2*b*.

$$(H^0 - H)^L = (H^0 - H)^L_{1,500 lb./sq. in. abs.} + \Delta \qquad (2)$$

The isothermal-pressure corrections to the ideal-gas-state enthalpy are given in British thermal units per pound. It would be more convenient to present this information in British thermal units per pound mole since process calculations are carried out on molal basis; however, this would entail a much smaller scale for the high-molecular-weight mixtures with a corresponding loss in accuracy in the values for the lighter mixtures plotted on the same scale. The information obtained from these plots can be converted to a molal basis by multiplication by the average molecular weight of the mixture.

IDEAL-GAS-STATE ENTHALPIES

In order to calculate the enthalpy of a hydrocarbon mixture it is necessary first to calculate the enthalpy of the mixture in the ideal gas state. As ideal gases, or real gases at very low pressure, do not exhibit thermal effects upon mixing, the enthalpy of the mixture is simply the molal average of the enthalpies of the pure components in the mixture.

$$H^0_{mixture} = \sum x_i H_i^0 \qquad (3)$$

or if one prefers to use heat capacities,

$$C^0_{p\,mixture} = \sum x_i C_{pi}^0 \qquad (4)$$

The most reliable tabulation of these ideal gas properties is the American Petroleum Institute Research Project 44 compilation (*13*). However, any compilation of ideal gas or zero-pressure properties that one is accustomed to using is suitable for this work. These properties will vary depending on individual preferences for the datum plane from which enthalpies for process calculations are computed.

COMPARISON WITH EXPERIMENTAL DATA

It is extremely difficult to evaluate a correlation such as the one presented here because of the lack of accurate experimental data for mixtures. One source of data, which was calculated from experimental P.V.T. data and therefore might be considered experimental data, is the work done by Sage and Lacey on hydrocarbon mixtures (*14*). They have reported isothermal-pressure corrections to the ideal gas partial-molal enthalpies of methane, ethane, *n*-butane, and *n*-pentane in binary mixtures of these four hydrocarbons. From these values the enthalpies of mixtures of methane-ethane, methane-butane, and methane-pentane can be determined. This was done, and on Figure 3 the values obtained from the Sage and Lacey work are compared with values obtained from the correlation presented here. It can be seen that there is excellent agreement for the methane-ethane system but rather poor agreement for the methane-butane and methane-pentane systems. This does not invalidate the correlation since the systems methane-butane and methane-pentane are a very stringent test for the correlation. The systems represent a mixture of two extremely different molecules. It would be just as reasonable to check this correlation with a mixture of pentane and some nonhydrocarbon. Further, it is very unlikely that one would be concerned with such a mixture in a practical process-design calculation. Normally mixtures which are encountered contain small amounts of light and heavy components with the major portion consisting of similar molecules.

Another source of experimental data is the investigation of Nelson and Holcomb (*10*) on three ternaries made up of propane, *n*-butane, and *n*-pentane. A comparison of these data with the correlation presented here is given in Figure 4. Surprisingly enough, the poorer agreement is in the vapor region, with excellent agreement in the liquid region. This can

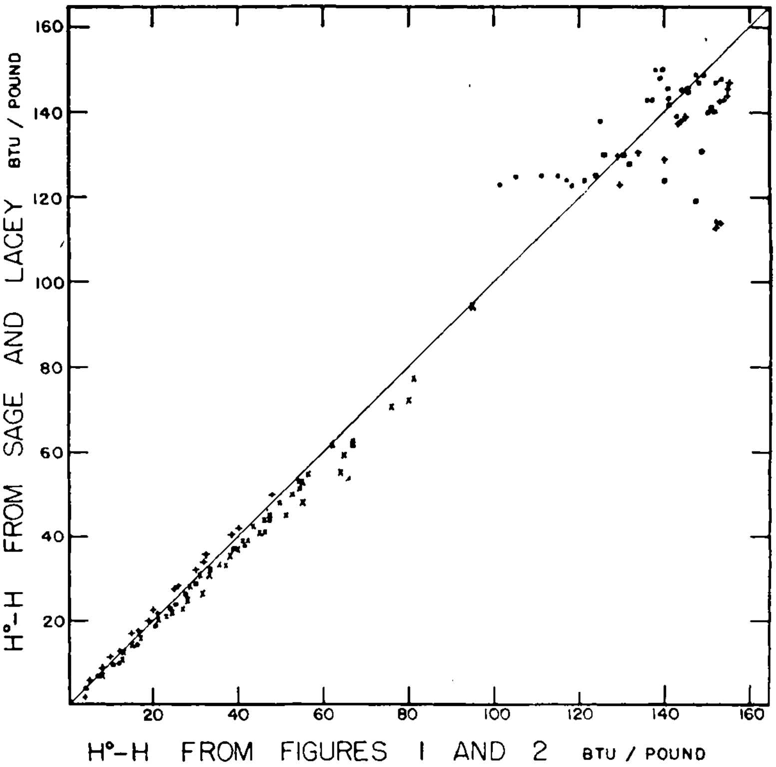

Fig. 3. Comparison of enthalpies of hydrocarbon mixtures calculated by Sage and Lacey with this work; × methane-ethane mixtures, ■ methane-butane mixtures, + methane-pentane mixtures.

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*The plots presented with this article are solely for the purpose of showing the form the correlation takes. Working plots with fine-line backgrounds are obtainable free of charge upon request from the Department of Chemical Engineering, Carnegie Institute of Technology, Pittsburgh 13, Pennsylvania.

be explained by pointing out that all the vapor data reported by Nelson and Holcomb fall in the lower left-hand corner of Figure 1, which is undoubtedly the least accurate portion of the chart. In spite of this the maximum difference between the data of Nelson and Holcomb in the vapor region and this correlation is about 10 B.t.u./lb. According to the original paper by Nelson and Holcomb this seems to be the same order of magnitude as the agreement they report for the correlations of Scheibel and Jenny (*15*) and Holcomb and Brown (7). It might be pointed out here that differences of this order of magnitude were encountered when the thermodynamic properties reported by different investigators for the same compound were compared.

A very recent paper by Edmister (*6*) dealing with isobaric integral heats of vaporization contains a sample calculation which might serve as a comparison of the different methods of calculating the isobaric integral heat of vaporization. Edminster considers a hypothetical mixture containing 5 lb. moles of methane, 15 lb. moles of ethane, 30 lb. moles of propane, and 50 lb. moles of normal butane. This corresponds to a hydrocarbon mixture having an M.A.B.P. of −30°F. and an average molecular weight of 47.5. Using the DePriester charts (*5*), he obtains a bubble point of 95°F. and a dew point of 185°F. for this mixture at 300 lb./sq. in. abs. In order to calculate the isobaric integral heat of vaporization for this mixture it is necessary to subtract the enthalpy of the liquid at 95°F. and 300 lb./sq. in. abs. from the enthalpy of the vapor at 185°F. and 300 lb./sq. in. abs. Edmister presents detailed calculations using the method described in his paper and the earlier partial-molal enthalpy paper by Canjar and Edmister (*4*). Using the Canjar-Edmister partial-molal enthalpies he finds the isobaric integral heat of vaporization for the above-mentioned mixture to be 8,079 B.t.u./lb. mole of mixture compared with 7,953 B.t.u./lb. mole of mixture found by use of the Edmister *K*-value method.

In the way of a comparison and sample calculation, the same calculation is presented here by means of Figures 1 and 2 of this work. From Figure 1 it can be seen that the pressure correction at 300 lb./sq. in abs. to the enthalpy of an ideal gas mixture with an M.A.B.P. of −30°F. at 185°F. is 22 B.t.u./lb., or 1,045 B.t.u./lb. mole (average molecular weight of 47.5). Figure 2*a* gives a pressure correction for a liquid at 1,500 lb./sq. in. abs. and 95°F. of 152 B.t.u./lb. To adjust this to 300 lb./sq. in. abs., Figure 2*b* is employed. The adjustment is found to be about +1 B.t.u./lb., giving a value of $H° - H$ for the liquid at 300 lb./sq. in. abs. of 153 B.t.u./lb., or 7,268 B.t.u./lb. mole. To find the enthalpy of the liquid and vapor it is simply a matter of determining the ideal gas enthalpies. Edmister interpolated these values from the A.P.I. tables (*6*). They are shown in the accompanying table.

Component	Mole fraction	$H°$ (B.t.u./lb. mole)* 185°F.	95°F.
Methane	0.05	5,266	4,466
Ethane	0.15	6,593	5,367
Propane	0.30	8,375	6,643
Butane	0.50	11,073	8,783
$H°_{mixture} = \Sigma x_i H_i° =$		9,301	7,413

* Reference: ideal gas at 0°R.

$$H^V = H° - (H° - H)^V = 9{,}301 - 1{,}045 = 8{,}256 \text{ B.t.u./lb. mole}$$
$$H^L = H° - (H° - H)^L = 7{,}413 - 7{,}268 = 145 \text{ B.t.u./lb. mole}$$
$$H^V - H^L = 8{,}256 - 145 = 8{,}111 \text{ B.t.u./lb. mole}$$

In summary:

	B.t.u./lb. mole
Edmister *K*-value method	7,953
Canjar-Edmister partial-enthalpy method	8,079
Present method	8,111

The agreement with the partial-enthalpy method is excellent in view of the fact that the partial enthalpies were derived from Kellogg *K* values, which are essentially mixture data, and that Figures 1 and 2 are based on pure-component data only. The agreement with the Edmister *K*-value method is poorer although still good, owing to the fact that in the derivations of the equations used in the Edmister method some approximate assumptions were made about the constancy of partial molal heat of vaporization over a wide temperature range.

CONCLUSIONS

An enthalpy correlation has been presented which can be expected to predict hydrocarbon-mixture enthalpies with a fair degree of accuracy. Strictly speaking, the correlation should be used only with the Kellogg (*2*) and DePriester (*5*) equilibrium-vaporization constants. There is a thermodynamic consistency in these *K* values with the enthalpies presented here through the M.A.B.P. concept. For this reason the correlation is strictly valid for hydrocarbon mixtures containing the lighter paraffins and olefins. In the absence of better methods for estimating enthalpies of mixture, however, this method can be extended with caution to

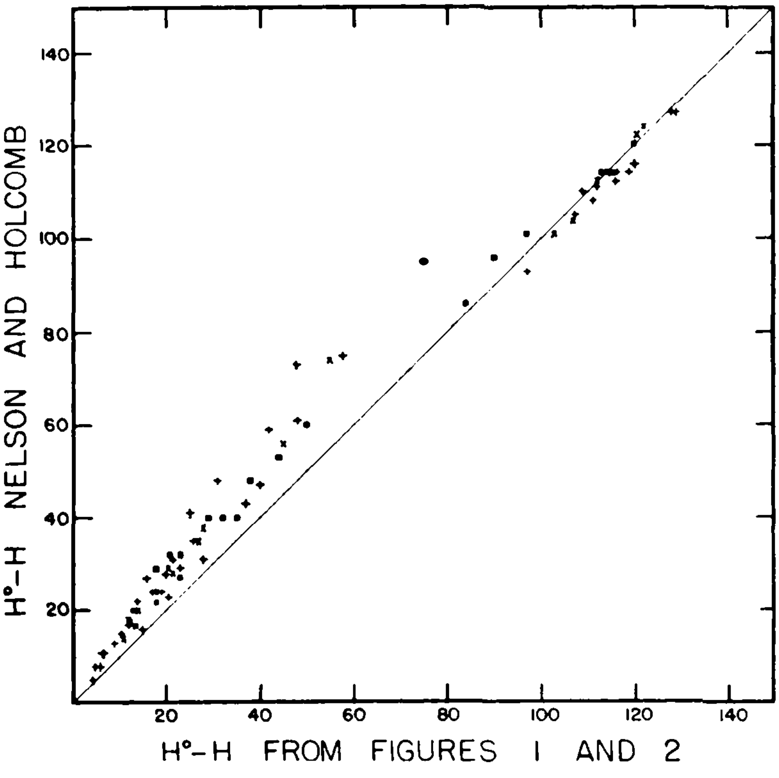

Fig. 4. Comparison of enthalpies of hydrocarbon mixtures determined by Nelson and Holcomb with this work; + mixture *A*, × mixture *B*, ■ mixture *C*.

mixtures containing other types of compounds such as aromatics and nonhydrocarbons. The correlation will fail completely if these other types of compounds are present in major amounts in the mixture.

It is impossible to estimate the accuracy of a correlation such as this because of the scarcity of good experimental data. The regions of greatest uncertainty in Figures 1 and 2 are those corresponding to high M.A.B.P.-low temperatures and the critical point of the region of high pressure-low temperature on Figure 1. The uncertainty in this latter region is due to uncertainty in PVT measurements on pure compounds in the vicinity of the critical point.

NOTATION

B = normal boiling point, °F.
C_p° = molal heat capacity for ideal gas state, B.t.u./(lb. mole)(°R.)
H = enthalpy of a real gas or liquid, B.t.u./lb. or B.t.u./lb. mole
H° = enthalpy of an ideal gas, B.t.u./lb. or B.t.u./lb. mole
M.A.B.P. = molal average boiling point, °F. ($\sum x_i B_i$)
P = pressure, lb./sq. in. abs.
T = temperature, °F.
x = mole fraction

Superscripts

L = liquid phase
V = vapor phase

Subscript

i = ith component in a mixture

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Vapor Pressures: The Saturated Aliphatic Hydrocarbons

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A rigorous analysis of the available data presented in the literature for all the saturated aliphatic hydrocarbons from methane through *n*-eicosane was conducted to establish the constants *A*, *B*, *C*, and *D* of the vapor-pressure equation developed by Frost and Kalkwarf (21). With all the constants determined, vapor pressures can be calculated accurately from the triple to the critical point. The actual constants *A*, *B*, *C*, and *D* have been calculated from the available reported vapor-pressure data of eighty-seven saturated aliphatic hydrocarbons and include all the normal paraffins through eicosane and all the isomeric paraffins through the nonanes.

In order to ascertain the validity of calculated-vapor-pressure constants, values of *A*, *B*, *C*, and *D* were produced from the molecular structure and normal boiling point for all the normal paraffins through eicosane and all the thirty-four isomeric nonanes. The normal paraffins were selected to cover the range of the saturated aliphatic hydrocarbons; whereas the nonanes were chosen because they represent the most complex structures for which reported vapor pressures are available.

With the calculated constants, vapor pressures were evaluated from the equation at several representative points and were compared with reported values to produce an overall absolute average percentage of deviation of 0.58 for the normal paraffins and 0.73 for the isomeric nonanes, or 0.68 for these fifty-four saturated aliphatic hydrocarbons.

In order to obtain information on the vapor-pressure behavior of substances for which experimental data are available in limited ranges, extrapolations and interpolations are necessary. The resulting degree of accuracy will depend upon the reliability of the methods used to extend the experimental data. To facilitate these extensions, several vapor-pressure expressions have been proposed. The familiar Clausius-Clapeyron vapor-pressure equation

$$\log P = A + \frac{B}{T} \qquad (1)$$

possesses considerable simplicity because of the assumptions used in its development from the rigorous thermodynamic relationship of Clapeyron and has been applied to define satisfactorily the vapor pressures of metals (*5, 41*). However, Equation (1) fails to represent properly the complete vapor-pressure behavior of many substances and must be applied over limited temperature ranges (*34*). Modifications of Equation (1) have been proposed by Antoine (*1*) and Cox (*16*).

Rankine (*44*), Kirchhoff (*31*), and Dupré (*18*) empirically proposed a refinement to Equation (1) with the introduction of a third constant to define the vapor-pressure equation as

$$\log P = A + \frac{B}{T} + C \log T \qquad (2)$$

Equation (2) can be developed from the Clapeyron equation by assuming the molar heat of vaporization to vary linearly with temperature. Although Equation (2) expresses the vapor-pressure behavior over wider ranges of temperature, still it fails generally to define satisfactorily the complete vapor-pressure function included between the triple and critical points. Modifications of Equation (2) have been proposed by van Laar (*56*), Riedel (*45*), and Gamson and Watson (*22*). Thodos (*53*) points out that a plot of precise experimental vapor pressures between the critical and triple points for normal paraffins produces an elongated S-shaped curve as presented in Figure 1. To retain the characteristics of the actual vapor-