Differential Heats of Condensation and Enthalpies of Saturated Liquid Hydrocarbon Mixtures

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By use of saturated-vapor enthalpies determined by accepted procedures in conjunction with differential latent heats of condensation, the saturated-liquid enthalpies are established for the system methane–ethane at 200, 400, and 600 lb./sq. in. abs. and for the systems ethane–*n*-butane and propane–*n*-butane at the two lower pressures. Where comparison is possible, the liquid-enthalpy values obtained by this method are in general agreement with those previously determined by Edmister and Canjar. The procedure used is thermodynamically rigorous and may be applied to any binary mixture, provided the Benedict-Rubin-Webb equation of state is valid in the vapor phase and *P-V-T-x* data are available.

As operating pressures in the petroleum and related industries increase, the heat effects and the vapor-liquid equilibrium relationships become difficult to predict. Designs for conditions of elevated pressures are often reduced to questionable estimates and the design engineer is frequently confronted with inconsistencies between the vapor-liquid equilibrium data and the enthalpy data. The Kellogg equilibrium-vaporization ratios (*13*), based on the Benedict-Rubin-Webb equation of state (*4*), have helped immeasurably in the prediction of accurate y/x data over wide pressure ranges; however, the determination of the heat effects has remained a problem.

At the present time the partial-enthalpy approach used in conjunction with the Benedict-Rubin-Webb equation appears to be the most promising method for obtaining precise thermal data on mixtures which will also be consistent with the equilibrium information. This approach has been used by Papadopoulos, Pigford, and Friend (*16*) and Edmister and Canjar (*11*). Although the Benedict-Rubin-Webb equation holds with a high degree of precision in the vapor phase, its applicability to the liquid phase, particularly when the liquid density is greater than 125% of the critical density, is open to some question. Hence it is desirable to determine the enthalpy of saturated-liquid mixtures by some other method which would provide the same degree of accuracy as can be obtained in the vapor phase. This accuracy can be achieved either by calculating the latent heat of condensation of the mixture and subtracting it from the vapor-phase enthalpy or by determining the liquid-phase enthalpy directly.

As no exact equation of state exists for liquid mixtures, the prediction of the latent heat of condensation offers the better prospect. With mixtures either of two latent heats may be considered, the integral heat and the differential heat. The integral heat of condensation may be determined under isothermal or isobaric conditions, and the isothermal integral heat of condensation may be calculated by the method of Bahlke and Kay (*2*). The isobaric integral heat is the heat emitted under constant pressure when a given amount of a mixture at its dew point is completely converted to a liquid at its bubble point. It may also be calculated rigorously, although this is not often done because of the large amount of experimental data required. Edmister (*10*) developed an expression by which the isobaric integral heat of vaporization may be approximated.

As an alternate approach, it is suggested that the enthalpy differences between the saturated liquid and vapor phases be obtained through the differential latent heat of condensation. These enthalpy differences are of great value, for they are the heat effects involved in many distillation operations. Further, the differential heat of condensation and, in turn, the enthalpy difference between the two saturated phases may be calculated from rigorous thermodynamic relationships which require considerably fewer experimental data than are needed for the exact determination of either of the integral heats of vaporization.

The differential heat of condensation on a molal basis is the heat given up when a mole of vapor is condensed from a gaseous mixture containing N moles, where N is so large that the composition of the gaseous mixture remains unchanged. The composition of the liquid formed is governed by the equilibrium relationship, and the temperature and pressure of the process are constant. This case is analogous to the one developed by Dodge (*7*). As the process occurs under isobaric and isothermal conditions and without change of composition of the vapor phase, the Clapeyron equation may be applied. This is pointed out by Dodge (*8*).

$$\left(\frac{\partial P}{\partial T}\right)_v = \frac{\Delta H_c}{T\Delta V} \tag{1}$$

In Equation (1) $(\partial P/\partial T)_v$ is the slope of the dew-point pressure-temperature curve of the mixture; T, the absolute temperature of condensation; and ΔH_c, the differential heat of condensation. Not only does the volume change ΔV involve the difference between the saturated vapor and liquid volumes, as is the case for a pure material, but the change in the volume of the vapor due to the condensation of 1 mole must also be taken into account. As shown by Dodge (*7*), the net volume change for the process is expressed by

$$\Delta V = V_b - V_d + (y - x)\left(\frac{\partial V_G}{\partial y}\right)_{T,P} \tag{2}$$

From Equations (1) and (2), it is apparent that precise dew-point pressure-temperature, volumetric, and equilibrium data are required to evaluate the differential heat of condensation. Such data have been reported for a number of binary systems, particularly those containing hydrocarbons.

The partial differential $(\partial V_G/\partial y)_{T,P}$ is the most difficult term in the equation to evaluate. To determine this quantity, an isotherm must be constructed on a plot of V_G vs. y, the pressure being held constant. The slope of the isotherm at its point of intersection with the saturated vapor curve must then be measured. It is apparent that volumetric data in the superheated vapor region, as well as the saturated vapor volume, are necessary to determine the value of $(\partial V_G/\partial y)_{T,P}$. The required volumetric data were calculated by the Benedict-Rubin-Webb equation of state,

$$P = RTd + (B_0RT - A_0 - C_0/T^2)d^2 + (bRT - a)d^3 + a\alpha d^6 + cd^3/T^2[(1 + \gamma d^2)e^{-\gamma d^2}] \tag{3}$$

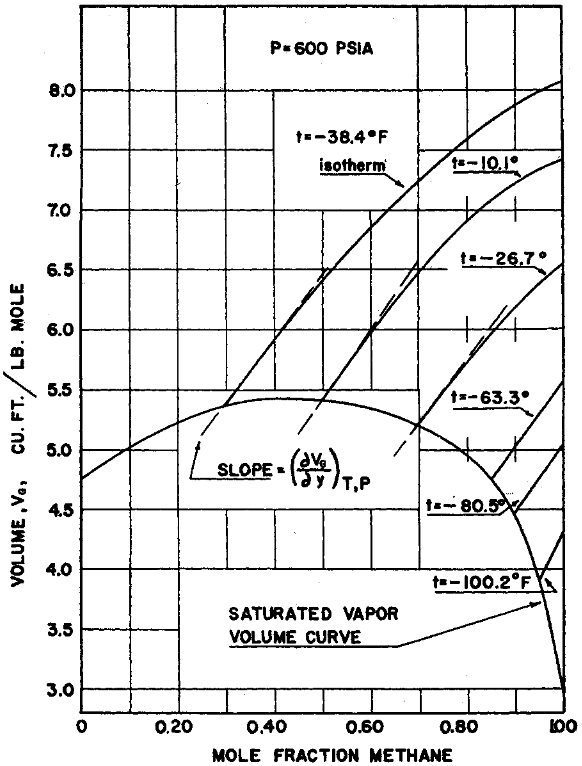

Fig. 1. Volume-composition diagram for methane-ethane system showing isotherms with slope equal to $(\partial V_G/\partial y)_{T,P}$.

For the systems investigated, sufficient experimental data are available to define the saturated vapor volume curves. The validity of the Benedict-Rubin-Webb equation of state was established by calculating saturated vapor volumes and comparing them with the experimental values. In no case did the two values differ by more than 1%. In most instances the calculated value agreed with the experimental value within 0.75%. As the Benedict-Rubin-Webb equation predicted the volumetric behavior of the saturated-vapor mixtures with such precision, it was felt that the equation could safely be used to predict the behavior of the superheated vapor mixtures.

To help illustrate the procedure used, the V_G vs. y plot for the methane-ethane system at 600 lb./sq. in. abs. is included as Figure 1. A number of isotherms were constructed on the plot to evaluate the quantity $(\partial V_G/\partial y)_{T,P}$ over the complete range of vapor composition.

With the term $(\partial V_G/\partial y)_{T,P}$ evaluated, the differential heat of condensation can be determined without difficulty through the use of Equations (1) and (2). The relationship between the differential latent heat of condensation and the saturated-vapor and -liquid enthalpies, as given by Dodge (*9*), is

$$\Delta H_c = H_b - H_a + (y - x)\left(\frac{\partial H_G}{\partial y}\right)_{T,P} \tag{4}$$

The term $(\partial H_G/\partial y)_{T,P}$ can be evaluated by a procedure similar to that outlined for the calculation of the term $(\partial V_G/\partial y)_{T,P}$. The Benedict-Rubin-Webb equation in the form

$$H = \sum_i x_i H_i^0 + (B_0RT - 2A_0 - 4C_0/T^2)d + (2bRT - 3a)d^2/2 + 6a\alpha d^5/5 + cd^2/T^2\left[3\,\frac{1 - \exp(-\gamma d^2)}{\gamma d^2} - \frac{\exp(-\gamma d^2)}{2} + \gamma d^2 \exp(-\gamma d^2)\right] \tag{5}$$

and the enthalpies in the ideal gas state obtained (*1*) were used to calculate enthalpies of the saturated and superheated vapors. Equation (4) can readily be solved for the single unknown, the saturated-liquid enthalpy.

The method of calculation outlined above was applied to three binary hydrocarbon systems, methane-ethane, ethane–*n*-butane, and propane–*n*-butane. These systems were used because the validity of

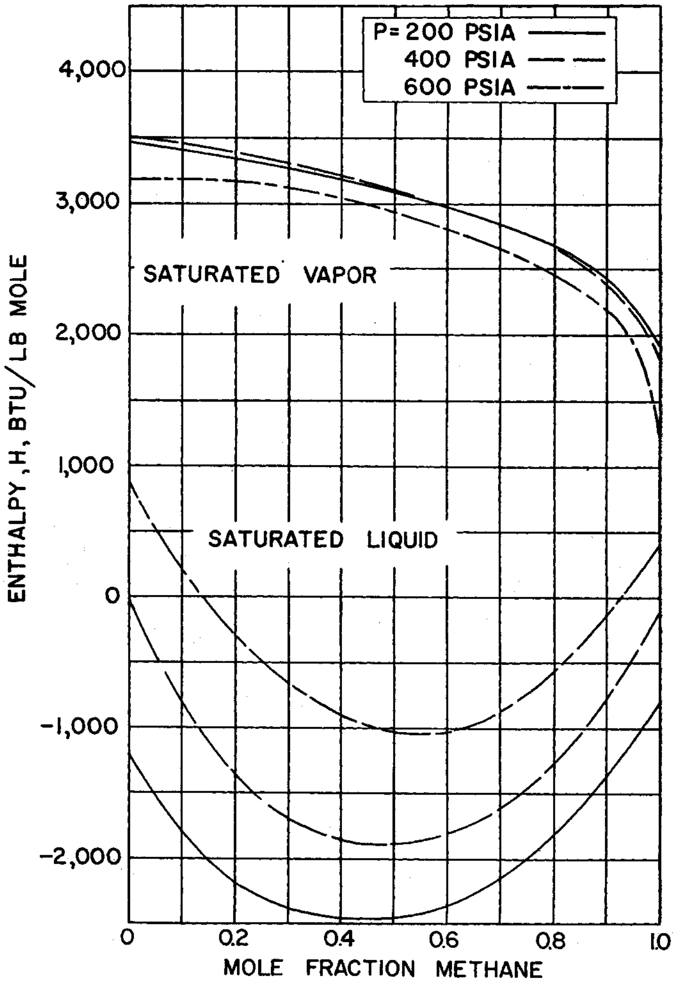

Fig. 2. Enthalpy-composition diagram for methane-ethane system. $H = 0$ for the pure components in the ideal gas state at unit fugacity and 0°R.

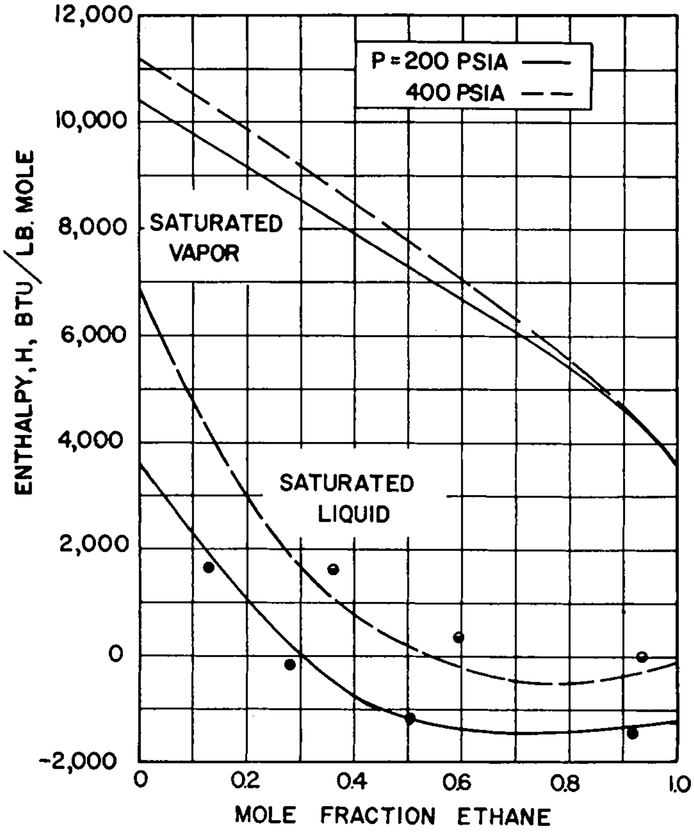

Fig. 3. Enthalpy-composition diagram for ethane-*n*-butane system. $H = 0$ for the pure components in the ideal gas state at unit fugacity and 0°R. Points represent data of Edmister and Canjar (*11*).

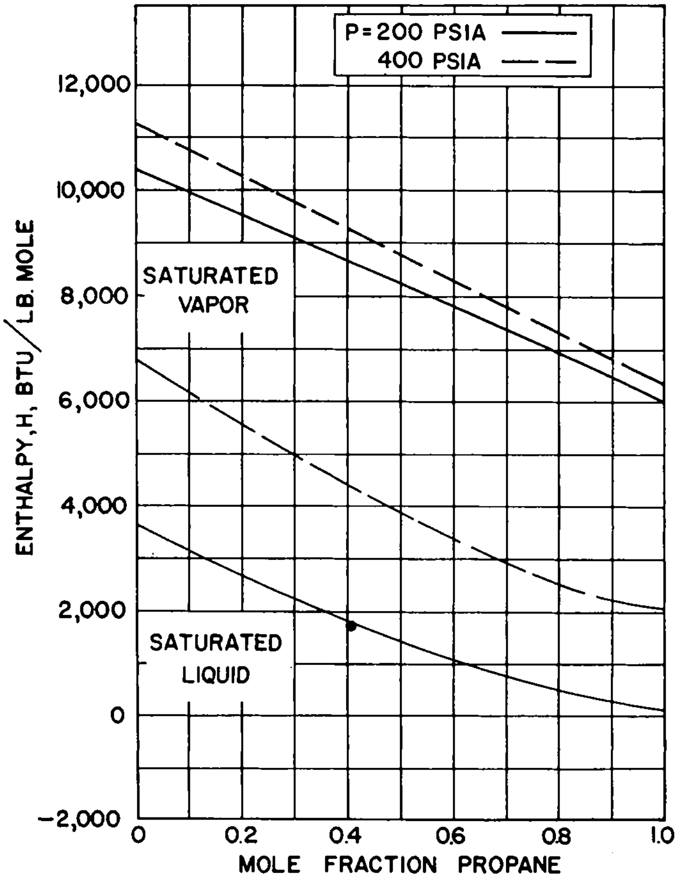

Fig. 4. Enthalpy-composition diagram for propane-*n*-butane system. $H = 0$ for the pure components in the ideal gas state at unit fugacity and 0°R. Point represents datum of Edmister and Canjar (*11*).

the Benedict-Rubin-Webb equation of state has been established for them and accurate equilibrium and volumetric data are available. The empirical constants of the various mixtures for the equation of state were calculated by the method outlined by Benedict-Rubin-Webb (*5*) with the exception of the A_0 for the methane-ethane system, which was calculated by the method of Bloomer, Gami, and Parent (*6*). The values of the constants for the pure materials used in the calculations were those given by Benedict-Rubin-Webb (*5*). The methane-ethane system was investigated at three pressures, 200, 400, and 600 lb./sq. in. abs., and the systems ethane-*n*-butane and propane-*n*-butane were investigated at the two lower pressures only.

The results are presented in graphical form in Figures 2 through 4 and in tabular form in Tables 1 through 3*. The tabulated data are reported to four significant figures, in order to keep the results consistent. The expected error in the enthalpy differences reported is approximately 3%, possible sources of error being in the inaccuracy of the Benedict-Rubin-Webb equation of state and the determination of the slopes of the numerous curves. The calculated-enthalpy differences were very sensitive to the values used for the slope of the dew-point pressure-vs.-temperature curve; hence it was necessary to determine these slopes with the highest possible degree of accuracy.

The ethane-*n*-butane system is the only one in which the liquid-phase enthalpies calculated in this work can be compared with those of Edmister and Canjar (*11*). The enthalpy values obtained by the two independent methods agree very well at 200 lb./sq. in. abs., but not so well at 400 lb./sq. in. abs. At these conditions the values of Edmister and Canjar tend to be above the values presented in this work.. Their values represent a maximum disagreement of 10% in enthalpy difference between the saturated liquid and vapor conditions. The disagreements are only in the liquid-phase enthalpies, as the vapor-phase enthalpies presented by Edmister and Canjar (*11*) agree very well with those calculated in this work.

SUMMARY AND CONCLUSIONS

Differential latent heats of condensation and saturated-liquid enthalpies have been calculated by a rigorous thermodynamic relationship for the system methane-ethane at 200, 400, and 600 lb./sq. in. abs. and for the systems ethane-*n*-butane and propane-*n*-butane at the two lower pressures, experimental

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*Complete tabular data may be obtained as document 4964 from an American Documentation Institute, Photoduplication Service, Library of Congress, Washington 25, D. C., for $1.25 for photoprints or 35-mm. microfilm.

P-V-T-x data and the Benedict-Rubin-Webb equation of state being used. Enthalpy-concentration diagrams for the three systems at the various pressures involved have been presented. For the ethane–*n*-butane system, where a number of comparisons were possible, the saturated-liquid enthalpies presented are in fair-to-excellent agreement with previously determined values.

When accurate *P-V-T-x* relationships are available, the method of calculation presented offers a thermodynamically rigorous means to obtain accurate enthalpy data of saturated-liquid mixtures. As more extensive experimental volumetric and equilibrium data become available, this method should be of considerable value in establishing accurate partial enthalpies for the liquid phase.

TABLE 1. ENTHALPY VALUES FOR SATURATED HYDROCARBON MIXTURES
Methane-ethane system
Pressure = 200 lb./sq. in. abs.

Saturation temperature, °F.	Mole fraction methane (*6*)		Enthalpy,* B.t.u./lb. mole		
	x	y	H_b	H_d	
−6.2	0	0	−1,230	3,463	(*3*)
−51.2	0.10	0.526	−1,808	3,040	
−85.5	0.20	0.764	−2,200	2,723	
−112.0	0.30	0.882	−2,392	2,477	
−130.7	0.40	0.935	−2,468	2,291	
−143.9	0.50	0.959	−2,472	2,171	
−153.8	0.60	0.975	−2,375	2,076	
−161.2	0.70	0.983	−2,165	2,018	
−167.1	0.80	0.990	−1,836	1,962	
−172.7	0.90	0.994	−1,378	1,926	
−178.5	1.00	1.00	− 812	1,867	(*14*)

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*H = 0 for the pure components in the ideal-gas state at unit fugacity and 0°R. The vapor- and liquid-phase enthalpies of the pure components, obtained from the literature sources cited, were in all instances adjusted to this reference state.

TABLE 2. ENTHALPY VALUES FOR SATURATED HYDROCARBON MIXTURES
Ethane–*n*-Butane system
Pressure = 200 lb./sq. in. abs.

Saturation temperature, °F.	Mole fraction ethane (*12*)		Enthalpy*, B.t.u./lb. mole		
	x	y	H_b	H_d	
202.7	0	0	3,616	10,487	(*17*)
159.5	0.10	0.393	2,252	7,939	
122.5	0.20	0.640	1,008	6,421	
93.0	0.30	0.784	+ 10	5,480	
69.0	0.40	0.866	− 757	4,902	
49.5	0.50	0.918	−1,170	4,478	
34.0	0.60	0.949	−1,368	4,158	
21.0	0.70	0.969	−1,445	3,936	
10.0	0.80	0.984	−1,440	3,751	
1.0	0.90	0.995	−1,355	3,620	
−6.2	1.00	1.00	−1,243	3,560	(*3*)

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*H = 0 for the pure components in the ideal-gas state at unit fugacity and 0°R. The vapor- and liquid-phase enthalpies of the pure components, obtained from the literature sources cited, were in all instances adjusted to this reference state.

TABLE 3. ENTHALPY VALUES FOR SATURATED HYDROCARBON MIXTURES
Propane–*n*-butane system
Pressure = 200 lb./sq. in. abs.

Saturation temperature, °F.	Mole fraction propane (*15*)		Enthalpy*, B.t.u./lb. mole		
	x	y	H_b	H_d	
202.7	0	0	3,648	10,440	(*17*)
188.0	0.10	0.198	3,148	9,338	
174.3	0.20	0.387	2,665	8,719	
161.8	0.30	0.536	2,225	8,092	
150.8	0.40	0.649	1,803	7,603	
141.3	0.50	0.738	1,409	7,208	
132.5	0.60	0.814	1,062	6,854	
124.6	0.70	0.874	755	6,572	
116.6	0.80	0.930	497	6,305	
109.9	0.90	0.974	258	6,091	
105.0	1.00	1.00	85	5,962	(*18*)

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*H = 0 for the pure components in the ideal-gas state at unit fugacity and 0°R. The vapor- and liquid-phase enthalpies of the pure components, obtained from the literature sources cited, were in all instances adjusted to this reference state.

NOTATION

H = enthalpy, B.t.u./lb. mole. $H = 0$ for a pure component in the ideal-gas state at unit fugacity and 0°R.
H° = enthalpy of a component in the ideal-gas state and unit fugacity, B.t.u./lb. mole
$\overline{\Delta H}$ = partial-enthalpy difference, $H - H^\circ$, B.t.u./lb. mole
ΔH_c = differential latent heat of vaporization, B.t.u./lb. mole
P = pressure, lb./sq. in. abs.
R = gas-law constant, 1.987 B.t.u./(lb. mole)(°R.)
T = absolute temperature, °R.
V = molal volume, cu. ft./lb. mole
d = density, lb. mole/cu. ft.
x = mole fraction in the liquid phase
y = mole fraction in the vapor phase
A_0, B_0, C_0, a, b, c, α, and γ = empirical constants of the Benedict-Rubin-Webb equation of state

Subscripts

G = vapor phase
b = bubble point
d = dew point
i = a component
j = total number of components

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