Liquid Phase Enthalpy Values for the Ethane–*n*-Pentane System

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SATURATED liquid phase enthalpies were presented (*9, 15, 16*) for five binary hydrocarbon systems over the pressure range of 100 to 600 p.s.i.a. The enthalpy data were calculated from *P-V-T-x* data and the differential heat of condensation. The basic relationships (*8*) are thermodynamically rigorous.

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

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

$$\Delta H_c = H_b - H_d + (y - x)\left(\frac{\partial H_G}{\partial y}\right)_{T,P} \tag{3}$$

More recently Houser and Weber (*10*) recalculated the saturated liquid phase enthalpy values for the methane-ethane system and, in addition, calculated partial enthalpies in the liquid phase. This was done by the use of Equations 1 to 3 and similar equations which describe a differential vaporization process. The additional relationships are

$$\left(\frac{\partial P}{\partial T}\right)_x = \frac{\Delta H_v}{T\Delta V_v} \tag{4}$$

$$\Delta V_v = V_d - V_b - (y - x)\left(\frac{\partial V_L}{\partial x}\right)_{T,P} \tag{5}$$

$$\Delta H_c = H_d - H_b - (y - x)\left(\frac{\partial H_L}{\partial x}\right)_{T,P} \tag{6}$$

In calculating enthalpy data for the methane-ethane system the effect of pressure over 50-p.s.i. intervals at constant temperature on the liquid phase volumes and enthalpies was neglected.

As part of a continuing attempt to evaluate liquid phase enthalpies, both total and partial quantities, the ethane–*n*-pentane system was investigated. Reamer, Sage, and Lacey (*13*) determined *P-V-T-x* data for this system over a temperature range of 40° to 460° F. and up to pressures of 10,000 p.s.i.a. Also, Reamer, Berry, and Sage (*12*) determined liquid phase partial volumes using the experimental data from the previous work; their results were used in this investigation. The data for ethane were obtained from Barkelew, Valentine, and Hurd (*2*) and for *n*-pentane from Brydon, Walen, and Canjar (*7*).

These references provided volumetric data for the liquid phase but were not sufficient for the vapor phase. Hence, it was necessary to calculate some dew-point volumes for ethane–*n*-pentane mixtures and all superheated vapor volumes. First, Black's equation of state (*5*)

$$V_m = RT/P + \left[\sum_i (b_i y_i) - \sum_i (a_i \xi_i)^{1/2} y_i\right]^2 / RT \tag{7}$$

was tested. His generalized constants were used, initially, and volumes of ethane–*n*-pentane mixtures at various pressures and temperatures were calculated and compared with the experimental data. The agreement between the two sets was not satisfactory. Individual constants for Black's equation were then developed for ethane and *n*-pentane from the available pure component data. These were combined, and volumes of mixtures recalculated. While individual constants yielded better results than the generalized constants, the predicted volumes were not accurate enough.

In previous investigations of this type (*9, 10, 15, 16*) the Benedict-Webb-Rubin equation (*3, 4*)

$$P = RT\mathrm{d} + (B_0RT - A_0 - C_0/T^2)\mathrm{d}^2 + (bRT - a)\mathrm{d}^3 + a\,\alpha\,\mathrm{d}^6 + c\mathrm{d}^3/T^2[(1 + \gamma\,\mathrm{d}^2)\,\mathrm{exp.}(-\gamma\,\mathrm{d}^2)] \tag{8}$$

was used to predict the volumetric behavior of the pure components and their mixtures.

The values of the constants given by Benedict and others (*4*) were satisfactory for ethane, but not for *n*-pentane. By changing the value of B_0 to 2.67 and γ to 1950, the predicted volumes had an average deviation of 0.6% from those determined experimentally, and the maximum deviation, which occurred at 600 p.s.i.a., was 0.9%.

The constants for the pure components, ethane and *n*-pentane, were then combined as outlined by Benedict, Webb, & Rubin, and volumes for gaseous mixtures were calculated. However, the predicted volumes were greater than the experimental ones over the entire composition range; the greatest deviation occurred in the center of the composition range. Bloomer, Gami, and Parent (*6*) recommended the combined, A_{0m}, be calculated in the manner

$$A_{0m} = \left[\sum_i (y_i A_{0i}^{1/2})\right]^2 + k\,y_1 y_2 \tag{9}$$

Under isobaric conditions, a value of *k* allowed the predicted volumes to be within ±1% of experimental values over the entire composition range. Further, *k* was determined to be a function of pressure in the following manner

$$k = 2000 + 40P - 0.05P^2 \tag{10}$$

With these changes it was possible to predict volumes of mixtures at their dew points within ±1% of the experimental values over the pressure range of this investigation. Since no volumetric data on superheated gaseous mixtures were available, the Benedict-Webb-Rubin equation, as modified, was used to predict these and partial volumes, the latter being necessary in Equation 2.

The Benedict-Webb-Rubin equation (*3*) in the form of

$$H - \sum_i x_i H_i^\circ = (B_0RT - 2A_0 - 4C_0/T^2)\mathrm{d} + (2bRT - 3a)\mathrm{d}^3/2 + 6a\alpha\mathrm{d}^5/5 + c\mathrm{d}^2/T^2 \left[3\,\frac{1 - \mathrm{exp.}\,(-\gamma\mathrm{d}^2)}{2_d 2} - \frac{\mathrm{exp.}\,(-\gamma\mathrm{d}^2)}{2} + \mathrm{exp.}\,(\gamma\mathrm{d}^2)\right] \tag{11}$$

was used to calculate enthalpies of gaseous mixtures at their dew points. The ideal gas state enthalpy values, H°, were obtained from API 44 (*1*). Papadopoulos, Pigford, and Friend (*11*) differentiated Equation 11 for the evaluation of

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partial enthalpies. Their relationship was used to evaluate the term $(\partial H_G/\partial_y)_{T,P}$ in Equation 3.

The slopes terms, $(\partial P/\partial T)_y$ and $(\partial P/\partial T)_x$, of Equations 1 and 4 were obtained, respectively, from the dew point and bubble point pressure–temperature data (*13*). The pressure-temperature data at various constant compositions were fitted to a modification of a relationship given by Sondak and Thodos (*14*) for correlating vapor-pressure temperature data for pure compounds. The modified relationship had the form

$$\log P = A' + B'/T + C'/T^2 \qquad (12)$$

The original equation had an additional term which is important at low pressures. The constants A', B', and C' were determined by the method of least squares. Once the constants were obtained, the equations were differentiated analytically and the necessary values of the slopes determined.

With the experimental and calculated data, the values of the saturated liquid phase enthalpies, H_b's, could be obtained by applying Equations 1, 2, and 3. H_b's at 50-p.s.i. intervals over the pressure range 100 to 600 p.s.i.a. and at temperatures greater than 100° F. were determined. The calculated results appeared consistent and fell along smooth curves. Below 100° F. there was a scattering in the results which became more pronounced as the temperature decreased. The probable reason for the difficulties encountered below this temperature was the lack of sufficient experimental data. Reamer, Sage, and Lacey (*13*) obtained data at 40° F., the only temperature below 100° F. The slopes $(\partial P/\partial T)_y$ and $(\partial P/\partial T)_x$, could not be evaluated accurately under these circumstances. Consequently, ideal behavior was assumed—i.e., that enthalpy of the mixture was an additive property and proportional to the respective mole fractions. Because enthalpy values at and near the critical conditions were subject to large uncertainties, values at these conditions were not reported.

After H_b was determined and Equations 4, 5, and 6 were applied the quantity $(y - x)$ $(\partial H_L/\partial x)_{T,P}$ and, in turn, $(\partial H_L/\partial x)_{T,P}$ could be calculated. Partial enthalpies in the liquid phase and the following relationships were calculated from these data.

$$H_b = x_1\bar{H}_{L1} + x_2\bar{H}_{L2} \qquad (13)$$

and

$$(\partial H_L/\partial x)_{T,P} = \bar{H}_{L1} - \bar{H}_{L2} \qquad (14)$$

The enthalpy data, dew point, bubble point, and partial quantities in the liquid phase, and dew and bubble point temperatures are reported for various compositions and pressures in Table I. Figure 1 shows the bubble point enthalpy data as a function of liquid phase composition and Figures 2 and 3 give graphical comparisons of the partial enthalpies in the liquid phase and the pure components of ethane and n-pentane, respectively. Composition and temperatures parameters are included on these two pressure *vs.* enthalpy diagrams.

NOMENCLATURE

H = enthalpy, B.t.u. per lb. mole
$\bar{H}$ = partial enthalpy, B.t.u. per lb. mole
ΔH_c = differential heat of condensation, B.t.u. per lb. mole
ΔH_v = differential heat of vaporization, B.t.u. per lb. mole
P = pressure, lbs. per sq. inch abs.
R = gas law constant, 10.731 (lbs. per sq. in.) (cu. ft.) per (lb. mole) (° R.)
T = temperature, ° R.
V = volume, cu. ft. per lb. mole

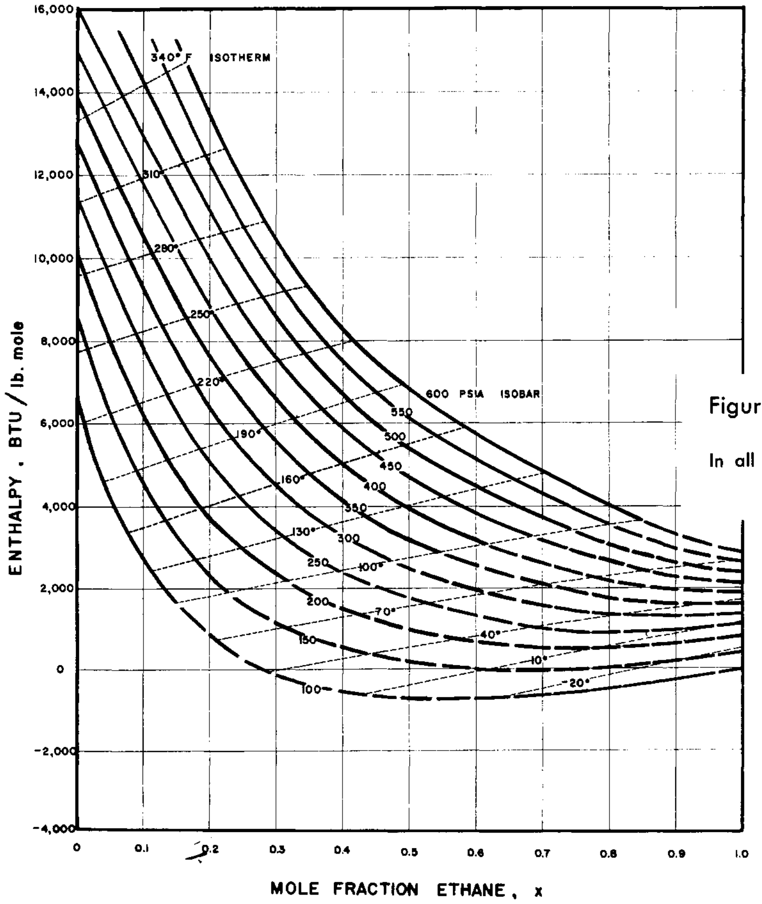

Figure 1. Enthalpy composition diagram for liquid phase mixtures of ethane–n-pentane

In all figures, H = 0 for the pure components in the ideal gas state, unit fugacity, and 0° R.

Table I. Enthalpy and Partial Enthalpy Values, Given in B.T.U. per Pound Mole, for Saturated Mixtures of Ethane and *n*-Pentane[a]

Mole Fraction Ethane	t_d, ° F.	H_d,	t_b, ° F.	H_b,	$\bar{H}_1$,	$\bar{H}_2$,
			Pressure = 100 P.S.I.A.			
0.00	224.2	14,280	224.2	4,950	. . .	4,950
0.10	215.1	12,850	139.3	662	1935	520
0.20	197.9	11,940	73.4	−1,178	590	−1,620
0.30	188.7	11,040	36.8	−2,184	−280	−3,000
0.40	180.0	10,150	14.3	−2,640	−750	−3,900
0.50	170.3	9,250	−2.2	−2,690	−1180	−4,200
0.60	157.7	8,350	−15.1	−2,728	−1480	−4,600
0.70	140.3	7,410	−24.8	−2,690	−1700	−5,000
0.80	115.3	6,450	−32.8	−2,504	−1825	−5,220
0.90	75.2	5,340	−39.8	−2,285	−1950	−5,300
1.00	−46.6	3,300	−46.6	−2,060	−2060	. . .
			Pressure = 150 P.S.I.A.			
0.00	259.9	14,888	259.9	6,719	. . .	6,719
0.10	246.7	13,750	183.4	2,588	3020	2,540
0.20	235.3	12,720	118.6	240	1480	−70
0.30	224.3	11,680	75.7	−863	600	−1,490
0.40	212.0	10,660	47.2	−1,550	−50	−2,550
0.50	197.6	9,670	27.3	−1,855	−490	−3,220
0.60	180.7	8,690	12.1	−2,014	−850	−3,760
0.70	160.5	7,700	0.3	−2,079	−1110	−4,340
0.80	134.5	6,660	−9.0	−1,986	−1320	−4,650
0.90	94.2	5,490	−16.6	−1,840	−1500	−4,900
1.00	−23.6	3,400	−23.6	−1,630	−1630	. . .
			Pressure = 200 P.S.I.A.			
0.00	287.5	15,600	287.5	8,190	. . .	8,190
0.10	272.3	14,350	216.8	4,269	3990	4,300
0.20	258.5	13,210	154.3	1,632	2280	1,470
0.30	245.4	12,110	108.2	329	1260	−70
0.40	232.0	11,050	75.4	−620	550	−1,400
0.50	217.2	10,000	52.0	−1,065	90	−2,220
0.60	199.8	8,970	34.5	−1,332	−300	−2,880
0.70	178.6	7,910	20.8	−1,506	−600	−3,620
0.80	150.6	6,830	10.0	−1,514	−870	−4,090
0.90	107.9	5,590	1.6	−1,435	−1100	−4,450
1.00	−5.8	3,460	−5.8	−1,230	−1230	. . .
			Pressure = 250 P.S.I.A.			
0.00	310.0	16,175	310.0	9,502	. . .	9,502
0.10	294.8	14,900	243.4	5,825	4790	5,940
0.20	280.5	13,660	183.1	3,002	3010	3,000
0.30	265.8	12,470	135.5	1,468	1860	1,300
0.40	250.0	11,310	100.3	286	1090	−250
0.50	232.8	10,200	74.5	−300	600	−1,200
0.60	214.2	9,100	54.6	−696	160	−1,980
0.70	192.4	8,040	39.4	−968	−170	−2,830
0.80	163.6	6,930	27.1	−1,160	−580	−3,480
0.90	116.9	5,650	17.5	−1,081	−760	−3,970
1.00	9.1	3,545	9.1	−900	−900	. . .
			Pressure = 300 P.S.I.A.			
0.00	329.6	16,656	329.6	10,738	. . .	10,738
0.10	313.4	15,280	269.4	7,260	5460	7,460
0.20	298.6	14,000	208.8	4,332	3660	4,500
0.30	284.0	12,750	159.1	2,561	2400	2,630
0.40	267.8	11,570	122.2	1,202	1580	950
0.50	249.1	10,420	94.5	425	1030	−180
0.60	228.2	9,280	73.6	−82	550	−1,030
0.70	204.9	8,150	56.1	−460	200	−2,000
0.80	175.7	7,000	41.8	−666	−130	−2,810
0.90	127.8	5,700	30.8	−733	−430	−3,460
1.00	21.8	3,515	21.8	−650	−650	. . .
			Pressure = 350 P.S.I.A.			
0.00	346.9	17,002	346.9	11,871	. . .	11,871
0.10	329.7	15,500	290.8	8,602	5920	8,900
0.20	313.1	14,160	232.2	5,598	4190	5,950
0.30	296.8	12,940	181.5	3,598	2870	3,910
0.40	279.8	11,730	142.1	2,076	2040	2,100
0.50	261.4	10,540	112.4	1,155	1410	900
0.60	240.1	9,370	89.5	544	920	−20
0.70	215.9	8,220	70.9	64	550	−1,070
0.80	185.6	7,030	55.3	−266	190	−2,090
0.90	136.2	5,680	42.8	−405	−130	−2,880
1.00	33.2	3,510	33.2	−400	−400	. . .
			Pressure = 400 P.S.I.A.			
0.00	362.2	17,161	362.2	12,917	. . .	12,917
0.10	345.1	15,680	310.1	9,833	6080	10,250
0.20	327.5	14,340	253.2	6,800	4600	7,350
0.30	309.9	13,050	201.6	4,627	3360	5,170
0.40	291.7	11,810	159.9	2,938	2470	3,250
0.50	272.5	10,620	129.0	1,890	1760	2,020
0.60	251.2	9,420	104.5	1,158	1250	1,020
0.70	225.9	8,260	84.6	589	850	−20
0.80	193.1	7,050	68.2	144	480	−1,200
0.90	143.2	5,680	54.6	−78	160	−2,220
1.00	43.3	3,495	43.3	−135	−135	. . .
			Pressure = 450 P.S.I.A.			
0.00	375.9	17,052	375.9	14,023	. . .	14,023
0.10	358.7	15,750	327.7	11,039	6080	11,590
0.20	341.2	14,430	272.2	7,978	4890	8,750
0.30	322.1	13,140	221.2	5,579	3780	6,350
0.40	302.1	11,890	177.2	3,788	2870	4,400
0.50	281.2	10,660	143.8	2,615	2080	3,150
0.60	259.1	9,460	118.2	1,802	1550	2,180
0.70	234.1	8,280	97.3	1,133	1130	1,140
0.80	200.2	7,070	79.8	634	750	−170
0.90	149.8	5,680	64.8	256	450	−1,490
1.00	52.6	3,460	52.6	120	120	. . .
			Pressure = 500 P.S.I.A.			
0.10	372.4	15,830	343.7	12,199	5890	12,900
0.20	353.9	14,440	290.2	9,100	5060	10,110
0.30	333.7	13,150	239.8	6,562	4140	7,600
0.40	311.8	11,890	195.1	4,634	3260	5,550
0.50	289.5	10,660	158.1	3,340	2380	4,300
0.60	266.1	9,450	130.6	2,430	1810	3,360
0.70	240.6	8,270	108.9	1,686	1380	2,400
0.80	207.1	7,050	90.2	1,036	1010	1,140
0.90	154.3	5,600	74.2	579	710	−600
1.00	61.4	3,400	61.4	365	365	. . .
			Pressure = 550 P.S.I.A.			
0.20	360.0	14,150	306.0	10,220	5140	11,490
0.30	339.9	13,030	256.2	7,526	4390	8,870
0.40	318.0	11,890	211.5	5,386	3640	6,550
0.50	296.1	10,660	173.4	4,070	2660	5,480
0.60	272.3	9,460	143.0	3,092	2080	4,610
0.70	246.5	8,280	119.5	2,278	1630	3,790
0.80	212.7	7,060	100.2	1,520	1250	2,600
0.90	158.5	5,580	83.4	919	960	550
1.00	69.1	3,305	69.1	605	605	. . .
			Pressure = 600 P.S.I.A.			
0.20	. . .	. . .	321.0	11,262	5110	12,800
0.30	346.9	12,660	272.6	8,470	4550	10,150
0.40	324.2	11,690	228.2	6,168	3990	7,620
0.50	301.0	10,640	187.5	4,775	2930	6,620
0.60	276.9	9,440	153.9	3,748	2320	5,890
0.70	250.8	8,250	128.7	2,876	1880	5,200
0.80	217.8	7,050	108.5	2,024	1480	4,200
0.90	162.5	5,530	91.6	1,267	1200	1,870
1.00	76.3	3,195	76.3	870	870	. . .

[a] $H = 0$ for pure components in ideal-gas state at unit fugacity and 0° R. Vapor- and-liquid-phase enthalpies of the pure components, obtained from literature sources cited, were adjusted to this reference state.

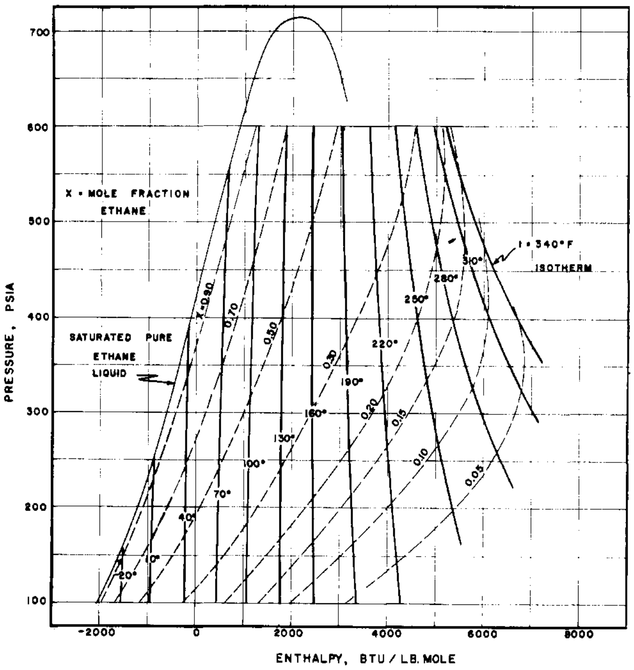

Figure 2. Pressure enthalpy diagram for ethane showing partial values in the liquid phase for the ethane–*n*-pentane system. Data for pure ethane are from Barkelew, Valentine, and Hurd (2)

ΔV_c = volume change accompanying differential condensation process, cu. ft. per lb. mole
ΔV_v = volume change accompanying differential vaporization
$\bar{V}$ = partial volume, cu. ft. per lb. mole
a = Van der Waals attraction constant
b = Van der Waals constant, covolume
d = density, lb. moles per cu. ft.
k = constant, Equation 9
x = mole fraction in liquid phase
y = mole fraction in vapor phase
A_0, B_0, C_0, a, b, c, α, γ = empirical constants of Benedict-Webb-Rubin equation of state
ξ = attraction coefficient in Black's equation of state
A', B', C' = constants, Equation 12

Subscript

G = gas phase
L = liquid phase
b = bubble point
d = dew point
i = component i in a mixture
m = mixture
1 = component 1 in a mixture

Superscript

° = property in ideal gas state

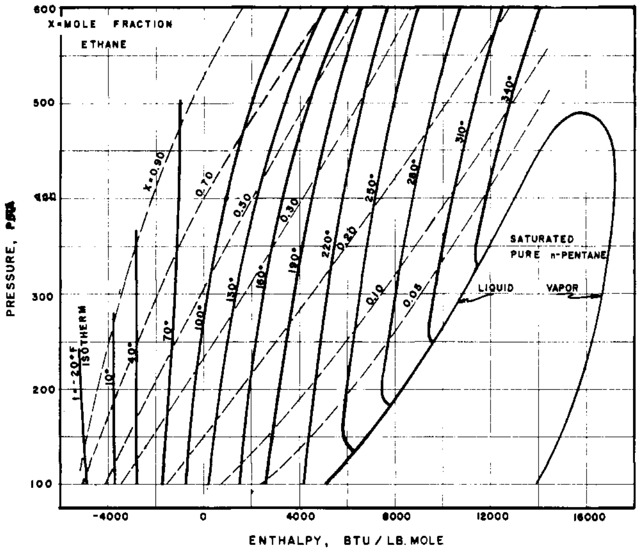

Figure 3. Pressure-Enthalpy Diagram for *n*-pentane showing partial values in the liquid phase for ethane–*n*-pentane system. Data for pure *n*-pentane are from Brydon, Walen, and Canjar (7)

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