

# Liquid Phase Enthalpy Values for the Ethane-*n*-Butane System

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Through the application of rigorous thermodynamic relationships and *P-V-T-x* data, total and partial liquid phase enthalpy values have been calculated for the ethane-*n*-butane system over the pressure range 100 to 550 p.s.i.a.

IN A PREVIOUS ARTICLE (12) saturated liquid phase enthalpy values were presented for the ethane-*n*-butane system at 200 and 400 p.s.i.a. These values were calculated from *P-V-T-x* data and the differential heat of condensation. The basic relationships (5) are thermodynamically rigorous.

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

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

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

Later, using the differential heat of vaporization as well as that of condensation, Houser and Weber (7) recalculated the saturated liquid phase enthalpy values for the methane-ethane system and, in addition, calculated partial enthalpies in the liquid phase. Vennix and Weber (13) performed the same type of calculation for the ethane-*n*-pentane system. The additional equations utilized were:

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

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

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

In both of these works the effect of pressure over 50 p.s.i. intervals at constant temperature on the liquid phase volumes and enthalpies were neglected.

As part of a continuing attempt to evaluate liquid phase enthalpies, both total and partial quantities, the ethane-*n*-butane system was restudied. In this case both the differential heats of condensation and vaporization were calculated and total and partial enthalpies in the liquid phase evaluated at 50 p.s.i. intervals over the pressure range 100-550 p.s.i.a. The *P-V-T-x* data for the binary system used with calculations were those of Kay (8) and the data on pure ethane were those of Barkelew, Valentine, and Hurd (2) and pure *n*-butane of Prengle, Greenhaus, and York (10).

While the amount of liquid phase volumetric data was insufficient to permit the exact application of Equation (5), by neglecting the effect of pressure on the liquid volume over a 50 p.s.i. range the equation could be used. Since volumetric data for the superheated vapor as well as the saturated vapor were required, the use of an equation of state for the vapor phase was necessary. Kay (8) reported only limited data for the saturated vapor. As in the previous

work (3, 4), the Benedict-Webb-Rubin equation

$$P = RTd + (B_0RT - A_0 - C_0/T^2)d^2 + (bRT - a)d^3 + a\alpha d^6 + cd^3/T^2[(1 + \gamma d^2)\exp(-\gamma d^2)] \quad (7)$$

was used. This equation, with the exception of one instance ( $y = 0.1749$ ) at 100 p.s.i.a., predicted vapor volumes in good agreement, average deviation of less than  $\pm 1\%$ , with those given by Kay (8). In general the predicted and experimental volumes agreed more closely as the pressure was increased. The equation of state was used to determine the quantity  $(\partial V_G/\partial y)_{T,P}$ , also.

The Benedict-Webb-Rubin equation (3, 4) in the form

$$H - \sum_i x_i H_i^o = (B_0RT - 2A_0 - 4C_0/T^2)d + (2bRT - 3a)d^2/2 + 6a\alpha d^5/5 + cd^2/T^2 \left[ 3 \frac{1 - \exp(-\gamma d^2)}{\gamma d^2} - \frac{\exp(-\gamma d^2)}{2} + \gamma d^2 \exp(-\gamma d^2) \right] \quad (8)$$

was used to calculate enthalpies of gaseous mixtures at their dew point. The ideal gas state enthalpy values,  $H_i^o$ , were obtained from API 44 (1). Papadopoulos, Pigford, and Friend (9) differentiated this relationship for the evaluation of partial enthalpies. Their relationship was used to evaluate the terms  $(\partial H_G/\partial y)_{T,P}$  in Equation 3.

Since the final liquid phase enthalpy values are very sensitive to the values of  $(\partial P/\partial T)_y$  and  $(\partial P/\partial T)_x$  used in Equations 1 and 4, considerable effort was expended in finding a suitable expression which would relate the pressure and temperature at the dew and bubble point conditions. A modified form of the expression given by Frost and Kalkwarf (6)

$$\ln P = A + B/T + DP/T^2 \quad (9)$$

the quantity  $C$  in  $T$  was deleted from the original expression, was found to be the most suitable of those investigated, the selection being made on the basis of the degree of consistency of the value of the derivatives. The constants were determined by the method of least squares in which a weighting factor was introduced. The procedure has been described by Smith and Tao (11).

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 550 p.s.i.a. were determined.

After  $H_b$  was determined, the quantity  $(\partial H_L/\partial x)_{T,P}$  could be calculated from Equations 4, 5, and 6. Partial enthalpies can then be calculated readily from

$$H_b = x_1 H_{L1} + x_2 H_{L2} \quad (10)$$

and

$$(\partial H_L/\partial x)_{T,P} = H_{L1} - H_{L2} \quad (11)$$

The enthalpy data for the saturated vapor and liquid phases, partial values for the liquid phase, bubble and dew point temperatures as well as compositions are reported in Table I. The saturated liquid phase enthalpies are shown in Figure 1. Figures 2, and 3 give graphical comparisons of the partial enthalpies in the liquid phase and the pure components of ethane and *n*-butane, respectively. Composition

and pressure parameters are included on the two enthalpy vs. temperature diagrams.

The liquid phase enthalpy values at 200 p.s.i.a. in this work are from 300 B.t.u.'s/lb. mole less to 200 more than those reported previously, while at 400 p.s.i.a., the present values are 100 to 800 B.t.u.'s/mole greater than the previous ones (12).

Table I. Enthalpy and Partial Enthalpy Values for Saturated Mixtures of Ethane and *n*-Butane<sup>a</sup>

Mole Fraction Ethane	$t_D$ ° F.	$H_D^*$ B.t.u. lb.-mole	$t_B$ ° F.	$H_{L1}$ B.t.u. lb.-mole	$H_{L2}$ B.t.u. lb.-mole	B.t.u. lb.-mole	Mole Fraction Ethane	$t_D$ ° F.	$H_D$ B.t.u. lb.-mole	$t_B$ ° F.	$H_{L1}$ B.t.u. lb.-mole	$H_{L2}$ B.t.u. lb.-mole	B.t.u. lb.-mole
Pressure-100 p.s.i.a.							Pressure-350 p.s.i.a.						
0.00	146.0	9,413	146.0	1,471	...	1,471	0.00	257.0	11,200	257.0	6,071	...	6,071
0.10	138.1	8,872	96.7	12	320	-22	0.10	244.0	10,470	219.7	4,320	5,350	4,205
0.20	129.3	8,327	58.9	-945	-232	-1,123	0.20	230.5	9,752	183.6	2,915	3,795	2,695
0.30	120.0	7,792	30.3	-1,585	-580	-2,015	0.30	216.2	9,037	152.3	1,872	2,660	1,530
0.40	110.0	7,264	10.3	-1,970	-856	-2,713	0.40	201.4	8,344	125.6	1,028	1,920	435
0.50	99.1	6,742	-4.9	-2,125	-1,140	-3,110	0.50	185.4	7,657	103.1	432	1,340	-475
0.60	86.0	6,205	-17.4	-2,142	-1,307	-3,395	0.60	168.1	6,981	84.3	86	910	-1,150
0.70	69.6	5,644	-27.8	-2,140	-1,450	-3,750	0.70	147.7	6,283	68.7	-122	563	-1,720
0.80	50.1	5,074	-36.0	-2,120	-1,600	-4,200 <sup>b</sup>	0.80	123.0	5,555	54.8	-250	250	-2,250
0.90	21.5	4,422	-42.0	-2,088	-1,856	-4,176 <sup>b</sup>	0.90	88.0	4,702	41.8	-322	-35	-2,905
1.00	-46.5	3,326	-46.5	-2,042	-2,042	...	1.00	32.8	3,560	32.8	-342	-342	...
Pressure-150 p.s.i.a.							Pressure-400 p.s.i.a.						
0.00	177.3	9,979	177.3	2,646	...	2,646	0.00	270.9	11,300	270.9	6,841	...	6,841
0.10	168.8	9,401	132.0	1,070	1,500	1,017	0.10	256.6	10,550	235.1	5,125	6,100	5,017
0.20	159.0	8,807	94.5	0	650	-162	0.20	242.2	9,822	200.6	3,650	4,535	3,428
0.30	148.5	8,220	64.6	-745	180	-1,140	0.30	227.4	9,104	169.1	2,498	3,280	2,163
0.40	137.3	7,644	42.2	-1,250	-225	-1,935	0.40	211.9	8,398	141.6	1,557	2,385	1,005
0.50	125.1	7,073	25.3	-1,523	-550	-2,496	0.50	195.3	7,700	118.1	880	1,765	-5
0.60	110.6	6,488	11.2	-1,624	-773	-2,900	0.60	177.4	7,012	98.5	468	1,300	-780
0.70	92.9	5,880	-0.6	-1,642	-930	-3,300	0.70	156.7	6,307	81.5	215	881	-1,340
0.80	72.0	5,265	-10.2	-1,640	-1,183	-3,468 <sup>b</sup>	0.80	131.1	5,555	66.7	53	535	-1,875
0.90	41.6	4,559	-18.0	-1,625	-1,390	-3,740 <sup>b</sup>	0.90	96.6	4,700	53.1	-46	245	-2,670
1.00	-23.8	3,436	-23.8	-1,598	-1,598	...	1.00	43.0	3,545	43.0	-88	-88	...
Pressure-200 p.s.i.a.							Pressure-450 p.s.i.a.						
0.00	202.7	10,430	202.7	3,643	...	3,643	0.00	283.5	11,320	283.5	7,606	...	7,606
0.10	193.1	9,802	159.7	1,990	2,525	1,930	0.10	268.6	10,610	249.8	5,825	6,860	5,710
0.20	182.3	9,166	123.0	788	1,563	594	0.20	253.5	9,880	216.7	4,310	5,250	4,075
0.30	170.8	8,539	92.9	-32	890	-427	0.30	237.7	9,144	184.7	3,118	3,830	2,813
0.40	158.4	7,918	68.7	-620	363	-1,275	0.40	221.4	8,425	155.9	2,116	2,830	1,640
0.50	144.2	7,288	49.2	-970	-28	-1,912	0.50	204.2	7,718	131.8	1,368	2,150	586
0.60	128.5	6,664	33.9	-1,125	-326	-2,322	0.60	185.8	7,023	111.2	883	1,620	-222
0.70	111.1	6,049	20.9	-1,188	-523	-2,740	0.70	164.5	6,305	93.7	588	1,200	-840
0.80	88.7	5,392	10.0	-1,220	-737	-3,150	0.80	138.4	5,540	77.9	390	823	-1,345
0.90	57.2	4,648	1.0	-1,228	-1,007	-3,217 <sup>b</sup>	0.90	103.7	4,669	63.3	260	500	-1,900
1.00	-6.1	3,502	-6.1	-1,226	-1,226	...	1.00	52.3	3,513	52.3	172	172	...
Pressure-250 p.s.i.a.							Pressure-500 p.s.i.a.						
0.00	223.3	10,750	223.3	4,521	...	4,521	0.00	295.0	11,210	295.0	8,433	...	8,433
0.10	212.9	10,100	182.1	2,850	3,385	2,790	0.10	279.4	10,590	263.2	6,608	8,020	6,450
0.20	201.2	9,432	145.8	1,566	2,310	1,380	0.20	263.4	9,875	230.7	5,020	5,940	4,790
0.30	188.5	8,762	116.1	611	1,540	212	0.30	246.6	9,129	198.9	3,735	4,290	3,497
0.40	175.5	8,119	91.1	-58	835	-720	0.40	229.4	8,400	169.7	2,696	3,245	2,330
0.50	160.7	7,465	70.0	-480	450	-1,410	0.50	212.0	7,703	144.6	1,862	2,522	1,200
0.60	144.4	6,818	53.0	-700	126	-1,940	0.60	193.6	7,020	123.0	1,297	1,995	250
0.70	124.9	6,150	39.1	-810	-140	-2,373	0.70	171.5	6,285	104.5	937	1,510	-400
0.80	101.8	5,469	27.0	-870	-383	-2,820	0.80	144.4	5,495	88.0	700	1,125	-1,000
0.90	70.0	4,703	16.9	-895	-650	-3,100 <sup>b</sup>	0.90	109.9	4,618	72.8	530	804	-1,940
1.00	8.7	3,541	8.7	-902	-902	...	1.00	60.8	3,461	60.8	433	433	...
Pressure-300 p.s.i.a.							Pressure-550 p.s.i.a.						
0.00	241.2	11,000	241.2	5,308	...	5,308	0.00	305.8	10,740	305.8	10,220	...	10,220
0.10	229.2	10,300	201.9	3,572	4,400	3,480	0.10	288.7	10,440	275.5	7,442	9,065	7,261
0.20	216.9	9,619	166.0	2,220	3,088	2,003	0.20	271.7	9,774	244.3	5,820	6,645	5,613
0.30	203.5	8,928	134.9	1,255	2,106	890	0.30	254.5	9,064	213.4	4,432	4,850	4,253
0.40	189.1	8,244	109.0	505	1,418	-103	0.40	236.8	8,348	183.7	3,320	3,675	3,083
0.50	173.7	7,573	87.1	2	922	-918	0.50	218.8	7,654	157.3	2,400	2,995	1,805
0.60	157.0	6,913	69.3	-280	550	-1,520	0.60	199.8	6,969	134.4	1,752	2,346	860
0.70	137.2	6,232	54.8	-458	214	-2,026	0.70	177.3	6,232	115.0	1,326	1,817	180
0.80	113.0	5,520	41.9	-560	-65	-2,541	0.80	149.9	5,434	97.6	1,030	1,442	-620
0.90	79.5	4,710	29.8	-610	-317	-3,246	0.90	115.5	4,548	81.5	796	1,051	-1,500
1.00	21.5	3,560	21.5	-614	-614	...	1.00	68.6	3,382	68.6	684	684	...

<sup>a</sup>0.0 for the pure components in the ideal-gas state at unit fugacity and 0° Rankine. 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.

<sup>b</sup>Extrapolated values.

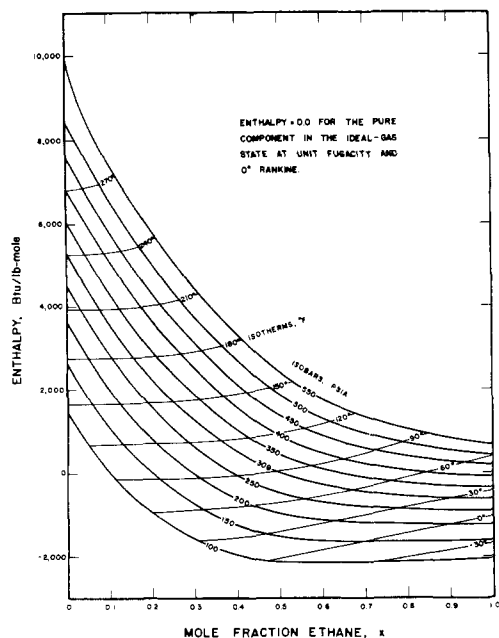


Figure 1. Liquid phase enthalpy vs. composition-ethane-n-butane system

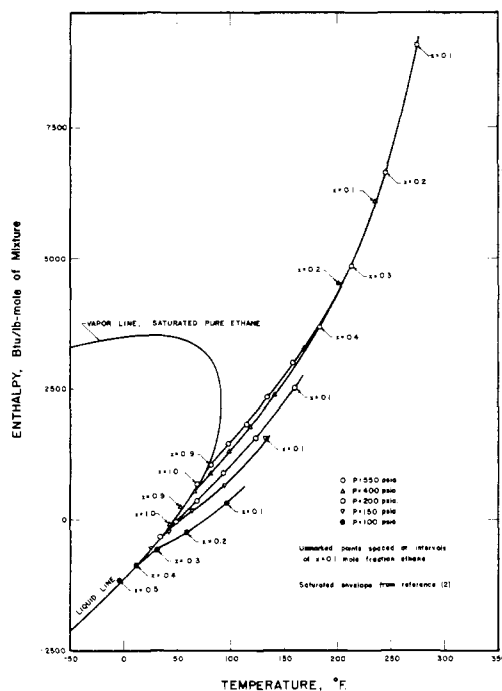


Figure 2. Enthalpy vs. temperature diagram for ethane. Partial enthalpies of liquid ethane in ethane-n-butane system included

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#### NOMENCLATURE

- $H$  = enthalpy, B.t.u. per lb. mole
- $\bar{H}$  = partial enthalpy, B.t.u. per lb. mole
- $\Delta H_c$  = differential heat of condensation, B.t.u. per lb. mole
- $\Delta H_v$  = 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

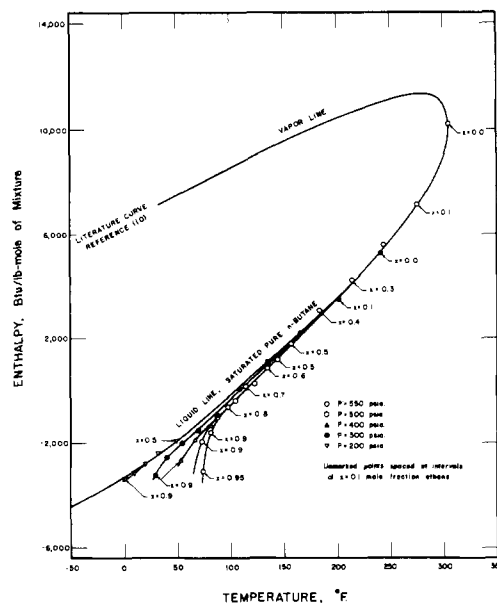


Figure 3. Enthalpy vs. temperature diagram for n-butane. Partial enthalpies of liquid n-butane in ethane-n-butane included

- $\Delta V_c$  = volume change accompanying differential condensation process, cu. ft. per lb. mole
- $\Delta V_v$  = volume change accompanying differential vaporization
- $\bar{V}$  = partial volume, cu. ft. per lb. mole
- $d$  = density, lb. moles per cu. ft.
- $x$  = mole fraction in liquid phase
- $y$  = mole fraction in vapor phase

$A_0, B_0, C_0, a, b, c, \alpha, \gamma,$  = empirical constants of Benedict-Webb-Rubin equation of state

$A, B, D$  = constants, Equation 9

#### Subscript

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

#### Superscript

- $^\circ$  = property in ideal gas state

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