Saturated Liquid Phase Enthalpies at High Pressures Ethane–*n*-Heptane System

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As part of a continuing study of thermal data of binary systems, saturated liquid phase enthalpies are presented for the system ethane–*n*-heptane at 100, 200, 300, 400, 500, and 600 p.s.i.a. Saturated liquid phase enthalpy data have been presented for other hydrocarbon systems (*5, 7*).

The method used for calculating the saturated liquid enthalpy data is outlined by Dodge (*4*) and has been discussed in detail (*5, 7*); the procedure is thermodynamically rigorous. The differential heat of condensation is calculated and, in turn, the saturated liquid enthalpy. The differential heat of condensation is the heat given up when one mole of liquid is condensed from a very large quantity of vapor, the process taking place under conditions of constant pressure and temperature. The basic expressions used in the calculations are

$$\Delta V = V_b - V_d + (y - x)\left(\frac{\partial V_G}{\partial y}\right)_{T,P} \quad (1)$$

$$\frac{\partial P}{\partial T}_y = \frac{\Delta H_c}{T\Delta V} \quad (2)$$

and

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

From Equations 1, 2, and 3 it is evident that volumetric data for the saturated and superheated vapor states and saturated liquid state are required. Vapor-liquid equilibrium data are also necessary, including pressure and temperature information.

Kay (*6*) obtained *P-V-T-x* data for the ethane–*n*-heptane system, including volumetric data for the saturated liquid and vapor states only. Additional saturated vapor and superheated vapor volumetric data were required; so the Benedict-Webb-Rubin equation state (*3*)

$$P = RTd + (B_0RT - A_0 - C_0/T^2)d^2 + (bRT - a)d^3 + a\alpha d^6 + cd^3/T^2\ (1 + \gamma d^2)\exp(-\gamma d^2) \quad (4)$$

was utilized. The validity of this relationship was established by comparing results calculated from the equation with the experimental results of Kay. With the exceptions of the critical regions, the calculated results and the experimental data for various mixtures were in good agreement, usually within ±1%. The differences at the critical points were 15.7, −14.4, and −12.1% at pressures of 400, 500, and 600 p.s.i., respectively. The positive percentage figure indicates the experimental value was greater than the calculated; the negative percentage figures indicate the opposite.

Once the validity of the Benedict-Webb-Rubin equation (*3*) was established, the necessary volumetric data for the solution of Equation 1 could be calculated. Also, by using the equation (*3*) and enthalpy data (*1*) for the pure components in the ideal gas state (*1*), the required vapor phase enthalpy data could be calculated. The relationship used was

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

Because ethane and *n*-heptane differ greatly in volatility, the determination of partial volumes, $(\partial V_G/\partial y)T,P$, and partial enthalpies $(\partial H_G/\partial y)T,P$, was difficult. The difficulties were greatest when the concentration of ethane in the vapor phase was high—e.g., when the mole fraction was between 0.995 and 0.95. The smoothing technique, described by Hobson and Weber (*5*), in which the quantities $(y - x)(\partial V_G/\partial y)T,P$, and $(y - x)(\partial H_G/\partial y)T,P$ are plotted against y was used to detect erroneous values. With the calculated data and the equilibrium data determined by Kay (*6*), the saturated liquid enthalpy values could be calculated by using Equations 1, 2, and 3.

The enthalpy values of pure ethane presented by Barkelew, Valentine, and Hurd (*2*) were used. These data had to be changed to the datum plane used in this work—namely, the enthalpies of the pure components in the ideal gas state at 0° R. and unit fugacity were set equal to zero. Equation 5 was used to calculate enthalpy values for pure *n*-heptane in the saturated vapor state. These calculated data and the latent heat of vaporization data for *n*-heptane (*8*) were used to determine the enthalpy values of *n*-heptane in the saturated liquid state.

The final results presented in Figure 1 and in Table I are believed to be accurate within ±3%. The enthalpy data are reported to four or five figures for consistency.

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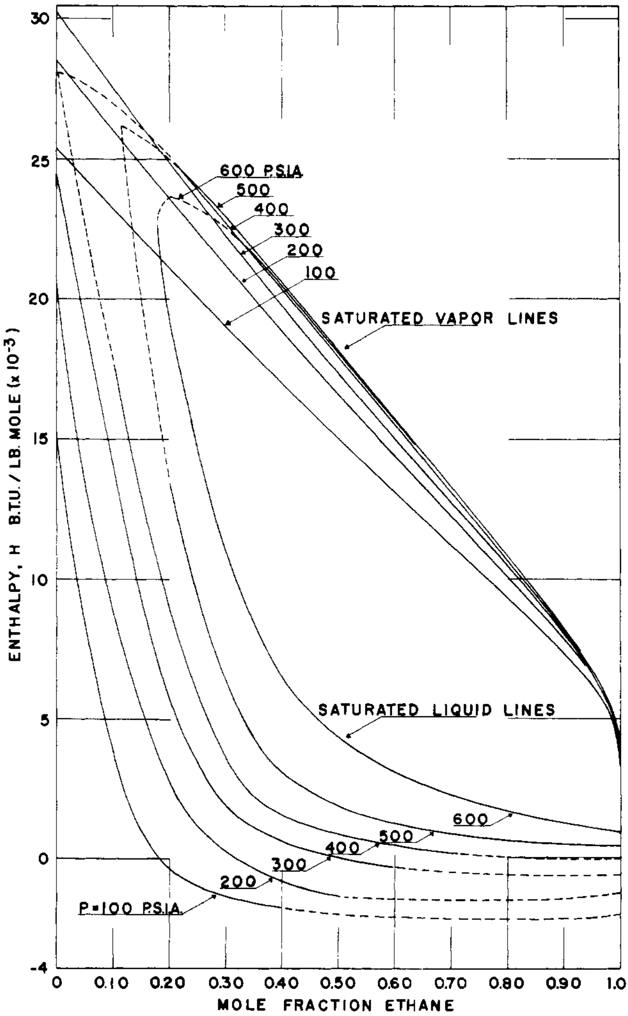

Figure 1. Enthalpy vs. composition diagram

Table 1. Enthalpy-composition Data for Ethane–*n*-Heptane System

Mole Fraction Ethane, z_{c_2}	Bubble Point Temp., t_b, °F.	Dew Point Temp., t_d, °F.	Enthalpy at^a Bubble Point, H_b, B.t.u./Lb. Mole	Enthalpy at^a Dew Point, H_d, B.t.u./Lb. Mole	
Pressure, 100 P.S.I.A.					
0	358	358	14,743	25,256	
0.10	165	347	+3,802	23,148	
0.20	83	334	-425	21,032	
0.30	41	320	-1,463	18,947	
0.40	14	305.5	-1,852	16,951	
0.50	-5	290	(-2,060)^b	15,014	
0.60	-18.5	272.5	(-2,170)	13,104	
0.70	-29	251	(-2,220)	11,245	
0.80	-37	223	(-2,290)	9,360	
0.90	. . .	179	(-2,240)	7,397	
0.96	. . .	132	. . .	6,057	
0.99	. . .	78	. . .	5,028	
0.995	. . .	55.5	. . .	4,687	
1.00	-46	-46	-2,061	3,299	(*2*)
Pressure, 200 P.S.I.A.					
0	430.5	430.5	20,165	28,396	
0.10	292	415	8,650	25,818	
0.20	176	399	2,716	23,429	
0.30	115	382	+ 205	20,997	
0.40	78.5	364.5	-902	18,755	
0.50	53	345	-1,375	16,487	
0.60	34.5	324	(-1,440)^b	14,364	
0.70	20	298	(-1,510)	12,231	
0.80	9.5	264	(-1,510)	10,051	
0.90	1.5	214.5	(-1,480)	7,852	
0.96	. . .	162	. . .	6,349	
0.99	. . .	102	. . .	5,178	
0.995	. . .	+78	. . .	4,780	
1.00	-6.2	-6.2	-1,230	3,467	(*2*)
Pressure, 300 P.S.I.A.					
0	478.2	478.2	24,268	30,195	
0.10	375.6	459.1	13,808	27,410	
0.20	254.2	439.1	5,392	24,760	
0.30	176.3	418.7	1,798	22,122	
0.40	126.7	397.8	+ 562	19,631	
0.50	93.6	376.8	-20	17,271	
0.60	71.2	354.3	-366	15,019	
0.70	54.7	326.4	(-504)^b	12,792	
0.80	41.8	290	(-600)	10,467	
0.90	31.2	235.3	(-600)	8,072	
0.96	. . .	178	. . .	6,436	
0.99	. . .	113	. . .	5,135	
0.995	. . .	90.5	. . .	4,751	
1.00	21.6	21.6	-650	3,515	(*2*)
Pressure, 400 P.S.I.A.					
0.003	512	512	(28,058)^b	(28,058)	
0.10	435.5	490	17,796	(26,950	
0.20	322	468	8,883	25,050	
0.30	232.5	445	3,502	22,658	
0.40	171	423	1,512	20,241	
0.50	131.5	400	807	17,855	
0.60	103	377.5	405	15,489	
0.70	82	348	195	13,085	
0.80	67	307.5	(+ 5)	10,683	
0.90	54	249	(-70)	8,156	
0.96	. . .	187	. . .	6,406	
0.99	. . .	120	. . .	5,039	
0.995	. . .	99	. . .	4,640	
1.00	42.8	42.8	-68	3,497	(*2*)
Pressure, 500 P.S.I.A.					
0.113	497.5	497.5	(26,130)^b	(26,130)^b	
0.20	382.3	483.5	13,633	(24,905)	
0.30	285.7	462.8	6,378	22,854	
0.40	220.8	440.5	2,992	20,495	
0.50	168.2	417.0	1,803	18,047	
0.60	130.6	390.5	1,212	15,603	
0.70	106.6	359.3	883	13,195	
0.80	89.3	320	604	10,798	
0.90	74.2	259	407	8,192	
0.96	. . .	192.5	. . .	6,326	
0.99	. . .	126	. . .	4,901	
0.995	. . .	104.5	. . .	4,469	
1.00	61.0	61.0	369	3,398	(*2*)
Pressure, 600 P.S.I.A.					
0.20	484	484	(23,622)^b	(23,622)^b	
0.177	475	. . .	22,720	. . .	
0.193	450	. . .	19,895	. . .	
0.236	400	. . .	15,832	. . .	
0.30	337	471	10,906	22,504	
0.40	256	450	6,397	20,317	
0.50	198	426	4,302	17,941	
0.60	158	400	3,098	15,597	
0.70	130	370	2,303	13,242	
0.80	110	328	1,711	10,790	
0.90	92.5	264	1,261	8,114	
0.96	. . .	198	. . .	6,236	
0.99	. . .	131	. . .	4,747	
0.995	. . .	109	. . .	4,251	
1.00	75.8	75.8	870	3,194	(*2*)

^{a}H = 0 for pure components in ideal gas state at unit fugacity and 0° R. ^{b}All values in parentheses are extrapolated data.

NOMENCLATURE

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
ΔH_c = differential heat of condensation, B.t.u./lb. mole
P = pressure, p.s.i.a.
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 liquid phase
y = mole fraction in vapor phase
z = mole fraction in either liquid or vapor phase
A_0, B_0, C_0, a, b, c, α and γ = empirical constants of Benedict-Webb-Rubin 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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