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Saturated Liquid Phase Enthalpies for the System *n*-Butane-*n*-Heptane at Elevated Pressures

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Accurate calculations for distillation operations require thermal as well as vapor-liquid equilibrium data. At the present time there are vapor-liquid equilibrium data for a number of binary systems for which thermal data are unavailable. Recently, Stiehl, Hobson, and Weber (*6*) utilized a thermodynamically rigorous method, outlined by Dodge (*3*), by which the saturated liquid phase enthalpies of binary mixtures may be calculated from the differential heats of condensation and vapor phase enthalpy data. As the saturated vapor phase enthalpies can be calculated from the Benedict-Webb-Rubin equation of state (*2*), complete enthalpy composition data are made available.

The method of calculation has been discussed thoroughly (*6*). The basic relationships which apply to the process of condensation for 1 mole of liquid from a large quantity of vapor under equilibrium conditions are

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

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

and

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

In the previous work enthalpy-composition data were presented for the system methane-ethane at 200, 400, and 600 pounds per square inch absolute and for the systems ethane-*n*-butane and propane-*n*-butane at the two lower pressures. In this work enthalpy composition data are presented for the system *n*-butane–*n*-heptane at 100, 200, 300, and 400 pounds per square inch absolute.

The vapor-liquid equilibrium data and the volumetric behavior of the coexisting phases for the *n*-butane–*n*-heptane system are reported by Kay (*4*). The Benedict-Webb-Rubin equation (2)

$$P = RTd + (B_0RT - A_0 - C_0/T^2)d^2 + (bRT - a)d^3 + a\alpha d^6 + cd^3/T^2[(1 + yd^2)\exp(-yd^2)] \tag{4}$$

was also used to calculate the saturated vapor volumes; the results agreed with the experimental data of Kay within ±1%. The single exception was the calculated value at the critical point at 400 pounds per square inch absolute, 511.8°F., and 1.1% *n*-heptane. In this case the molal volume predicted by the equation was 3.6% greater than the experimental value.

As the validity of the Benedict-Webb-Rubin equation was established for this binary system, this relationship was used to predict volumetric data in the superheated vapor region. Through the use of the calculated data, the experimental results of Kay (*4*), and the volumetric data for pure *n*-butane (*5*), the term $(\partial V/\partial y)_{T,P}$ in Equation 1 can be determined as a function of composition along any given isotherm at the pressure under consideration. The partial differential must be evaluated accurately. This is rendered difficult for three reasons: First, the slope is determined graphically; second, the slope of the isotherm must be determined at its point of intersection with the saturated vapor curve; and third, at high percentage compositions of the

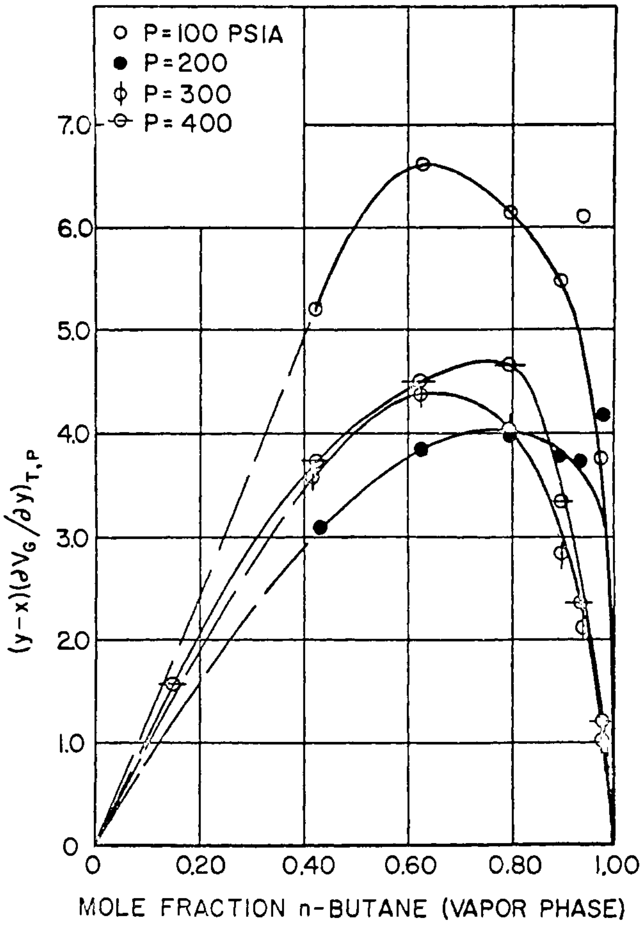

Figure 1. $(y - x)(\partial V_G/\partial y)_{T,P}$ *vs. y diagram for n-butane–n-heptane system*

more volatile component a small change in the molal volume, considerably less than 1%, produces a very large change in the slope of the isobaric isotherm.

In view of the above, additional means were sought to obtain consistent $(\partial V_G/\partial y)_{T,P}$ data. A simple plot of $(\partial V_G/\partial y)_{T,P}$ values at a single pressure vs. y failed to yield the desired results, because the points did not produce a smooth curve. However, a plot of the product $(y - x)(\partial V_G/\partial y)_{T,P}$ vs. y produced a smooth curve, parabolic in shape, for each pressure. This type of plot has an additional advantage because the product is equal to zero at $y = 0$ and $y = 1$. This fixed the two terminal points of the parabolic curve. A plot of $(y - x)(\partial V_G/\partial y)_{T,P}$ vs. y at the four pressures investigated is given in Figure 1 to illustrate the method which was used to smooth the slope data. Figure 1 shows that two calculated points, both in the range of high *n*-butane compositions and one on both the 100 and 200 pounds per square inch absolute pressure parameters, deviated considerably from their respective curves. The smoothing technique permitted the detection of these deviations.

Equation 1 can now be solved for the term ΔV, as the other terms are known. Also, the differential heat of condensation, ΔH_c, can be calculated from Equation 2. The data of Kay (*4*) were used to calculate the value of the term $(\partial P/\partial T)_y$ and to obtain the correct temperature.

The only enthalpy data available for the *n*-butane–*n*-heptane system are the values for the pure compounds in the saturated liquid and vapor states and the superheated vapor state (*5, 7*). These data were used in this work after they had been converted to the proper datum point. For convenience, the reference state used in (*1*), $H = 0$ for the pure components in the ideal gas state and unit fugacity at 0°R, was also selected as the datum point for this work.

The procedure used in evaluating the term $(\partial H_G/\partial y)_{T,P}$ was similar to the procedure used for $(\partial V_G/\partial y)_{T,P}$. As the validity of the Benedict-Webb-Rubin equation had been established, the equation in the form

$$H = \sum_i x_i H_i^0 + (B_0RT - 2A_0 - 4C_0/T^2)d + (2bRT - 3a)d^2/_2 + 6a\alpha d^5/5 + cd^2/T^2\left[3\,\frac{1 - \exp(-\gamma d^2)}{d^2}\right. \left.\frac{\exp(-\gamma d^2)}{2} + d^2\exp(-\gamma d^2)\right] \quad (5)$$

Table I. Enthalpy-Composition Data for *n*-Butane–*n*-Heptane System

Saturation Temp., °F.	Mole Fraction *n*-Butane (*4*)		Enthalpy[a], B.T.U./Lb. Mole		Ref.
	x	y	H_b	H_d	
Pressure = 100 Pounds per Square Inch Absolute					
358	0	0	10,673	21,186	(*7*)
315	0.10	0.380	8,338	19,330	
278.5	0.20	0.628	6,615	16,198	
248	0.30	0.773	5,338	13,951	
223.5	0.40	0.856	4,370	12,558	
204	0.50	0.908	3,658	11,650	
188	0.60	0.944	3,045	10,965	
173.8	0.70	0.969	2,502	10,405	
160.5	0.80	0.985	2,070	9,954	
151	0.90	0.996	1,732	9,560	
146	1.00	1.00	1,310	9,227	(*5*)
Pressure = 200 Pounds per Square Inch Absolute					
430.7	0	0	16,350	24,581	(*7*)
394.8	0.10	0.270	12,798	22,928	
359.5	0.20	0.497	10,270	20,120	
328.4	0.30	0.658	8,443	17,412	
301.3	0.40	0.773	7,050	15,392	
278.6	0.50	0.850	5,998	13,915	
258.9	0.60	0.902	5,168	12,905	
241.0	0.70	0.940	4,540	12,032	
225.5	0.80	0.968	4,081	11,355	
212.2	0.90	0.988	3,765	10,802	
202.7	1.00	1.00	3,616	10,487	(*5*)
Pressure = 300 Pounds per Square Inch Absolute					
478.2	0	0	20,866	26,793	(*7*)
446.2	0.10	0.207	17,955	25,050	
414.2	0.20	0.400	15,138	22,715	
383.5	0.30	0.565	12,455	19,770	
355.0	0.40	0.696	10,101	17,392	
329.2	0.50	0.794	8,435	15,595	
307.0	0.60	0.862	7,218	14,285	
287.8	0.70	0.911	6,298	13,238	
270.0	0.80	0.949	5,732	12,385	
254.0	0.90	0.978	5,450	11,602	
241.0	1.00	1.00	5,288	10,995	(*5*)
Pressure = 400 Pounds per Square Inch Gage					
511.8	0.011	0.011	...	(27,380)[b]	
487.0	0.10	0.151	23,720	26,430	
457.0	0.20	0.322	19,586	24,560	
426.5	0.30	0.484	15,758	21,808	
397.3	0.40	0.623	13,095	19,240	
370.5	0.50	0.732	11,035	17,148	
347.0	0.60	0.813	9,508	15,505	
325.4	0.70	0.877	8,390	14,252	
304.8	0.80	0.928	7,585	13,102	
286.0	0.90	0.970	7,041	12,075	
270.3	1.00	1.00	6,900	11,282	(*5*)

[a] $H = 0$ for pure components in ideal gas state at unit fugacity and 0°R.

[b] Critical point. Value in parenthesis is an extrapolated datum.

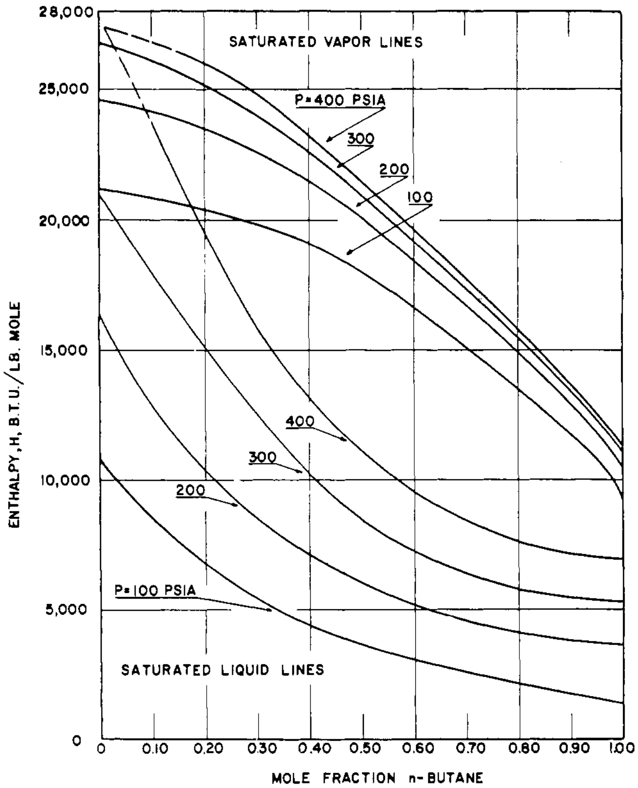

Figure 2. Enthalpy *vs.* composition diagram for *n*-butane–*n*-heptane system

was used to calculate the enthalpies of the saturated and superheated vapors of *n*-butane–*n*-heptane mixtures. The necessary values of H^0 were obtained from (*1*).

With these calculated data and the available information on pure *n*-butane, the term $(\partial H_G/\partial y)_{T,P}$ could be evaluated graphically. The slope data were smoothed by plotting $(y - x)(\partial H_G/\partial y)_{T,P}$ *vs.* y for each pressure. Again, four parabolic shaped curves were obtained. The enthalpy, H_b, of the saturated liquid mixtures can now be calculated by Equation 3. As the enthalpy values at points $x = 0$ and $x = 1$ are known, the H_b *vs.* x curve can be completed by repeating the series of calculations for a number of different compositions in the vapor phase.

RESULTS AND CONCLUSIONS

Using the data for the pure components available in the literature (*5*, *7*), the Benedict-Webb-Rubin equation of state (*2*) and the method of calculation described above, enthalpy *vs.* composition diagrams at 100, 200, 300, and 400 pounds per square inch absolute, were constructed for the system *n*-butane–*n*-heptane. The final results are presented in Table I and in graphical form in Figure 2. The tabulated values are believed to be accurate within ± 3% and are reported to four or five significant figures for consistency. Although these data cannot be used directly to obtain partial enthalpy data, they can be used to check enthalpies of mixtures obtained through the use of partial enthalpies or any other method.

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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^0 = 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, pounds per square inch absolute
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
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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Phase Equilibria in Hydrocarbon Systems

Volumetric Behavior of Cyclohexane

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Little experimental information is available concerning the influence of pressure and temperature upon the molal volume of cyclohexane. Rossini (*12*) reviewed the available information concerning the physical properties of cyclohexane at atmospheric pressure and these data are used as the basis for establishing the purity of the cyclohexane used in this investigation. Geist and Cannon (*4*), as well as Parks and coworkers (*8*), determined a number of the properties of cyclohexane at atmospheric pressure. The critical temperature and pressure were reported by