Enthalpy Changes upon Vaporization in the *n*-Butane–*n*-Decane System

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The enthalpy changes upon vaporization of mixtures of *n*-butane and *n*-decane were experimentally determined by calorimetric measurements at temperatures between 100° and 340° F. The results are presented in graphical and tabular form.

NO DIRECT calorimetric measurements of the enthalpy changes upon vaporization of mixtures of *n*-butane and *n*-decane appear to be available. However, the enthalpy change upon vaporization of *n*-butane has been measured at temperatures between 70° and 250° F. (*13*) and of *n*-decane at temperatures between 160° and 340° F. (*2*). The volumetric behavior of the liquid phase of the *n*-butane–decane system has been investigated at pressures up to 10,000 p.s.i.a. in the temperature interval between 100° and 460° F. (*11*). Recently, the phase behavior of this system was studied at temperatures between 160° and 460° F. (*10*). Furthermore, measurements of the volumetric and phase behavior of *n*-butane (*6*) and of *n*-decane (*9*) have been made throughout the temperature interval between 100° and 460° F. These volumetric and phase behavior measurements serve to delineate the characteristics of the system in sufficient detail to permit resolution of the calorimetric data in terms of the changes in enthalpy between the phases.

As a result of the absence of direct calorimetric measurements of the change in enthalpies upon vaporization in the *n*-butane–*n*-decane system, such measurements were made throughout the greater part of the composition interval at temperatures between 100° and 340° F.

METHODS

In principle, the method involved the evaporation of a liquid phase of *n*-butane and *n*-decane and the withdrawal of the necessary amount of the gas phase to maintain the system under isothermal conditions. The quantity of the gas phase withdrawn was established gravimetrically. The apparatus, which has been described in detail (*5, 12*), involves an isochoric vessel in which a heterogeneous mixture of *n*-butane and *n*-decane was confined. The vessel is mounted within a vacuum jacket, and it is provided with a mechanical agitator and an electric heater. The mixture of *n*-decane and *n*-butane in the gas phase was withdrawn and the quantity determined by weighing bomb techniques. The rate of addition of electrical energy was so controlled as to maintain the system under isothermal conditions. Pressure within the isochoric vessel was measured as a function of time by means of a dead weight, piston-cylinder combination. The contents of the calorimeter were separated from the oil-filled system associated with the pressure-measuring equipment by an aneroid-type steel diaphragm. Mechanical agitation was maintained during the withdrawal process. Appropriate corrections for the energy introduced by conduction and radiation to the isochoric chamber and the viscous dissipation associated with the mechanical agitation were taken into account. Also, small corrections for local variations from isothermal conditions and the small superheat of the vapor were accounted for.

The thermodynamic analysis of this process is similar to that proposed by Osborne and coworkers (*7, 8*) and presented by McKay (*4*). A somewhat more direct analysis of the process associated with the evaporation of a binary hydrocarbon system is available (ADI). For the analysis of the current measurements, the following differential expression was employed:

$$\sum_{k=1}^{k=n} (\bar{H}_{kg} - \bar{H}_{kl})y_k = \left\{\frac{V_g - V_l}{V_g\mathrm{d}m_a + m_g\mathrm{d}V_g + m_l\mathrm{d}V_l}\right\}$$
$$\left\{m_g \sum_{k=1}^{k=n} (\bar{H}_{kg} - \bar{H}_{kl})\mathrm{d}y_k - \underline{q} + (m_gC_{Pg} + m_lC_{Pl} + C_c)\mathrm{d}T - \right.$$
$$\left.\left[m_gT\left(\frac{\partial V_g}{\partial T}\right)_{Py} + m_lT\left(\frac{\partial V_l}{\partial T}\right)_{Px}\right]\mathrm{d}P\right\} \quad (1)$$

Equation 1 assumes a constant total volume for the calorimeter and local equilibrium insofar as the composition of the coexisting phases is concerned. If the small variation in temperature during evaporation is neglected, along with the difference in temperature of the gas and liquid phases, the following integrated form of Equation 1 results:

$$\left\{\sum_{k=1}^{k=2} (\bar{H}_{kg} - \bar{H}_{kl})y_k\right\}^* = \left\{\frac{V_g^* - V_l^*}{V_g^* - \Delta m_a} + \frac{V_g^* - V_l^*}{m_g^*\Delta V_g + m_l^*\Delta V_l}\right\}$$
$$\left\{-\underline{Q} - \left[m_gT\left(\frac{\partial V_g}{\partial T}\right)_{Py} + m_lT\left(\frac{\partial V_l}{\partial T}\right)_{Px}\right]^*\Delta P + \right.$$
$$\left. m_g^* \sum_{k=1}^{k=2} (\bar{H}_{kg} - \bar{H}_{kl})^*\Delta y_k\right\} \quad (2)$$

In some instances, one component may be treated as nonvolatile and, under these circumstances, Equation 1 reduces to:

$$H_{kg}^{\circ} - \bar{H}_{kl} = \left\{\frac{V_g - V_l}{V_g\mathrm{d}m_a + m_g\mathrm{d}V_g + m_l\mathrm{d}V_l}\right\}$$
$$\left\{-\underline{q} - \left[m_gT\left(\frac{\partial V_g}{\partial T}\right)_{Py} + m_lT\left(\frac{\partial V_l}{\partial T}\right)_{Px}\right]\mathrm{d}P\right\} \quad (3)$$

In the resolution of the current measurements, Equation 1 was employed. After a review of each of the quantities entering into the evaluation of the results, a probable uncertainty introduced from each has been set forth in Table I. This information indicates that the over-all uncertainty is probably not more than 0.25% if each of the factors is considered to be independent. The necessary volumetric and phase equilibrium data required in an evaluation of Equation 1 were obtained from earlier volu-

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Table I. Estimated Uncertainties in Calorimetric Measurements

Quantity	Probable Uncertainty, %
Energy added electrically	0.03
Energy added by agitation	0.12
Energy exchange with jacket	0.01
Energy effect of pressure drop	0.04
Change in temperature of liquid and gas phases	0.03
Weight of material withdrawn	0.02
Change in weight of gas phase	0.10
Effects associated with deviation from equilibrium	0.05

metric measurements (*6*, *9-11*). The applicability of these data rests entirely upon the assumption of local equilibrium (*3*).

MATERIALS

The *n*-butane employed in this investigation was obtained from the Phillips Petroleum Co., and it was reported to contain less than 0.0006 mole fraction of impurities. It was repeatedly frozen at liquid nitrogen temperatures and subjected to evacuation over an extended period. Comparisons of the vapor pressure of the *n*-butane so treated indicated good agreement with available data, and there was less than 0.2 p.s.i. variation in vapor pressure with change in quality from 0.1 to 0.8 at 100° F. On the basis of this experience, the sample of *n*-butane is believed to contain less than 0.0013 mole fraction of material other than *n*-butane. The *n*-decane was obtained as research grade from the Phillips Petroleum Co., and it was reported to contain not more than 0.0051 mole fraction of impurities. The specific weight of the deaerated material was 45.338 pounds per cubic foot at 77° F. as compared to a value of 45.337 pounds per cubic foot reported for an air-saturated sample at the same temperature (*1*). A measurement of the refractive index relative to the D-lines of sodium at 77° F. showed a value of 1.40963 which compares favorably with a value of 1.40967 reported for the same temperature (*1*). The probable impurities for both the *n*-butane and the *n*-decane are isomers of their respective hydrocarbons. The presence of small quantities of isomeric impurities does not influence measured values of the enthalpy change upon vaporization to the extent that such impurities affect measurements such as bubble-point or dew-point pressure.

EXPERIMENTAL RESULTS

Experimental measurements were made at five different temperatures between 100° and 340° F. A typical set of data for 220° F. is set forth in Table II. All of the experimental results are available from the American Documentation Institute. Values of the quantity:

$$\sum_{k=1}^{k=2} (\bar{H}_{kg} - \bar{H}_{kl}) y_k$$

are presented in Figure 1 as a function of the weight fraction of *n*-butane in the liquid phase. The standard error of estimate of the smoothed curves drawn through the data was 0.35 B.t.u. per pound. Table III records values of the quantity for even values of weight fraction *n*-butane in the liquid phase. It is possible to compare the measured quantity

$$\sum_{k=1}^{k=2} (\bar{H}_{kg} - \bar{H}_{kl}) y_k$$

with a related quantity, assuming that the partial enthalpy change of each component between the gas and liquid phase is equal to the latent heat of vaporization of the pure

Table II. Typical Experimental Results for 220° F.

Identification	Pressure, P.S.I.A.		Wt. Fraction *n*-Butane		Energy Added, B.t.u./Lb.			$\underline{l}_p^a \Delta P$ B.t.u.	Weight of Material, Lb.				Partial Enthalpy Change[d], B.t.u./Lb.			
										Vaporized[b]						
	P_1	P_2	Gas y_4	Liquid x_4	Electrically	Agitation	Conduction and radiation		Withdrawn	*n*-Butane	*n*-Decane	Calorimeter[c]	$\Delta\bar{H}_{10}$ *n*-Decane	$(\Delta\bar{H}_{10})y_{10}$	$\sum_{k=1}^{k=2} (\Delta\bar{H}_k)y_k$	$\Delta\bar{H}_4$ *n*-Butane
457	29.1	21.4	0.8595	0.048	2.8639	0.1074	−0.0003	0.0563	0.022871	−0.00125	0.00003	1.0669	135.5[e]	19.0	134.6	134.5
449	100.0	95.4	0.9650	0.249	3.9790	0.0420	−0.0037	0.0288	0.030620	0.00050	0.00004	1.3846	134.4	4.7	128.0	127.8
442	128.6	126.2	0.9745	0.364	5.3938	0.0371	0.0004	0.0197	0.042451	0.00049	0.00002	1.2469	133.9	3.4	124.2	124.0
470	169.9	166.6	0.9895	0.554	4.7875	0.0453	−0.0005	0.0325	0.038910	0.00170	0.00006	1.0426	133.4	1.4	118.0	117.8
467	189.0	187.8	0.9895	0.664	3.5429	0.0341	0.0030	0.0111	0.029020	0.00205	0.00003	1.3836	133.1	1.4	114.8	114.6

[a] $\underline{l}_p = [m_g l_{pg} + m_l l_{pl}]$. [b] Change in vapor weight, Δm_g. [c] Calorimeter contents. [d] $\Delta\bar{H}_k = \bar{H}_{kg} - \bar{H}_{kl}$.

[e] Estimated from enthalpy change upon vaporization of pure *n*-decane.

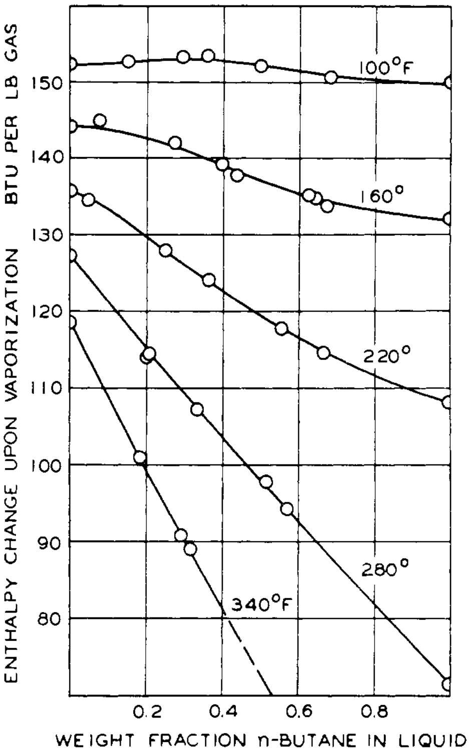

Figure 1. Influence of composition on enthalpy change upon vaporization

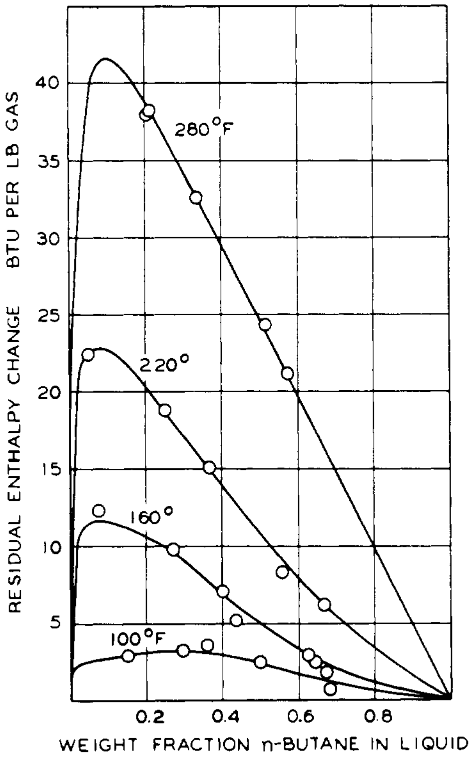

Figure 2. Residual enthalpy change upon vaporization

component at the same temperature. The ordinate of Figure 2 represents the difference between these two quantities. The deviations from such simplifying assumptions increase rapidly with an increase in temperature. In the evaluation of the data shown in Figure 2, the enthalpy change upon vaporization of *n*-butane (*13*) and for *n*-decane (*2*) was obtained from earlier calorimetric measurements.

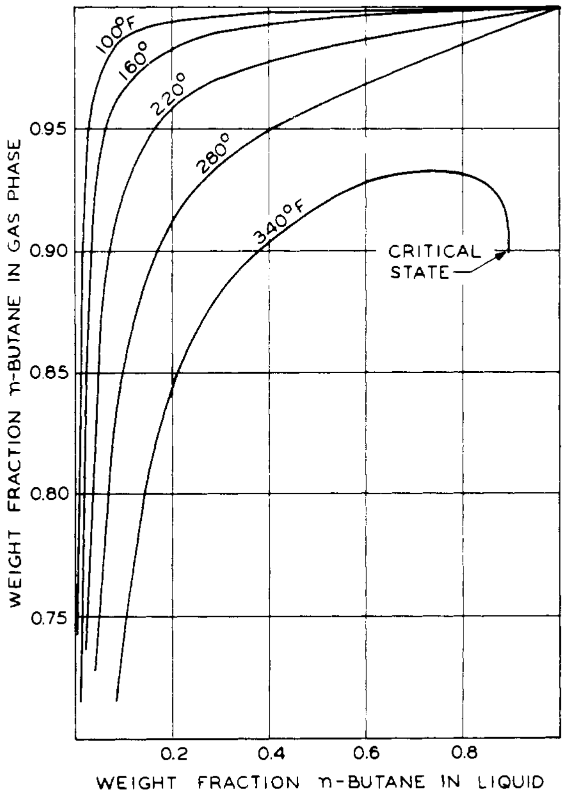

Figure 3. Gas-liquid composition diagram for the *n*-butane–*n*-decane system

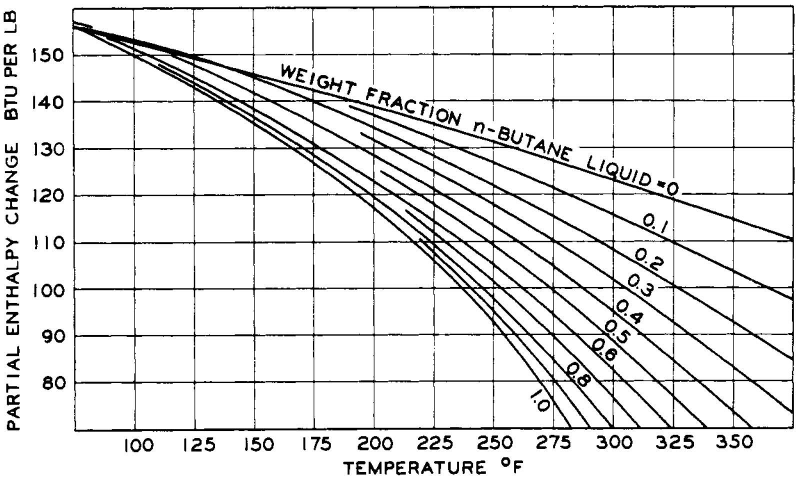

Figure 4. Partial enthalpy change upon vaporization for *n*-butane

Table III. Enthalpy Change upon Vaporization

Wt. Fraction *n*-Butane in Liquid	Temperature, ° F.				
	100	160	220	280	340
0.0	152.4[a]	144.2	135.8	127.3	118.7
0.1	152.6	143.9	133.2	121.2	109.0
0.2	153.0	142.9	129.7	115.1	99.4
0.3	153.2	141.3	126.3	109.3	90.4
0.4	152.9	139.1	122.9	103.7	81.5
0.5	152.2	137.1	119.6	98.2	72.7
0.6	151.5	135.4	116.6	92.8	...
0.7	150.8	134.1	114.0	87.4	...
0.8	150.4	133.3	111.8	82.1	...
0.9	150.1	132.7	110.0	76.7	...
1.0	149.9	132.0	108.3	71.5	...

[a] Values of $\sum_{k=1}^{k=2} (H_{kg} - H_{kl})y_k$ expressed in B.t.u./lb.

Table IV. Partial Enthalpy Change upon Vaporization for n-Butane

Wt. Fraction n-Butane in Liquid	Temperature, ° F.										
	70	100	130	160	190	220	250	280	310	340	370
0.0	156.4[a]	152.4	148.3	144.2	140.1	135.8	131.2	126.4	121.4	116.3	111.1
0.1	156.6	152.6	148.4	143.9	138.6	132.9	126.7	120.1	113.2	105.9	98.5
0.2	157.1	153.0	148.4	143.0	136.0	129.5	122.0	114.0	105.2	96.0	86.2
0.3	157.6	153.2	147.7	141.2	134.0	126.1	117.7	108.3	97.9	86.8	74.8
0.4	157.7	153.0	146.5	139.0	131.2	122.8	113.3	102.7	90.7	78.0	64.3
0.5	157.3	152.2	144.9	136.9	128.6	119.5	109.1	97.2	83.8	69.1	...
0.6	156.6	151.5	143.9	135.2	126.1	116.4	105.0	91.9	77.2	...	...
0.7	156.4	150.7	142.9	134.0	124.4	113.7	101.2	86.6	70.4	...	...
0.8	156.5	150.3	142.4	133.2	123.2	111.5	97.6	81.4	...	...	...
0.9	156.9	150.1	141.9	132.7	122.2	109.7	94.6	76.4	...	...	...
1.0	157.2	149.9	141.4	132.1	121.1	108.3	92.3	71.5	...	...	...

[a] Values of $(\bar{H}_{kg} - \bar{H}_{kl})$ expressed in B.t.u./lb.

Figure 3 shows the weight fraction of n-butane in the gas phase as a function of weight fraction n-butane in the liquid phase for each of the several temperatures. Except for the higher temperatures, the weight fraction of n-decane in the gas phase is small compared with the weight fraction of n-butane. For this reason it is possible to assume that the difference in the partial enthalpy of n-decane in the gas and liquid phases may be approximated by the latent heat of vaporization. On the basis of this assumption, the differences in the partial enthalpy of n-butane can be computed. Such calculations are recorded in Table IV and are depicted in Figure 4.

An error of 10% in the evaluation of the differences in the partial enthalpy of n-decane will yield less than 1% added uncertainty in the evaluation of the differences in the partial enthalpy of n-butane above the experimental uncertainties. For this reason, the values for the differences in partial enthalpy for n-butane recorded in Table IV and shown in Figure 4 probably do not involve over-all uncertainties greater than 2%, except at temperatures above 280° F. Many other diagrams and methods of presenting these data may be employed. However, the tabular information in Tables III and IV may be readily transformed by use of available volumetric data (*6, 9–11*) to yield the internal energy changes upon vaporization (ADI).

ACKNOWLEDGMENT

The senior author was the recipient of a fellowship supported by the Standard Oil Company of California. In addition, the Shell Companies Foundation contributed funds for the continuation of the experimental investigation for a period of two months.

NOMENCLATURE

C_c = heat capacity of calorimeter, B.t.u./° F.
C_p = isobaric heat capacity, B.t.u./lb. ° F.
H = enthalpy, B.t.u./lb.
$\bar{H}_k$ = partial enthalpy of component k, B.t.u./lb.
l_p = latent heat of pressure change, $l_p = -T[(\partial V)/(\partial T)]_{Pn}$ (B.t.u./lb.)/p.s.i. (Table II)
$\underline{l}_p$ = total latent heat of pressure change, B.t.u. (Table II)
m = weight, lb.
n = number of components; weight fraction of a component
P = pressure, p.s.i.a.
$\underline{Q}$ = heat associated with change in state of system, B.t.u.
$\underline{q}$ = total energy added to calorimeter, B.t.u.
T = thermodynamic temperature, ° R.
V = specific volume, cu.ft./lb.
y_k = weight fraction of component k in gas phase
d = differential operator
∂ = partial differential operator
Δ = difference
$\sum$ = summation operator

Subscripts

a = relating to properties of material added to system
g = gas phase
k = component k
l = liquid phase
n = number of components; weight fraction
P = pressure
x = constant composition in liquid phase
y = constant composition in gas phase
1 = initial conditions
2 = final conditions
4 = n-butane
10 = n-decane

Superscripts

o = pure component
* = average value

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RECEIVED for review March 16, 1965. Accepted May 4, 1965. This paper was accepted as a contribution to this journal by R.L. Pigford, Editor of *Ind. Eng. Chem. Fundamentals*. Material supplementary to this article has been deposited as Document No. 8457 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the document number and by remitting $1.25 for photoprints, or $1.25 for 35 mm. microfilm. Advance payment is required. Make checks or money orders payable to: Chief, Photoduplication Service, Library of Congress.