Latent Heat of Vaporization of 1-Butene

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CALORIMETRIC EVALUATION of the latent heat of vaporization of 1-butene does not appear to be available. The volumetric behavior of 1-butene was studied by Olds (5) who also reviewed the earlier experimental information. The data obtained by Olds extended from a temperature of 100° to 340° F. and provided information concerning the specific volume of the bubble-point liquid and the dew-point gas. In addition, Olds evaluated the vapor pressure at temperatures from 100° F. to near the critical state. Rossini (1) has reported critically chosen values of the critical temperature and pressure, as well as several characteristics at 21° and 77° F. As a result of the paucity of directly measured values of the enthalpy change upon vaporization, a calorimetric study of this quantity was made for 1-butene at temperatures from 100° to 220° F. Measurements were not obtained at higher temperatures because of the approach to the critical state where the volumetric behavior exerts a pronounced effect upon the values obtained from the calorimetric measurements.

EXPERIMENTAL MEASUREMENTS

In principle, the methods employed in this investigation are similar to those developed by Osborne and co-workers (6, 7). The apparatus, which has been described in detail (4, 8), involves an isochoric vessel within which a heterogeneous mixture of 1-butene is confined. The vessel was located in an adiabatic vacuum jacket and was provided with an agitator and an electric heater. The 1-butene was withdrawn as a gas and the quantity thus withdrawn determined by gravimetric methods. Electrical energy was added at such a rate as to maintain the system under isothermal conditions. A detailed thermodynamic analysis of the process is available (3).

Under ideal conditions, defined as those existing at constant and spatially uniform temperature and pressure, the enthalpy change upon vaporization is related to the net energy added and to the change in weight of the system by the following expression:

$$l = (H_g - H_l) = \frac{Q_{1,2}^*}{m_1 - m_2} \frac{V_g - V_l}{V_g} \qquad (1)$$

During actual operation, minor variations in pressure and temperature occur in varying degrees and the liquid is superheated to some extent. Deviations from isobaric, isothermal conditions and the superheat of the liquid necessitate a relatively complete analysis (3, 4) of the process. Corrections for the energy added by the agitator located in the liquid phase of the 1-butene and for the thermal transfers to or from the calorimeter, have been described (4) and were included in the term $Q_{1,2}^*$. In the current measurements, the deviations from ideal conditions did not introduce correction to the measured enthalpy change upon vaporization of more than 0.0032 fraction of the total value. The uncertainty of measurement estimated for each of the several variables is set forth in Table I. These values are expressed in terms of the fraction of the measured enthalpy change upon vaporization of 1-butene at the temperature of measurement.

From Equation 1, it is seen that the volumetric correction factor, $(V_g - V_l)/V_g$, is necessary in order to relate the quantity of 1-butene evaporated in the isochoric vessel to that withdrawn. The volumetric behavior of 1-butene reported by Olds (5) was used to establish preliminary values for the volumetric correction factor. This factor decreases to zero at the critical state which exists at 295.6° F. and 583 p.s.i.a. (1).

The internal energy change upon vaporization can be evaluated from the latent heat of vaporization by application of the following equation:

$$E_g - E_l = H_g - H_l - P(V_g - V_l) \qquad (2)$$

The accuracy of the change in internal energy is not materially affected by the uncertainties of the volumetric data in the temperature range between 100° and 220° F. For example, a 1% increase in the specific volume of the gas phase results in a decrease in internal energy upon vaporization of 0.11% at 100° F., or 0.04% at 220° F.

MATERIALS

The 1-butene employed in this investigation was obtained as research grade from Phillips Petroleum Co. and was reported to contain 0.0030 mole fraction of impurities. A chromatographic analysis indicated the sample to contain 0.0015 mole fraction 1,3-butadiene, 0.0014 mole fraction n-butane and 0.0003 mole fraction propane. It should be recognized that the presence of small quantities of impurities does not influence the values determined for the enthalpy change upon vaporization as markedly as such impurities affect the measurement of other thermodynamic properties such as vapor pressure.

EXPERIMENTAL RESULTS

The individual experimental results obtained for 1-butene are recorded in Table II. The volumetric correction factors, shown in Figure 1, are based upon the earlier volumetric data of Olds (5).

The data recorded in Table II takes into account all the perturbations from isobaric, isothermal conditions (3, 4), but are still dependent upon the actual value of the volumetric correction factor. From a combination of the Clapeyron equation and Equation 1, the following expression for the specific volume of the dew-point gas results.

$$V_g = \frac{1}{T(dP''/dT)} \frac{Q_{1,2}^*}{m_1 - m_2} \qquad (3)$$

The values of (dP''/dT) were obtained by application of

Table I. Estimated Uncertainties of Measurement

Quantity	Estd. Uncertainty, %
Energy added electrically	0.03
Energy added by agitation	0.20
Energy exchange between calorimeter and jacket	0.007
Change in temperature of liquid and vapor	0.05
Weight of material withdrawn	0.02
Volumetric correction factor	0.05
Superheat of liquid	0.04

Table II. Experimental Results for 1-Butene

| Identn. | Temp., ° F. | Energy Added, B.t.u. | | | Weight of Material Withdrawn, Lb. | Super-heat of Liquid, ° F. | Specific Vol., Cu. Ft./Lb. | | Vol. Correction Factor | Latent Heat of Vaporization, B.t.u./Lb. |
		Electrically	By agitator	By conduction and radiation			Dew point	Bubble point		
304	99.997	2.8169	0.0494	0.0018	0.018918	0.11	1.5246	0.02821	0.98150	148.85
310	99.996	4.3082	0.0514	0.0000	0.028690	0.15	1.5246	0.02821	0.98150	149.21
301	130.005	2.4472	0.0634	0.0075	0.017488	0.06	0.9982	0.02948	0.97047	139.77
312	130.000	5.7300	0.0412	0.0006	0.040020	0.19	0.9982	0.02948	0.97047	140.05
308	160.002	4.3784	0.0223	−0.0033	0.032298	0.21	0.6756	0.03092	0.95423	130.03
303	190.002	3.8457	0.0421	0.0021	0.030786	0.07	0.4647	0.03260	0.92985	117.53
314	219.996	6.3695	0.0372	−0.0030	0.055237	0.09	0.3222	0.03474	0.89218	103.49
315	220.025	4.9761	0.0290	−0.0053	0.043269	0.09	0.3222	0.03474	0.89218	103.15

residual graphical methods to the vapor pressure values reported by Olds (5). The vapor pressure values employed were found to be in good agreement with the data of Beattie (2). The standard error of estimate in the calculated values of the specific volume at dew point was less than 0.0016 fraction.

To permit a more meaningful evaluation of the deviations of the available data on the latent heat of vaporization of 1-butene, residual methods have been employed. The residual latent heat of vaporization has been related to the temperature by the empirical expression

$$l = l - (29{,}584 - 90.78t)^{1/2} \qquad (4)$$

The available calorimetric data for 1-butene are shown in Figure 2. These data were calculated from the calorimetric measurement by application of Equation 1. The average deviation with and without regard to sign and the standard error of estimate of the several sources of experimental data (1, 5, 9) from the smooth curve drawn through the present experimental points are recorded in Table III. The results of Olds (5) and Weber (9) are based on P-V-T measurements, while the present results were obtained from calorimatric measurements. As indicated in Table III the evaluation of the latent heat of vaporization from the current calorimetric measurements by Method I involved the application of Equation 1 and the volumetric measurements of Olds (5). Method II utilized Equation 3 and employed the vapor pressure measurements and experimental data of Olds (5) concerning the specific volume of the liquid phase only. Critically chosen values of the properties of 1-butene based upon the present investigation are set forth in Table IV. Included are the latent heat of vaporization, the internal energy change upon vaporization, and the specific volume of the dew-point gas evaluated from the data of Olds (5).

On a residual basis, Figure 3 shows the comparison of the directly measured specific volumes of the dew-point gas reported by Olds (5), and data obtained by the application of Equation 3 with the corrections described. The values below 100° F. represent an extrapolation to cover the same range of temperature as shown in Figure 2. The deviation from the directly measured volumetric data of Olds (5) of the computed data are set forth in Table V. Reasonable agreement was obtained between the directly measured and calculated volumetric data. The uncertainty in the evaluation of the volumetric correction factor in Equation 1 is less than 0.1 of the uncertainty involved in the specific volume of the dew-point gas.

ACKNOWLEDGMENT

Table III. Comparison of Results of Several Investigators

| Source | Temp.,[a] ° F. | Average Deviation | | Standard Error of Estimate,[d] B.t.u./lb. |
		Without sign[b] B.t.u./lb.	With sign[c] B.t.u./lb.	
Olds (5)	100–250	1.64	−1.39	1.89
Rossini (1)	21–77	0.82	0.04	0.82
Weber (9)	100–250	2.35	−2.35	2.64
Authors' Method I[e]	100–220	0.19	−0.02	0.21
Method II[f]	100–220	0.26	0.11	0.30

[a] Range.

$$^{b}\left[\sum_{1}^{N}\left| (l_A - l_s)\right|\right]/N$$

$$^{c}\left[\sum_{1}^{N}(l_A - l_s)\right]/N$$

$$^{d}\left\{\left[\sum_{1}^{N}(l_A - l_s)^2\right]/N\right\}^{1/2}$$

$$^{e}l = \left(\frac{Q^{*}_{1,2}}{\Delta m}\right)\left(\frac{V_g - V_l}{V_g}\right)$$

$$^{f}l = \frac{Q^{*}_{1,2}}{\Delta m} - V_l T \frac{dP''}{dT}$$
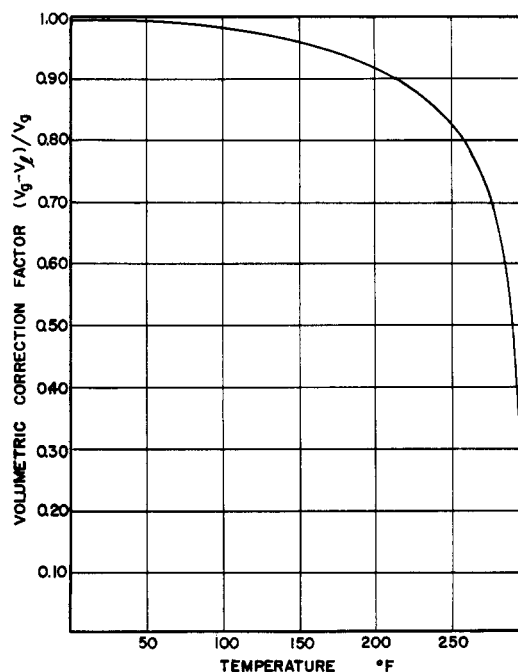
Figure 1. Volumetric correction factor for 1-Butene

Table IV. Critically Chosen Values of Some Properties of 1-Butene

Temp., °F.	Specific Vol. at Dew Point, Cu. Ft./Lb.	Internal Energy Change on Vaporization, B.t.u./Lb.	Latent Heat of Vaporization, B.t.u./Lb.
10	7.503	155.01	171.03
20	6.093	152.72	168.96
30	4.994	150.33	166.78
40	4.128	147.87	164.49
50	3.439	145.33	162.12
60	2.887	142.73	159.67
70	2.439	140.08	157.15
80	2.074	137.36	154.53
90	1.775	134.58	151.83[a]
100	1.525	131.75	149.03
110	1.307	128.94	146.10
120	1.137	125.88	143.07
130	0.9982	122.63	139.92
140	0.8771	119.33	136.64
150	0.7698	116.00	133.22
160	0.6756	112.61	129.65
170	0.5956	109.02	125.88
180	0.5258	105.29	121.91
190	0.4647	101.40	117.72
200	0.4123	97.24	113.25
210	0.3650	92.87	108.45
220	0.3222	88.31	103.34
230	0.2844	83.35	97.77[b]
240	0.2493	78.06	91.68
250	0.2183	72.19	84.93

[a] Lower temperature values based on Rossini (1) data.
[b] Higher temperature values based in part on Olds (5) data.

Table V. Comparisons of Specific Volumes at Dew Point

Temp., °F.	Cu. Ft./Lb. Vol.,[a]	Cu. Ft./Lb. Calorimetric[b]	Deviation,[c] %
99.997	1.5246	1.5303	−0.37
99.996	1.5246	1.5340	−0.62
130.005	0.9982	0.9948	0.34
130.000	0.9982	0.9968	0.14
160.002	0.6756	0.6682	1.10
190.002	0.4647	0.4534	2.43
219.996	0.3222	0.3139	2.58
220.025	0.3222	0.3129	2.89

[a] Measured by Olds (5). [b] Obtained by use of Equation 3 with the corrections described. [c] Deviation = $(V_v - V_c)/V_v$ reported as per cent.

NOMENCLATURE

b = specific gas constant, ft./° R.
d = differential operator
E = internal energy, B.t.u./lb.
H = enthalpy, B.t.u./lb.
l = latent heat of vaporization, B.t.u./lb.
$\bar{l}$ = residual latent heat of vaporization, B.t.u./lb.
m = weight of material, lb.
N = number of experimental observations
P = pressure, p.s.i.a.
P'' = vapor pressure, p.s.i.a.
Q = heat, B.t.u.
$Q^*_{1,2}$ = net energy added to calorimeter under ideal conditions, B.t.u.
T = absolute temperature, ° R.
t = temperature, ° F.
V = specific volume, cu. ft./lb.
$\bar{V}$ = residual specific volume, $[(bT/P) - V]$, cu. ft./lb.
$\sum$ = summation operator
σ = standard error of estimate

Subscripts

A = authors'
C = calorimetric
e = experimental
g = gas phase
l = liquid phase
s = source of data indicated
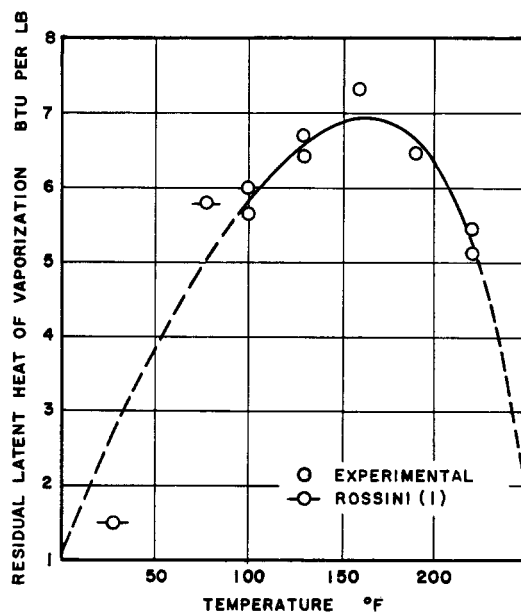V = volumetric
1 = initial state
2 = final state

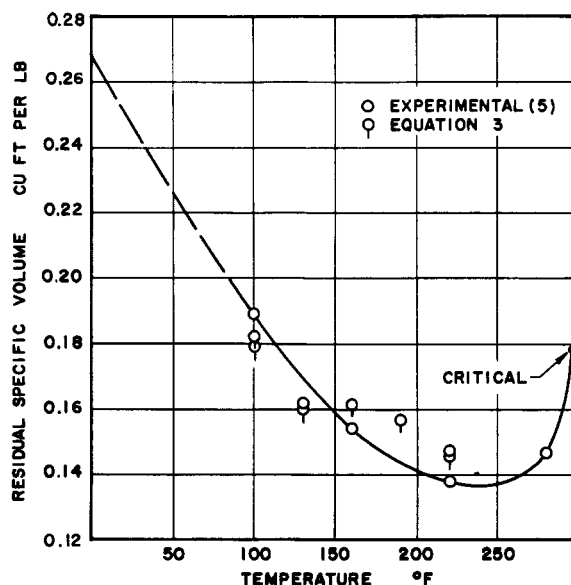Figure 2. Residual latent heat of vaporization

Figure 3. Residual specific volume of the dew-point gas

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