Latent Heat of Vaporization of *n*-Pentane

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THE DIRECT calorimetric evaluation of the latent heat of vaporization of *n*-pentane has been the subject of limited experimental investigation. Griffiths and Awbery (*1*) carried out measurements upon a sample of commercial *n*-pentane at temperatures between −4° and 86° F., and in reporting their data considered the latent heat of vaporization to be a linear function of temperature. Young (*11*) studied the volumetric behavior of the saturated liquid and saturated gas of *n*-pentane, and from measurements of the vapor pressure computed the latent heat of vaporization by application of the Clapeyron equation. More recently (*8*), calorimetric measurements of the latent heat of vaporization were made between 82° and 200° F. However, there existed significant differences between the calorimetric measurements of Griffiths and Awbery (*1*), the values obtained from the volumetric measurements of Young (*11*), and the earlier calorimetric data (*8*). For this reason, a further investigation of the latent heat of vaporization of *n*-pentane seemed desirable, particularly since relatively pure *n*-pentane is now readily available. Rossini (*7*) has made a critical review of the thermal properties of *n*-pentane and has reported values of the latent heat of vaporization near atmospheric pressure.

EXPERIMENTAL METHODS

There is no essential difference in principle of the methods employed in these investigations from those used by Osborne and coworkers (*4, 5*). The apparatus has been described in detail (*3, 9*). It involves a heterogeneous mixture of *n*-pentane confined in an isochoric vessel. This vessel was located in an adiabatic vacuum jacket and provided with an agitator and electric heater. Electrical energy was added to the isochoric vessel, and the quantity of *n*-pentane withdrawn as a gas was determined by gravimetric methods. A small orifice, operating at sonic velocity, maintained a steady discharge rate under isobaric conditions in the calorimeter. Electrical energy was adjusted to maintain nearly isobaric-isothermal conditions. A thermodynamic analysis of the process is available (*2*). The total quantity evaporated during a given operation was determined by weighing bomb techniques (*10*).

Under idealized conditions, the heat of vaporization is related to the electrical energy added and to the change in weight of a system by the following expression.

$$l = (H_g - H_l) = \frac{Q_{2,1}}{m_1 - m_2}\frac{V_g - V_l}{V_g} = \frac{\mathbf{q}/d\theta}{dm/d\theta}\,\frac{V_g - V_l}{V_g} \qquad (1)$$

During an actual evaporation, minor variations in temperature and pressure occur, and there are losses or gains in energy from the calorimeter as a result of small differences in temperature between the surface of the calorimeter itself and the adiabatic jacket. The gas leaving the calorimeter is not exactly in equilibrium with the coexisting liquid which also is superheated slightly as a results of the transport process. Such deviations from isobaric-isothermal conditions yield a relatively complicated expression involving several line integrals describing the actual evaporative process (*2, 3*). It does not appear worthwhile to reproduce this rather complicated expression, but it should be remembered that Equation 1 represents only the idealized process, and minor corrections must be made in accordance with the deviations from isobaric-isothermal evaporative processes.

Correction for the energy added by agitation, and as a result of thermal transfers from the calorimeter to or from the jacket, has been described (*3*). Throughout these measurements the deviations from idealized conditions did not introduce corrections to the measured latent heat of vaporization of more than 0.0015 fraction of the heat of vaporization.

The estimated uncertainty in each of the variables measured is set forth in Table I, expressed in terms of per cent of the measured latent heat of vaporization of *n*-pentane at the average temperature of measurement.

As indicated in Equation 1, it is necessary to evaluate the volumetric correction factor, $(V_g - V_l)/V_g$, in order to relate the quantity of *n*-pentane evaporated to that withdrawn from the isochoric vessel. To accomplish this evaluation, an earlier study (*6*) of the volumetric properties of *n*-pentane was employed. As the critical temperature is approached, the importance of this volumetric correction factor increases rapidly, as is shown in Figure 1. For this reason, calorimetric measurements as described here are not useful for *n*-pentane at temperatures above 300° F. This results from the fact that the uncertainties in the volumetric correction factor are probably the controlling error in the evaluation of the latent heat of vaporization. For this reason, it is probably better to apply the Clapeyron equation to volumetric data to establish the latent heat of vaporization at states near the critical. For example, an uncertainty of 1% in the specific volume of the gas phase at 340° F. introduces an error in the measured latent heat of vaporization of 0.22%.

The internal energy change upon vaporization may be readily calculated from the latent heat of vaporization by application of the familiar expression

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

Uncertainties in the volumetric data do not materially influence the accuracy with which the change in internal energy may be evaluated at temperatures from 100° to 310° F. For example, an uncertainty of 1% in the specific volume of the gas phase results in an over-all error of 0.03% in the internal energy change upon vaporization at

Table I. Estimated Uncertainties of Measurement

Quantity	Probable Uncertainty, %
Energy added electrically	0.03
Energy added by agitation	0.15
Energy exchange between calorimeter and jacket	0.005
Change in temperature of liquid	0.05
Weight of material withdrawn	0.015
Volumetric correction factor	0.05

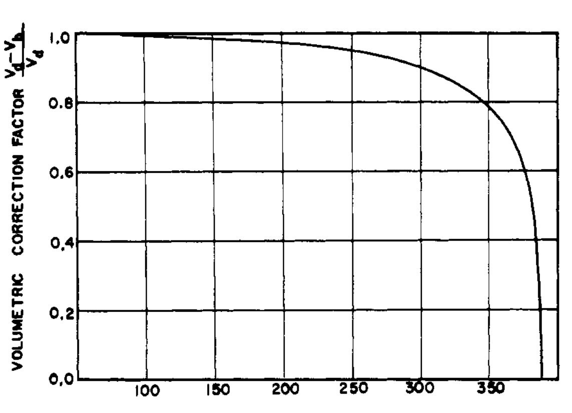

Figure 1. Volumetric correction factor as a function of temperature

310° F. At higher reduced temperatures than covered in this experimental investigation, uncertainties in the specific volume of the dew point gas are reflected in the change in internal energy on vaporization.

MATERIALS

The *n*-pentane employed in this investigation was obtained as research grade from the Phillips Petroleum Co., which reported it to contain not more than 0.0002 mole fraction of impurities. The air-free sample yielded an index of refraction of 1.3549 relative to the *D*-lines of sodium at 77° F., as compared to a value of 1.35472 reported by Rossini (7) for an air-saturated sample at the same temperature. From these indications, it is believed that the sample of *n*-pentane employed contained less than 0.0002 mole fraction of impurities. It should be recognized that the influence of small quantities of impurities is not as great as in many other types of thermodynamic measurements.

EXPERIMENTAL RESULTS

The individual experimental measurements on *n*-pentane are recorded in Table II. Recorded for each measurement are the electrical energy added, the numerous corrections for thermal losses, energy added by the agitator and the like, the weight of material withdrawn, the difference in temperature between the liquid and gas phases, the volumetric correction factor, and the latent heat of vaporization. The values of the latent heat of vaporization set forth in Table II are depicted graphically as a function of temperature in Figure 2. This diagram illustrates the density of experimental measurement and the general trend of the values.

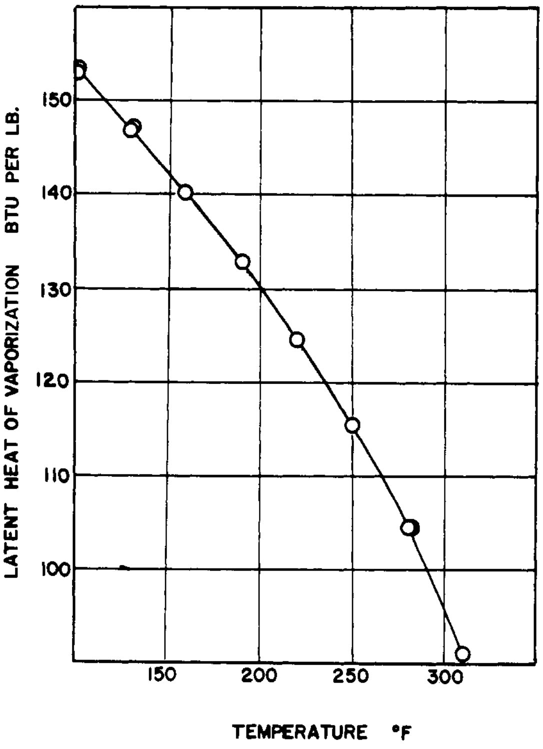

Figure 2. Effect of temperature on heat of vaporization for *n*-pentane

To indicate the deviations of the available data on *n*-pentane more clearly, residual methods have been employed. The following relatively simple analytical expression of the residual values of the latent heat of vaporization from several investigators was used in calculating the data shown in Figure 3:

$$\underset{\sim}{l} = l - (31694.45 - 82.127t)^{1/2} \qquad (3)$$

The full line corresponds to the smoothing of the data obtained from the current investigation. The average deviation, with and without regard to sign, and the standard deviations expressed in B.t.u. per pound for each investigator, are reported in Table III, along with the range of temperatures over which a comparison was possible. No effort was made to include data below 50° F. in these comparisons.

Table IV records for even temperature values, the latent heat of vaporization, and the internal energy change on vaporization of *n*-pentane based on the experimental data which are depicted by the smooth curve in Figure 3. From a consideration of Table I, it appears that the probable uncertainty is not greater than 0.18% at temperatures below 280° F., and perhaps somewhat greater at the higher temperatures.

Table II. Experimental Results for *n*-Pentane

Identification	Temp., ° F.	Energy Added, B.t.u.			Material Withdrawn, Lb.	Superheat of Liquid, ° F.	Vol. Corr. Factor	Latent Heat of Vaporization, B.t.u./Lb.
		Electrically	By agitator	By conduction and radiation				
249	100.000	4.7748	0.0780	0.0000	0.031502	0.30	0.99480	153.37
241	100.887	6.8270	0.0000	−0.0080	0.044377	0.30	0.99480	152.99
239	130.000	3.6519	0.1026	0.0000	0.025358	0.12	0.99144	146.84
259	130.042	3.7889	0.1022	0.0000	0.026276	0.12	0.99144	146.87
243	160.000	4.5944	0.0767	0.0000	0.032906	0.13	0.98574	139.99
244	190.044	5.9814	0.0606	0.0000	0.044511	0.14	0.97805	132.83
245	220.000	4.9357	0.0313	0.0000	0.038574	0.17	0.96614	124.49
246	249.978	7.6785	0.0407	−0.0023	0.063545	0.17	0.94922	115.26
248	280.011	5.6325	0.0206	0.0000	0.050028	0.14	0.92383	104.46
247	280.121	7.2765	0.0266	−0.0016	0.064656	0.14	0.92383	104.40
251	310.000	4.2330	0.0377	0.0047	0.041551	0.04	0.88491	91.07

Table III. Comparison of Experimental Results from Different Investigators

Source	Temp.[a], ° F.	Av. Deviation: With sign[b], B.t.u./lb.	Av. Deviation: Without sign[c], B.t.u./lb.	Standard Error, Est.[d], B.t.u./Lb.
Rossini (*7*)	77[e]	. . .	. . .	. . .
Sage, others (*8*)	100–200	0.72	0.72	0.84
Young (*11*)	104–302	−0.68	0.68	0.73

[a] Range of temperature within which comparison with present measurements was possible.
[b] $[\sum(l_S - l_A)]/N$
[c] $[\sum|(l_S - l_A)|]/N$
[d] $\{[\sum(l_S - l_A)^2]/N\}^{1/2}$
[e] Single value.

ACKNOWLEDGMENT

The experimental work was carried out through the financial support of the California Research Corp. over a period of years. The original calorimetric equipment was made available through the courtesty of the Jet Propulsion Laboratory at the California Institute of Technology, and its original construction was jointly sponsored by Project MX121 of the Air Materiel Command and by the Ordnance Department. R.A. McKay contributed to the revision of the equipment and to the accumulation of some of the measurements. E.R. Boller assisted one of the authors in accumulation of the experimental facts. Virginia Berry contributed to the calculation of the experimental results, and B. Lawson Miller assisted in the preparation of the manuscript.

Table IV. Critically Chosen Values for Latent Heat of Vaporization

Temp., ° F.	Internal Energy Change on Vaporization, B.t.u./Lb.	Latent Heat of Vaporization, B.t.u./Lb.
100	138.75	153.12
110	136.63	151.09
120	134.41	149.00
130	132.14	146.94
140	129.90	144.62
150	127.66	142.35
160	125.33	140.01
170	123.00	137.63
180	120.55	135.18
190	118.19	132.63
200	115.63	130.04
210	112.98	128.34
220	110.42	124.49
230	107.55	121.54
240	104.65	118.46
250	101.73	115.26
260	98.68	111.86
270	95.55	108.28
280	92.35	104.47
290	88.60	100.36
300	84.62	95.95
310	80.32	91.16
320	75.51	86.05[a]
330	70.39	80.42
340	65.13	74.21
350	59.95	67.20
360	54.96	59.06
370	49.21	48.94
380	38.45	34.41
385.9[b]	0	0

[a] Values at this and higher temperatures extrapolated from the data at lower temperatures.
[b] Critical (*7*).

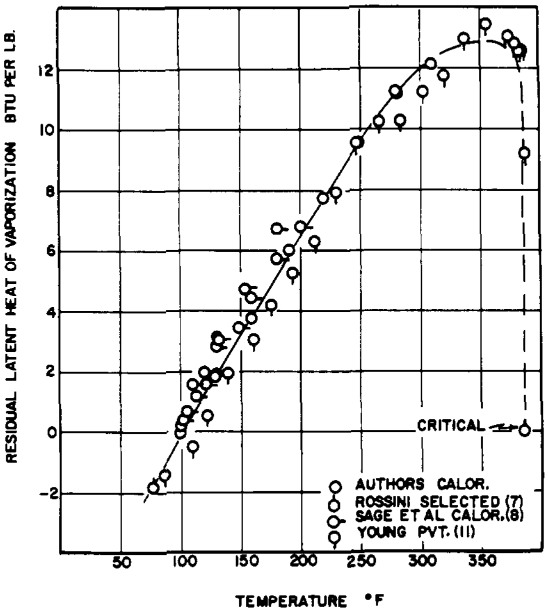

Figure 3. Comparison of heat of vaporization for *n*-pentane from several sources

NOMENCLATURE

E = internal energy, B.t.u./lb.
H = enthalpy, B.t.u./lb.
l = latent heat of vaporization, B.t.u./lb.
$\underset{\sim}{l}$ = residual heat of vaporization, B.t.u./lb.
m = weight of material, lb.
$dm/d\theta$ = weight rate of flow, lb./sec.
N = number of experimental observations
P = pressure, p.s.i.a.
Q = heat, B.t.u.
$q/d\theta$ = thermal flux, B.t.u./sec.
t = temperature, ° F.
V = specific volume, cu. ft./lb.
$\sum$ = summation operator

Subscripts

A = authors'
g = gas phase
l = liquid phase
s = source of data indicated
1 = initial condition
2 = final condition

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RECEIVED for review December 21, 1959. Accepted January 25, 1960.