Latent Heat of Vaporization for *n*-Octane

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THE DIRECT evaluation of the latent heat of vaporization for pure substances by calorimetric techniques is not new. Osborne and coworkers (*6, 7*) contributed much to the techniques of measurement of the heat of vaporization of water and have determined such vaporization data for several hydrocarbons (*5*). *n*-Heptane has been chosen (*2*) as a standard substance for the comparison of calorimeters. The critically chosen data (*2*) for such comparisons have been limited to heat capacity. In the present instance, the measurements of Osborne (*5*) on the heat of vaporization of *n*-heptane are perhaps the best available (*2*) and have been used for comparison purposes in this study. Osborne (*5*) also investigated the heat of vaporization of *n*-octane at 77° F. Further work is reported by Rossini (*8*) at 258° F. and Barrow (*1*) at 213° and 257° F. Young (*11*) studied the volumetric behavior of *n*-octane and measured its vapor pressure. From these data, values of the latent heat of vaporization were computed. Such values were reported (*11*) at temperatures from 248° to above 350° F.

As a result of the lack of a systematic experimental study of the latent heat of vaporization of *n*-octane over a wide range of temperatures, further measurements were undertaken. Data were obtained in this investigation at temperatures between 100° and 340° F. It was not feasible to carry the measurements to a higher temperature because of some indications of thermal rearrangement of *n*-octane above 340° F.

EXPERIMENTAL METHODS

In principle, the methods are very similar to those used by Osborne and coworkers (*6, 7*). The apparatus, which has been described in detail (*9*), involves the calorimeter, *A*, of Figure 1 which is surrounded by the adiabatic jacket, *B*. The space between the calorimeter and the jacket is evacuated to a pressure below 10^{-8} inch of mercury. A small mechanical agitator within the calorimeter at *C* and an electrical heater, *D*, add the requisite energy for the vaporization. The temperature of the evaporating liquid is determined from a resistance thermometer located within the calorimeter while the pressure is determined through the mercury-in-steel U-tube, *E*, by a pressure balance, *F* (*10*). The rate of evaporation is maintained at nearly a constant value for a given temperature by a sharp-edged orifice at *G*.

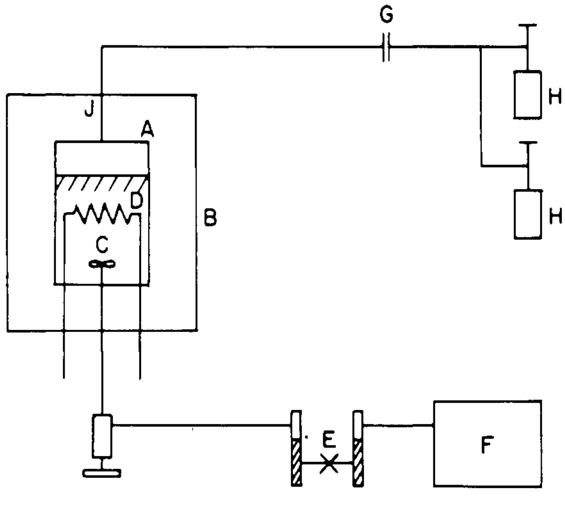

Figure 1. Schematic arrangement of calorimeter

The total quantity evaporated during a given period was determined by weighing bomb techniques (*10*) involving the dual arrangement shown at *H* and *H'* in Figure 1.

The thermodynamic analysis of such a hetrogeneous system of variable weight (*3*) is straightforward but rather lengthy. It has been omitted from this discussion therefore, but is available (*4*). The heat for an idealized isobaric-isothermal evaporation is given by

$$l = (H_g - H_l) = \frac{\underline{Q}_{2,1}}{m_1 - m_2}\,\frac{V_g - V_l}{V_g} = \frac{\mathring{\underline{Q}}}{\mathring{\underline{m}}}\,\frac{V_g - V_l}{V_g} \qquad (1)$$

In any actual calorimetric process, minor variations in temperature and pressure with time occur. Furthermore, there exist some losses or gains in energy from or to the calorimeter as a result of differences in temperature between the calorimeter, *A*, and the jacket, *B*. In addition, the gas leaving the calorimeter at *J* may not be at exactly the temperature at which the evaporation takes place. The small variations in temperature necessitate corrections for the heat capacity of the calorimeter and contents. The thermal losses or gains must also be accounted for. An analysis which includes these details, following conventional calorimetric techniques and the derivation (*4*) of an expression for such a process, leads to

$$\begin{aligned}(H_d - H_b)^* = {} & \frac{1}{\displaystyle\int_{m_1}^{m_2} \frac{V_g + m_g\dfrac{dV_g}{dm} + m_l\dfrac{dV_l}{dm}}{V_g - V_l}\,dm} \times \\ & \left[\int_1^2 - \underline{q} + \int_{m_1}^{m_2} \left\{ m_l\left[l_p - P\left(\frac{\partial V}{\partial P}\right)_T\right]_l + \right.\right. \\ & \left. m_g\left[l_p - P\left(\frac{\partial V}{\partial P}\right)_T\right]_g \right\} \frac{dP}{dm}\,dm + \int_{m_1}^{m_2} \left\{ m_l\left[C_p - P\left(\frac{\partial V}{\partial T}\right)_p\right]_l + \right. \\ & \left. m_g\left[C_p - P\left(\frac{\partial V}{\partial T}\right)_p\right]_g - C_A \right\} \frac{dT}{dm}\,dm + \qquad (2) \\ & \int_{m_1}^{m_2} P\left(m_g\frac{dV_g}{dm} + m_l\frac{dV_l}{dm}\right)dm + \\ & \left. \int_{m_1}^{m_2} \frac{\Big[(H_g - H_d) - (H_l - H_b)\Big]\left(V_g + m_g\dfrac{dV_g}{dm} + m_l\dfrac{dV_l}{dm}\right)}{V_g - V_l}\,dm \right]\end{aligned}$$

The change in internal energy upon vaporization can be evaluated from:

$$E_g - E_l = H_g - H_l - P(V_g - V_l) \qquad (3)$$

Each of the terms in Equation 2 is a function of state of the system and can be readily related to the temperature. The net energy added to the calorimeter can be evaluated in the following way:

$$\underline{Q}_{2,1} = \int_1^2 \underline{q} = \int_1^2 (\mathring{\epsilon} + \mathring{\underline{q}}_s + \mathring{\underline{q}}_{c-r})\,d\Theta \qquad (4)$$

In this analysis the quantities have been considered as heat because they are transferred as a result of temperature difference. Equation 4 can be expanded in terms of constants and values of experimentally measured quantities to yield

$$\underline{Q}_{2,1} = \int_{\theta_1}^{\theta_2} [k_E E_H E_I + k_s + k_{c+r} (T_B - T_A)] \, d\Theta \qquad (5)$$

For the small temperature difference, $T_B - T_A$, the exchange of energy by radiation can be treated as linear with respect to temperature difference rather than varying as the difference in fourth power of the temperatures. Each of the constants in Equation 5 can be determined through appropriate calibrations of the instrument. Both of the correction terms involving the constants k_{c+r} and k_s can be readily maintained at a value less than 0.02 of the total of the value of the first term involving the constant k_E, so it is unnecessary to establish the coefficients of the correction terms with high accuracy. The value of the constant k_E arises directly from the parameters of the calorimeter heater circuit.

The deviation from isothermal conditions was sufficiently small, and the energy losses to or gains from the jacket were controlled within such small limits, that the application of Equations 1 and 2 yielded values which differed by less than 0.002 fraction of the heat of vaporization.

The uncertainty in measurement of the latent heat of vaporization involves several quantities, as is evident from Equations 4 and 5. The estimated uncertainty of measurement of each of the several terms is recorded in Table I. Equation 2 indicates that a substantial amount of volumetric data is required, but, except for the specific volume of the pure component in the gas and liquid phases, each of the other volumetric terms is concerned with the deviation from steady state conditions. These deviations can be maintained to involve less than 0.05° F., so their contribution to the uncertainty in measurement of the latent heat of vaporization is small. It is necessary to evaluate accurately the state of the pure component in the gas phase as it leaves the calorimeter. In the present investigation the measurements of Young (*11*) were used. The volumetric correction factor, $(V_g - V_l)/V_g$, used in determining the latent heat of vaporization, is insensitive to errors in the specific volume of the gas phase in regions removed from the critical state. An uncertainty of 1.0% in the specific volume of the gas phase results in an uncertainty of 0.00017 fraction or less in the latent heat of vaporization. The internal energy change upon vaporization may be readily calculated from the latent heat of vaporization and the pressure-volume-temperature data of Young (*11*). An uncertainty of 1.0% in the specific volume of the gas phase introduces an uncertainty of 0.002 fraction or less in the values of the internal energy change upon vaporization.

There is recorded in Table I the contribution to the overall uncertainty of each of the several terms of Equations 4 and 5. These apply to *n*-octane and somewhat different values probably would exist for other substances. The overall uncertainty of measurement, excluding the specific volume of the gas phase, is less than 0.0022 fraction.

The specific volume of the saturated gas could be evaluated by applying the Clapeyron equation (*11*) to the measured values of the latent heat of vaporization and to the available information concerning the specific volume of the saturated liquid and the slope of the vapor-pressure curve.

Table I. Estimated Uncertainty of Measurement

Quantity	Probable Uncertainty, %
Energy added electrically	0.05
Energy added by agitation	0.2
Energy exchange between calorimeter and jacket	0.006
Change in temperature of liquid	0.08
Weight of material withdrawn	0.02

MATERIALS

The *n*-heptane utilized in determining the performance of the calorimeter was obtained as pure grade from the Phillips Petroleum Co. who reported it to contain not more than 0.01 mole fraction of impurities. This sample of *n*-heptane showed an index of refraction of 1.3851 relative to the *D*-lines of sodium at 77° F., which agrees with a value of 1.3851 reported by Rossini (*8*). The specific weight of the sample at 77° F. was 42.429 pounds per cubic foot as compared to 42.419 pounds per cubic foot reported by Rossini (*8*) for an air-saturated sample at the same temperature. It is believed that the sample of *n*-heptane contained less than 0.0102 mole fraction of materials other than *n*-heptane. The significant amount of impurities present in this sample of *n*-heptane has a markedly smaller effect upon the latent heat of vaporization than might be expected.

The sample of *n*-octane was obtained as research grade from the Phillips Petroleum Co. and was reported to contain less than 0.0017 mole fraction of impurities. The index of refraction of this sample of *n*-octane was 1.3952 relative to the *D*-lines of sodium at 77° F. as compared to 1.39505 at 77° F. reported by Rossini (*8*). The specific weight at 77° F. and atmosperic pressure was 43.614 pounds per cubic foot as compared to 43.604 pounds per cubic foot at the same temperature reported for an air-saturated sample by Rossini (*8*). From these data it appears that the sample of *n*-octane contained less than 0.0017 mole fraction of impurities.

CALIBRATION

To determine whether the calorimeter was free of systematic errors, the latent heat of vaporization of *n*-heptane was measured. Table II presents the experimental data, the values of each of the significant correction terms used in Equations 2 and 4, and the corrected values for the latent heat of vaporization.

The maximum deviation of the present measurements from those of Osborne (*5*) is 0.0009 fraction, so it was concluded that the calorimeter was relatively free of systematic errors because the deviation between the present measurements and those of Osborne was less than the estimated experimental uncertainty of either set of data.

EXPERIMENTAL RESULTS

The experimental results obtained upon *n*-octane and *n*-heptane and the numerical values of each of the several terms appearing in Equations 4 and 5 are recorded in Table II. Figure 2 shows the electric power added to the heater and the temperature of the liquid and the gas phases during a vaporization measurement. The variation in the temperature within each phase was less than 0.02° F. The electric power was manually adjusted at approximately 1000, 1500, and 2900 seconds to maintain substantially a steady rate of discharge from the calorimeter. The total energy added to the calorimeter was established by intregration of the information shown in the lower part of Figure 2. The data in Figure 2 are typical of all of the experimental data obtained for *n*-octane.

Figure 3 portrays the variation in the heat of vaporization and the change in internal energy upon vaporization for *n*-octane over the temperature range. The measurements of Barrow (*1*) and Osborne (*5*) have been included, together with the values reported by Rossini (*8*) and the data based upon the Clapeyron equation reported by Young (*11*). The current measurements are in excellent agreement with the data of Osborne (*5*) at about 77° F., slightly below the values reported by Barrow (*1*) and Rossini (*8*), and someabove the information computed upon the basis of the Clapeyron equation and reported by Young (*11*). The standard deviation of the experimental points recorded in Table II from the smooth curve drawn through these data was 0.37 B.t.u. per pound.

Table II. Experimental Results for *n*-Octane and *n*-Heptane

Identification	Temp., ° F.	Energy Added Electrically, B.t.u.	Energy Added by Agitator, B.t.u.	Energy Added by Conduction and Radiation, B.t.u.	Weight of Material Withdrawn, lb.	Superheat of Liquid, ° F.	Volumetric Correction Factor	Latent Heat of Vaporization, B.t.u./lb.
				n-Octane				
197	100.003	49.496	1.0973	−0.0077	0.033100	0.19	0.99976	152.83
199	130.007	39.447	0.4961	−0.0082	0.026862	0.21	0.99948	148.67
200	130.013	52.846	0.6658	−0.0229	0.036093	0.21	0.99948	148.20
201	160.000	61.007	0.3685	0.0019	0.042721	0.43	0.99899	143.71
202	189.990	43.294	0.7952	0.0268	0.031726	0.15	0.99848	138.84
214	219.992	48.448	0.5121	0.0157	0.036317	0.25	0.99674	134.55
215	219.994	47.738	0.5073	0.0107	0.035797	0.25	0.99674	134.50
218	250.003	45.900	0.5982	−0.0076	0.035835	0.21	0.99465	129.13
219	279.984	41.563	0.3459	0.0243	0.033113	0.32	0.99156	125.73
233	310.002	29.911	0.5227	−0.0060	0.025071	0.16	0.98714	119.88
234	339.995	32.890	0.4280	0.0020	0.028693	0.21	0.98096	114.07
				n-Heptane				
186	100.002	61.601	0.8421	−0.0641	0.040670	...	...	153.81

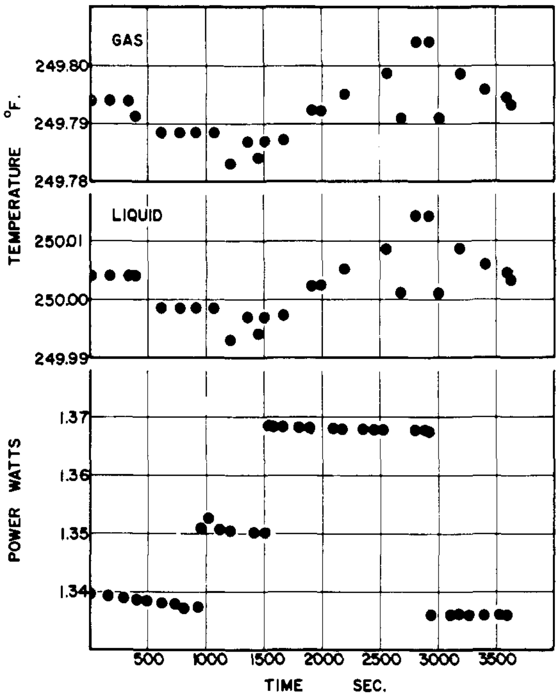

Figure 2. Variation in conditions during vaporization

Table III presents the values of the change in internal energy and the latent heat of vaporization for *n*-octane. The changes in internal energy are less dependable than those for the latent heat of vaporization because of the uncertainties in the specific volume of the gas phase as evaluated from the literature. However, both quantities require a correction which approaches unity at low temperatures but becomes significant at the higher temperatures involving the volumetric behavior of the gas and liquid phases. Considering the information in Table I, it is believed that the values for latent heat of vaporization presented in Table III do not involve uncertainties larger than 0.25%. The uncertainties in the change in internal energy, however, may be large as 0.45%, as a result of added uncertainty in the volumetric data available for *n*-octane.

NOMENCLATURE

C_A = heat capacity of calorimeter, B.t.u./(lb.)(° F.)
C_p = isobaric heat capacity, B.t.u./(lb.)(° F.)
d = differential operator
E = internal energy, B.t.u./lb.

Table III. Latent Heat of Vaporization of *n*-Octane

Temperature, ° F.	Internal Energy Change upon Vaporization, B.t.u./lb.	Latent Heat of Vaporization B.t.u./lb.
100	143.17	152.83
130	138.11	148.23
160	133.16	143.71
190	128.15	139.13
220	123.27	134.55
250	118.25	129.84
280	113.20	125.03
310	107.86	119.84
340	102.29	114.32

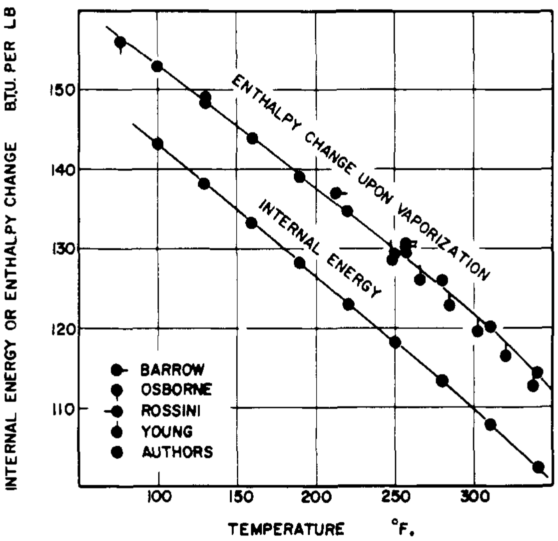

Figure 3. Comparison of heat of vaporization by several investigators and the internal energy change upon vaporization for *n*-octane

E_H = voltage across heater
E_I = voltage across current resistor
$\overset{o}{\epsilon}$ = energy flux, B.t.u./sec.
H = enthalpy, B.t.u./ib.
k = parameter
l = latent heat of vaporization, B.t.u./lb.
l_p = latent heat of pressure change, (B.t.u./lb.)/(lb./sq. ft.)
m = weight of material, lb.
$\overset{o}{m}$ = weight rate of flow, lb./sec.
P = pressure, lb./sq. in.

$\underline{Q}$ = heat, B.t.u.
$\underline{\mathring{Q}}$ = thermal flux, B.t.u./sec.
$\not{q}$ = heat, an infinitesimal, B.t.u.
$\underline{\mathring{q}}$ = net thermal flux, B.t.u./sec.
T = temperature, ° R.
V = specific volume, cu. ft./lb.
θ = time, sec.
∂ = partial differential operator
$\not\int$ = line integral

Subscripts

A = calorimeter
B = jacket
b = bubble point
c = conduction
d = dew point
E = electrical
g = gas phase
H = heater
I = current
l = liquid phase
r = radiation
s = agitation
1 = initial condition
2 = final condition

Superscript

$*$ = average

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Thermodynamic Properties of Perfluoro-2- butyltetrahydrofuran

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THE FLUOROCARBONS show great promise for industrial applications where operating conditions are unusually severe, because of their marked chemical inertness and great thermal stability (*1*). In this class are the fluorinated cyclic ethers, which are stable to temperatures in excess of 400° C. and have electrical insulating properties much superior to hydrocarbon oils (*2*). As an aid in their industrial application, data are needed on their physical and thermal properties. This article presents the thermodynamic properties of an important cyclic ether, perfluoro-2-butyltetrahydrofuran. The values were calculated by applying the rigorous thermodynamic equations to the data on the heat capacities and *P-V-T* relations of this compound. The temperature and pressure ranges covered are from the standard bolining point (102.6° C.) to 300° C. and a pressure of 44 atm.

Since the preparation of the manuscript, a chromatographic analysis of the sample that was studied showed that the sample was a mixture of close boiling isomers of indeterminate amounts. While the perfluoro-2-butyltetrahydrofuran [perfluoro-cyclic oxide ($C_8F_{16}O$)] is undoubtedly a major component, it is only one of several. The boiling range of the sample at atmospheric pressure was approximately 0.1° C.

PROPERTIES OF PERFLUORO-2-BUTYL-TETRAHYDROFURAN

Data on the heat capacities of perfluoro-2-butyltetrahydrofuran at 1 atm. as a function of temperature have been determined (*6, 7*) and are summarized by the following equations for the liquid,

$$C = 50.75 + 0.1752\ T \qquad (1)$$

and for the vapor,

$$C_p = 72.73 + 0.6745\ T \qquad (2)$$

where C and C_p are the heat capacities in calories per gram-mole, ° C., and T is ° K. The over-all accuracy of the data calculated by means of the equations is ±1.1% for the liquid and ±1.3% for the vapor.

The *P-V-T* relations were reported by Throckmorton (*5*). Data were given for the vapor pressure and saturated liquid and vapor specific volumes from 160° C. to the critical point, the specific volume of the liquid from 25° to 110° C., and *P-V-T* relations for the superheated vapor from 160° to 300° C. at pressures from 3.4 to 44 atm. Saturated vapor volumes at 100° and 110° C. and superheated vapor volumes for pressures near 1 atm. were measured by Leverett (*3*). Vapor pressure data between 60° and 100° C. have been reported by the Minnesota Mining and Manufacturing Co. (*4*).

Values of the vapor pressure between 110° and 160° C. are missing. These were estimated by extrapolating the experimental data with the aid of the standard vapor pressure equation, $\log P_{\text{calcd.}} = A/T + B$. The constants, A and B, were calculated using the values of the pressure and