Conclusions. The close accord between the observed and calculated values for the enthalpy of combustion is an indication that the internal strains in the triethylenediamine molecule, whatever its conformation, are relatively small.

ACKNOWLEDGMENT

The authors thank the National Science Foundation for the financial support of this research under a departmental NSFURP grant and the Houdry Process Corporation for the donation of the triethylenediamine used in this work. They are also grateful to Edgar F. Westrum, Jr. of The University of Michigan and Francis E. Condon of The City College of New York for their keen interest and many helpful suggestions.

LITERATURE CITED

(1) Chang, S.S., Westrum, E.F., Jr., *J. Phys. Chem.* **64**, 1551 (1960).
(2) Dunning, W.J., *Phys. Chem. Solids* **18**, 21 (1961).
(3) Guthrie, G.B., McCullough, J.P., *Ibid.*, **18**, 53 (1961).
(4) Hendrickson, J.B., *Chem. Eng. News* **39**, No. 47, 40 (1961).
(5) Hendrickson, J.B., *J. Am. Chem. Soc.* **83**, 4537 (1961).
(6) *Ibid.* **84**, 3355 (1962).
(7) Jaffe, I., M.S. thesis, University of Maryland, College Park, Md., 1958.
(8) Jessup, R.D., "Precise Measurement of Heat of Combustion with a Bomb Calorimeter," *Natl. Bur. Std. (U. S.) Monograph* **7**, p. 12, 1960.
(9) Macfarlane, J.J., Ross, I.G., *J. Chem. Soc.* **1960**, p. 4169.
(10) Pauling, L., "The Nature of the Chemical Bond," 3rd. ed., p. 85, University Press, Ithaca, N. Y., 1960.
(11) Prosen, E.J., in "Experimental Thermochemistry," p. 129, Interscience, New York, 1956.
(12) *Ibid.*, p. 143.
(13) Rossini, F.D., Wagman, D.D., Evans, W.H., Levine, S., Jaffe, I., "Selected Values of Thermodynamic Properties," *Natl. Bur. Std. (U. S.) Circ.* **500**, 1952.
(14) Shepard, M., *Anal. Chem.* **19**, 77 (1947).
(15) Trowbridge, J.C., Westrum, E.F., Jr., *J. Phys. Chem.* **67**, 2381 (1963).
(16) Wada, R., Kishida, E., Tomiie, Y., Suga, H., Seki, S., Nitta, I., *Bull. Chem. Soc. Japan* **33**, 1317 (1960).
(17) Westrum, E.F., Jr., *Phys. Chem. Solids* **18**, 83 (1961).

RECEIVED for review October 10, 1963. Resubmitted November 29, 1963. Accepted December 18, 1963.

Latent Heat of Vaporization of *n*-Hexane

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The enthalpy change upon vaporization of *n*-hexane was experimentally determined by calorimetric measurements at temperatures between 110° and 340° F. The results are presented in tabular and graphical form. Good agreement is indicated with the limited data available.

LIMITED calorimetric measurements of the latent heat of vaporization of *n*-hexane over a range of temperatures appear to be available. Waddington and Douslin (*10*) measured values of the latent heat of vaporization at temperatures between 77° and 156° F. Both Young (*12*) and Kay (*2*) measured the vapor pressure and the specific weight of the saturated liquid and gas from 140° to 455° F. Values of vapor pressure and latent heat of vaporization are also available from a recent correlation (*1*). Stewart and coworkers (*9*) reported values of the specific weight of the liquid. Thermodynamic properties of *n*-hexane have been reported by Weber (*11*). In the latter work the latent heats of vaporization of Waddington and Douslin (*10*) were used at temperatures between 77° and 156° F. and the Clapeyron equation was employed at other temperatures. The present investigation involves calorimetric measurements of the latent heat of vaporization of *n*-hexane at temperatures between 100° and 340° F.

METHODS

The experimental apparatus employed in this investigation has been described in some detail (*4, 7*). Principles and methods are similar to those developed by Osborne and coworkers (*5, 6*). An isochoric vessel containing a heterogeneous mixture of *n*-hexane was located within an adiabatic vacuum jacket. A mechanical agitator and electrical heater were provided within the isochoric vessel. The *n*-hexane was withdrawn as a gas and the quantity withdrawn determined by conventional weighing bomb techniques (*8*). A detailed thermodynamic analysis of the process is available (*3, 4*) which permitted the minor digressions from isobaric, isothermal conditions during the evaporation to be taken into account. Corrections were applied for the mechanical energy added to the system as a result of the agitation of the liquid phase and the minor thermal transfers between the calorimeter and the nearly adiabatic jacket. The fact that the gas phase was withdrawn from the isochoric chamber at a slightly different temperature than the evaporating liquid temperature was also taken into account. It is beyond the scope of this discussion to review the thermodynamic analysis (*3, 4*) of the process.

The latent heat of vaporization under idealized isobaric, isothermal conditions is given by the following expression:

$$l = (H_g - H_l) = [Q]_{T,P}\left(\frac{V_g - V_l}{V_g}\right) \qquad (1)$$

where the quantity $[Q]_{T,P}$ represents the net energy required per unit weight of material withdrawn from the isochoric calorimeter under isothermal conditions.

In the current measurements, the deviations from idealized isobaric, isothermal conditions did not introduce corrections to the latent heat of vaporization of more than 0.3%. The energy associated with the agitation was less than 1.3% of the electrical energy input at all states investigated. The estimated uncertainties of the several variables associated with measurements of the enthalpy change upon vaporization of *n*-hexane are set forth in Table I. The information in Table I is presented in terms of the fraction of the measured enthalpy change upon vaporization of *n*-hexane at a temperature of 280° F.

Equation 1 indicates that a knowledge of the volumetric behavior of the coexisting liquid and gas phases is necessary even under idealized conditions in order to relate the measured energy input $[Q]_{T,P}$ to the latent heat of vaporization l. It appeared desirable to eliminate the use of directly measured specific volumes of the saturated gas since these are subject to uncertainties as the result of absorption.

By combining the Clapeyron equation with Equation 1, the latent heat of vaporization of *n*-hexane may be evaluated in the following way:

$$l = [Q]_{T,P} - V_l T\,(\mathrm{d}P''/\mathrm{d}T) \qquad (2)$$

In the application of Equation 2 the volumetric measurements of Stewart (*9*) were employed to establish the specific volume of the saturated liquid as a function of temperature. The vapor pressure measurements reported by Young (*12*) as well as values submited in a critical review (*1*) were employed in the present measurements to evaluate the quantity $\mathrm{d}P''/\mathrm{d}T$. Residual techniques were employed in these operations and it is believed that the derivative $\mathrm{d}P''/\mathrm{d}T$ does not involve uncertainties of more than 0.2% from the measured values of vapor pressure reported (*1*). The specific volume of the dew-point gas was evaluated from the current measurements of the latent heat of vaporization by application of the Clapeyron equation:

$$V_g = V_l + \frac{l}{T(\mathrm{d}P''/\mathrm{d}T)} \qquad (3)$$

MATERIALS

The *n*-hexane utilized in this experimental investigation was obtained as research grade from the Phillips Petroleum Co. which reported it to contain not more than 0.0004 mole fraction of impurities. The specific weight of the material was 40.881 pounds per cubic foot at 77° F. which compared with a value of 40.878 pounds per cubic foot reported (*1*) for an air-saturated sample at the same temperature. Measurements of the index of refraction relative to the *D*-lines of sodium at 77° F. indicated an index of 1.3723 as compared to a value of 1.37226 reported (*1*) for an air-saturated sample at the same temperatures. A review of these data leads the authors to believe that the sample of *n*-hexane employed had a purity of at least 0.9996 mole fraction. The probable impurities are isomers of this hydrocarbon. It should be recognized that traces of impurities in calorimetric measurements of the latent heat of vaporization do not introduce uncertainties of the same magnitude as similar quantities of impurities would in the case of volumetric or vapor pressure measurements.

Table I. Estimated Uncertainties of Measurement

Quantity	Probable Uncertainty, Per Cent
Energy added electrically	0.03
Energy added by agitation	0.15
Energy exchange between calorimeter and jacket	0.01
Change in temperature of liquid and vapor	0.03
Weight of material withdrawn	0.02
Volumetric correction factor	0.05
Superheat of liquid	0.04

EXPERIMENTAL RESULTS

The results of the experimental measurements upon *n*-hexane are reported in Table II. It should be recognized that an error of 1% in the slope of the vapor pressure curve which is recorded in Table II introduces less than 0.08% uncertainty in the measured enthalpy change at the highest temperature recorded. The specific volume at dew point was calculated by application of Equation 3 and the and the compressibility factor recorded was evaluated, employing a molecular weight of *n*-hexane of 86.172 and a value of the universal gas constant of R = 10.73147 (p.s.i.) (cu. ft.)/(lb.-mole)(° R.). Values of the latent heat of vaporization recorded in Table II are presented in Figure 1. Critically chosen values (*1*) have been included for comparison.

In order to permit a more precise comparison of the present measurements with data reported by other investigators, residual techniques were employed. In the present instance, the residual latent heat of vaporization has been calculated by the following expression:

$$\mathbf{l} = l - (173.00 - 0.22t) \qquad (4)$$

Values of the residual latent heat of vaporization obtained in the present measurements are set forth in Figure 2 along with critically chosen values (*1*) and the experimental measurements of Waddington and Douslin (*10*). The "standard error of estimate" of the current measurements of the latent heat of vaporization from the smooth curve shown in Figure 2 was 0.21 B.t.u. per pound. This measure of uncertainty is defined by:

$$\sigma = \left[\left\{\sum_{1}^{N} (x_e - x_s)^2\right\}/(N-1)\right]^{1/2} \qquad (5)$$

In equation 5, σ is the standard error of estimate, x_e the experimental value, x_s the smooth value, and N the number of experimental points. The corresponding measure of uncertainty of the experimental work of Waddington and Douslin (*10*) was 0.58 B.t.u. per pound. Smooth values of the latent heat of vaporization are reported as a function of temperature in Table III. The internal energy change upon vaporization and the specific volume at dew point are presented also.

The compressibility factor for the dew-point or saturated gas as a function of pressure is shown in Figure 3. The

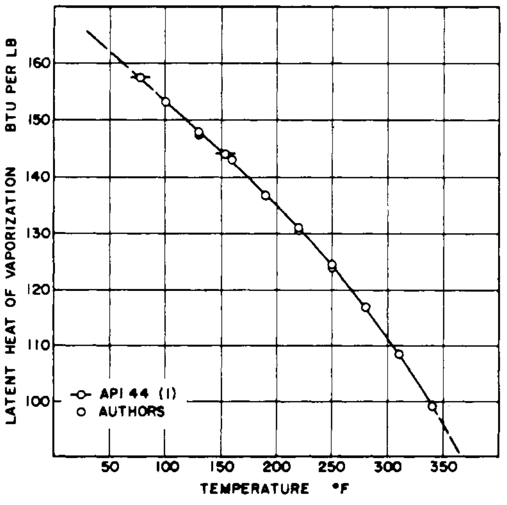

Figure 1. Latent heat of vaporization for *n*-hexane

Table II. Experimental Results for n-Hexane

Identification	Temp., ° F.	Press.[a] P.S.I.A.	Energy Added: Electrically, B.t.u.	Energy Added: By agitation, B.t.u.	Energy Added: By conduction and radiation, B.t.u.	Weight of Material Withdrawn, Lb.	Superheat of Liquid, ° F.	dP''/dT P.S.I./° R.	Specific Volume: Dew point cu. ft./lb.	Specific Volume: Bubble point[a] cu. ft./lb.	Compressibility Factor	Volumetric Correction Factor[b]	Latent Heat of Vaporization B.t.u./Lb.
382	100	4.95	5.3126	0.0887	−0.0017	0.035224	0.15	0.1077	13.75	0.02493	0.9764	0.99819	153.08
384	130	9.16	5.3946	0.0773	−0.0023	0.036916	0.17	0.1765	7.696	0.02553	0.9600	0.99669	147.74
386	130	9.16	5.3818	0.0828	−0.0016	0.037931	0.19	0.1765	7.682	0.02553	0.9582	0.99668	147.46
396	160	15.82	5.5704	0.0830	−0.0014	0.039344	0.16	0.2728	4.594	0.02618	0.9418	0.99430	142.91
388	190	25.76	5.2113	0.0764	0.0047	0.038383	0.12	0.3948	2.906	0.02691	0.9253	0.99074	136.67
389	190	25.76	3.7980	0.0556	0.0003	0.027936	0.11	0.3948	2.908	0.02691	0.9257	0.99075	136.73
390	220	39.87	2.4040	0.0491	−0.0029	0.018468	0.10	0.5521	1.910	0.02775	0.8996	0.98544	130.70
391	220	39.87	3.9475	0.0804	0.0090	0.030386	0.09	0.5521	1.914	0.02775	0.9015	0.98547	130.97
393	250	59.24	3.4772	0.0413	−0.0007	0.027772	0.12	0.7450	1.295	0.02868	0.8683	0.97784	123.93
398	250	59.24	5.5968	0.0570	−0.0032	0.044467	0.12	0.7450	1.299	0.02868	0.8710	0.97791	124.33
400	280	84.93	6.4212	0.0435	−0.0030	0.053526	0.15	0.9755	0.9047	0.02977	0.8341	0.96706	116.83
402	310	118.2	4.0326	0.0456	0.0010	0.035810	0.07	1.2484	0.6408	0.03103	0.7902	0.95162	108.43
405	340	160.3	5.3351	0.0404	−0.0016	0.050426	0.06	1.5681	0.4594	0.03256	0.7395	0.92904	99.05

[a] Stewart et al (9). [b] Not used directly in evaluation of latent heat of vaporization.

Table III. Critically Chosen Values of Some Properties of n-Hexane

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.
50	42.90	150.30	161.90
60	33.73	148.35	160.15
70	26.45	146.36	158.37
80	21.09	144.41	156.60
90	16.80[a]	142.44	154.80[a]
100	13.71	140.55	153.08
110	11.21	138.61	151.31
120	9.290	136.70	149.56
130	7.699	134.78	147.79
140	6.474	132.88	146.03
150	5.460	130.99	144.27
160	4.605	129.11	142.51
170	3.922	127.21	140.73
180	3.348	125.30	138.90
190	2.902	123.29	137.00
200	2.495	121.23	135.02
210	2.187	119.10	132.96
220	1.913	116.94	130.85
230	1.684	114.73	128.67
240	1.488	112.48	126.43
250	1.299	110.20	124.13
260	1.152	107.87	121.76
270	1.019	105.48	119.31
280	0.9046	103.03	116.78
290	0.8109	100.50	114.14
300	0.7109	97.87	111.37
310	0.6406	95.10	108.43
320	0.5742	92.25	105.40
330	0.5102	89.37	102.28
340	0.4594	86.39	99.05
350	0.4139	83.34	95.73

[a] Values at this and lower temperatures extrapolated from data at higher temperatures.

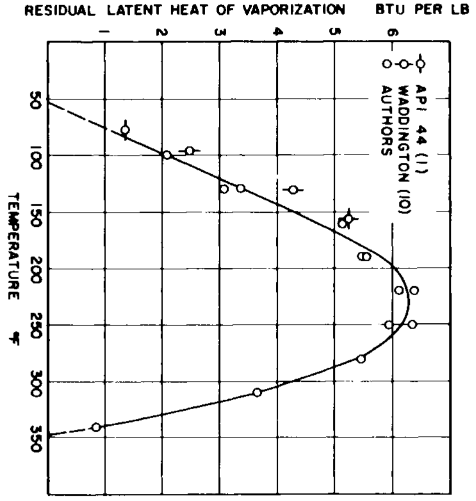

Figure 2 . Residual latent heat of vaporization

standard error of estimate of the experimental values of the compressibility factor of the dew-point gas recorded in Table II from the smooth curve shown in Figure 3 is 0.0017. As a matter of interest, the compressibility factor calculated from the directly measured values of the specific volume of the dew-point gas as reported by Young (*12*) has been included for comparison. These data indicate a standard error of estimate of the experimental values reported by Young (*12*) of 0.0072 from the smooth curve. Likewise, the values of the compressibility factor calculated from the more recent compilation of the thermodynamic properties of n-hexane by Weber (*11*) have been included. It is understood that the specific volumes of the dew-point gas reported by Weber (*11*) were at least in part based on the data of Young (*12*). The standard error of estimate of the values tabulated by Weber from the smooth curve shown in Figure 3 is 0.0063.

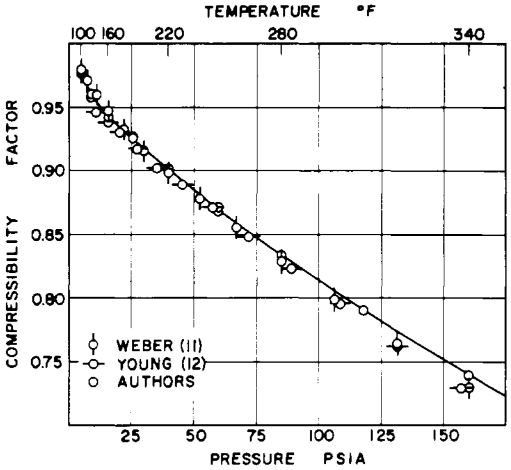

Figure 3. Compressibility factor for dew-point gas

ACKNOWLEDGMENT

The experimental work reported was carried out with the financial support of the Standard Oil Company of California which made available a fellowship to John Huisman. The calorimetric equipment was originally constructed through the support of the Jet Propulsion Laboratory of this Institute by Project MX-121 of the Air Materiel Command and by the Ordnance Department. Viginia Berry contributed to the calculation of the experimental results and B. Lawson Miller to the preparation of the manuscript.

NOMENCLATURE

d = differential operator
l = latent heat of vaporization, B.t.u./lb.
$\boldsymbol{l}$ = residual latent heat of vaporization, B.t.u./lb.
H = enthalpy, B.t.u./lb.
P'' = vapor pressure, p.s.i.a.
$[Q]$ = heat added per unit weight of material withdrawn under idealized conditions, B.t.u./lb.
T = thermodynamic temperature, ° R.
t = temperature, ° F.
V = specific volume, cu. ft./lb.

Subscripts

g = gas phase
l = liquid phase
P = pressure
T = temperature

LITERATURE CITED

(1) American Petroleum Research Project 44, Petrol. Res. Lab., Carnegie Inst. Technol., Pittsburgh, Pa., "Selected Values of Properties of Hydrocarbons and Related Compounds."
(2) Kay, W.B., *J. Am. Chem. Soc.* **68**, 1336 (1946).
(3) McKay, R.A., Sage, B.H., Doc. No. **6072**, Am. Doc. Inst., Washington, D.C., 1959.
(4) McKay, R.A., Sage, B.H., J. CHEM. ENG. DATA **5**, 21 (1960).
(5) Osborne, N.S., Stimson, H.F., Fiock, E.F., *Bur. Std. J. Res.* **5**, 411 (1930).
(6) Osborne, N.S., Stimson, H.F., Ginnings, D.C., *Ibid.*, **23**, 197 (1939).
(7) Sage, B.H., Hough, E.W., *Anal. Chem.* **22**, 1304 (1950).
(8) Sage, B.H., Lacey, W.N., *Trans. Am. Inst. Mining Met. Engrs.* **136**, 136 (1940).
(9) Stewart, D.E., Sage, B.H., Lacey, W.N., *Ind. Eng. Chem.* **46**, 2529 (1954).
(10) Waddington, Guy, Douslin, D.R., *J. Am. Chem. Soc.*, **69**, 2275 (1947).
(11) Weber, J.H., *A.I.Ch.E.J.* **2**, 514 (1956).
(12) Young, Sidney, *Sci. Proc. Roy. Dublin Soc.* **12**, 374 (1909–10).

RECEIVED for review September 23, 1963. Accepted December 30, 1963.