Table IX. Heats and Free Energies at 25° C. of Decomposition Reactions of the Type $XMH_4(c) \longrightarrow XH(c) + M(c) + 3/2H_2(g)$

Complex Hydride	ΔH^0, Kcal./Mole	ΔF^0, Kcal./Mole
$LiAlH_4$	+6.8	−3.9
$NaAlH_4$	+13.5	+3.0
$KAlH_4$	+26.0	+14.9
$CsAlH_4$	+27.5	+16.5
$LiBH_4$	+24.70	+14.0
$NaBH_4$	+32.14	+21.6
KBH_4	+40.88	+29.8

free energies, the aluminum hydrides are considerably (15 to 18 kcal. at 25° C.) less stable toward this type of decomposition than the corresponding borohydrides. Of the seven complex hydrides, lithium aluminum hydride is the only one for which the ΔF^0 is negative in sign. It is therefore the only hydride which is thermodynamically unstable at 25° C.

Lithium aluminum hydride is about 7 kcal. less stable thermodynamically than sodium aluminum hydride, which in turn is about 12 kcal. less stable than potassium aluminum hydride. Isothermal rate-of-decomposition data place the three compounds in the same order of increasing stability. This stepwise increase in stability from the lithium to the sodium to the potassium compound is also exhibited by the borohydrides. Finally, the decomposition reactions for all seven hydrides are endothermic, hence these reactions cannot become "runaway."

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LITERATURE CITED

(1) Coughlin, J.P., *J. Phys. Chem.* **62**, 419 (1958).
(2) Davis, W.D., Mason, L.S., Stegeman, G., *J. Am. Chem. Soc.* **71**, 2775 (1949).
(3) Douglas, T.B., Harman, A.W., *J. Res. Natl. Bur. Std.* **60**, 117 (1958).
(4) Finke, H.L., Gross, M.E., Waddington, G., Huffman, H.M., *J. Am. Chem. Soc.* **76**, 333 (1954).
(5) Gunn, S.R., Green, L.G., *Ibid.*, **80**, 4782 (1958).
(6) Herold, A., *Compt. rend.* **228**, 686 (1949).
(7) Hurd, D.T., "An Introduction to the Chemistry of the Hydrides," Wiley, New York, 1952.
(8) Johnson, W.H., Schumm, R.H., Wilson, I.H., Prosen, E.J., *J. Res. Natl. Bur. Std.* **65A**, 97 (1961).
(9) Kelley, K.K., King, E.G., "Entropies of the Elements and Inorganic Compounds," Bull. **592**, Bureau of Mines (1961).
(10) Klemm, W., *Z. Anorg. Allgem. Chem.* **249**, 23 (1942).
(11) Nat. Bur. Std., "Selected Values of Chemical Thermodynamic Properties," Circ. **500**, (1952).
(12) Shomate, C.H., Huffman, E.H., *J. Am. Chem. Soc.* **65**, 1625 (1943).
(13) Wrewsky, M.S., Kaigorodoff, A.I., *Z. physik. Chem.* **112**, 83 (1924).

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Latent Heat of Vaporization of *n*-Decane

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The latent heat of vaporization of *n*-decane was determined by calorimetric measurements at temperatures between 160° and 340° F. The results are presented in graphical and tabular form by application of the Clapeyron equation. The specific volume of the dew-point gas was evaluated throughout the above-indicated range of temperature. The current measurements are in good agreement with earlier volumetric data and critically chosen values of the latent heat of vaporization which have been reported.

DIRECT CALORIMETRIC MEASUREMENTS of the latent heat of vaporization of *n*-decane over a range of temperatures do not appear to be available. Rossini (*6*) reports values at 77° and 345° F. The volumetric behavior of the liquid phase of *n*-decane has been studied by Reamer and others (*5*). Likewise, the vapor pressure has been determined over a wide range of temperatures by Young (*9*), Reamer (*5*), and Willingham and coworkers (*8*). The volumetric data extend from a temperature of 40° to 460° F., and the vapor pressures cover a similar range of temperatures. Rossini (*6*) has also recorded several critically chosen values of the properties of *n*-decane at 77° F. As a result of the absence of directly measured values of the latent heat of vaporization of this paraffin hydrocarbon over a wide range of temperatures, the current investigation was initiated. This study involves measurements of the latent heat of vaporization of *n*-decane at temperatures between 160° and 340° F.

METHODS

Methods similar to those developed by Osborne and coworkers (*3, 4*) were employed. The apparatus has been described in detail (*2, 7*). It involves an isochoric vessel in which a heterogeneous mixture of *n*-decane was confined. The vessel, located within a vacuum jacket, is provided with an agitator and an electric heater. The *n*-decane was withdrawn as a gas and the quantity withdrawn determined by weighing bomb techniques. Electrical energy was added at such a rate as to maintain the system under isobaric, isothermal conditions. A detailed thermodynamic analysis of the process is available (*1*).

Under isobaric, isothermal conditions the enthalpy change upon vaporization is related to the net energy added to accomplish the change in weight in the isochoric system by the following idealized expression:

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

Actually minor variations in temperature and pressure occur in varying degrees, and the liquid is superheated to a limited extent. Such deviations from isobaric, isothermal conditions and the superheat of the liquid necessitate a rather complete thermodynamic analysis (*1, 2*) of the process. Corrections for the mechanical energy added by the agitator located in the liquid phase of the *n*-decane and for the thermal transfers between the calorimeter and the essentially adiabatic jacket have been described (*2*). In the current measurements, the maximum deviations from ideal isobaric, isothermal conditions did not introduce corrections to the measured enthalpy change upon vaporization of more than 0.0054 fraction of the total change. The estimated uncertainty in each of the several variables associated with these measurements is set forth in Table I. These values are expressed in terms of the fraction of the measured enthalpy change upon vaporization of *n*-decane at a temperature of 340° F. Inspection of Equation 1 indicates that the volumetric correction factor, $(V_g - V_l)/V_g$, is necessary in order to relate the quantity of *n*-decane evaporated to that withdrawn. Experimental information concerning the volumetric behavior of the dew-point gas of *n*-decane is not available.

Table I. Estimated Uncertainties of Measurement

Quantity	Probable Uncertainty, %
Energy added electrically	0.03
Energy added by agitation	0.18
Energy exchange between calorimeter and jacket	0.008
Change in temperature of liquid and vapor	0.05
Weight of material withdrawn	0.02
Volumetric correction factor	0.03
Superheat of liquid	0.07

A combination of the Clapeyron equation with Equation 1 results in the following expression for the latent heat of vaporization of *n*-decane:

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

It should be recognized that the quantity $[Q]_{T,P}$ in Equation 2 represents the thermal transfer required per unit weight of material withdrawn from the isochoric calorimeter under idealized conditions. It is necessary to apply the minor corrections that have been described (*2*) to account for the superheat of the liquid and the deviation from isobaric, isothermal conditions. As a result of the absence of volumetric data, the specific volume of the dew-point gas was evaluated from:

$$V_g = \left(\frac{Q^*_{1,2}}{m_1 - m_2}\right) \left(\frac{1}{T(\mathrm{d}P''/\mathrm{d}T)}\right) \qquad (3)$$

MATERIALS

The *n*-decane employed was obtained as research grade from the Phillips Petroleum Co. and was reported to contain not more than 0.0066 mole fraction of impurities. The specific weight of the material was 45.339 pounds per cubic foot at 77° F. as compared to 45.337 pounds per cubic foot reported by Rossini (*6*) for an air-saturated sample at the same temperature. The index of refraction relative to the D-lines of sodium at 77° F. was found to be 1.4097 as compared to a value of 1.40967 reported for an air-saturated sample at the same temperature (*6*). Review of these data leads the authors to believe that the sample of *n*-decane did not contain more than 0.0066 mole fraction of material other than *n*-decane. The probably impurities are the isomers of this hydrocarbon. The presence of small quantities of material other than *n*-decane does not influence the values of the latent heat of vaporization to the extent that such impurities might affect measurements of other properties such as vapor pressure.

EXPERIMENTAL RESULTS

The experimental results of the measurements upon *n*-decane are reported in Table II. Values of the slope

Table II. Experimental Results for *n*-Decane

No.	Temp., ° F.	Pressure[a], P.S.I.A.	Energy Added, B.t.u.: Electric	Energy Added, B.t.u.: Agitation	Energy Added, B.t.u.: Conduction and Radiation	Wt. Withdrawn Lb.	Superheat of Liquid, ° F.	$\mathrm{d}P''/\mathrm{d}T$ p.s.i./° R.	Specific Volume, Cu. Ft./Lb.: Dew point	Specific Volume, Cu. Ft./Lb.: Bubble point[b]	Vol. Correction Factor[c]	Latent Heat of Vaporization, B.t.u./Lb.
367	160	0.40	3.8328	0.1248	−0.0027	0.027447	0.12	0.01060	116.4	0.02321	0.99980	144.12
368	160	0.40	3.3375	0.1092	−0.0028	0.023855	0.12	0.01060	116.4	0.02321	0.99980	144.39
371	190	0.84	4.7201	0.0828	0.0022	0.034306	0.00	0.02012	57.9	0.02370	0.99959	140.10
372	190	0.84	4.2639	0.0738	−0.0004	0.030939	0.20	0.02012	57.9	0.02370	0.99959	140.23
373	220	1.65	6.2177	0.0731	0.0030	0.046369	0.24	0.03540	30.5	0.02420	0.99921	135.74
374	220	1.65	5.9721	0.0706	0.0000	0.044687	0.27	0.03540	30.5	0.02420	0.99921	135.24
375	250	3.04	3.6583	0.0752	0.0000	0.028267	0.15	0.05867	17.1	0.02470	0.99856	131.96
376	280	5.27	4.2949	0.0762	−0.0012	0.034258	0.12	0.09171	10.2	0.02520	0.99752	127.30
377	310	8.66	2.7888	0.0832	0.0019	0.023374	0.05	0.13644	6.4	0.02573	0.99595	122.48
379	340	13.61	3.4606	0.0596	0.0022	0.029495	0.07	0.19423	4.2	0.02630	0.99367	118.71

[a] Based on Willinghan (*8*) up to 220° F. and Reamer (*5*) up to 340° F. [b] Reamer *et al.* (*5*). [c] Not used directly in evaluation of latent heat of vaporization.

of the vapor pressure curve were obtained from the measurements of Reamer (*5*) and Willingham (*8*) by use of the residual methods. It should be recognized that a 2% uncertainty in the value of the slope of the vapor pressure curve does not introduce more than 0.00013 fraction uncertainty in the measured enthalpy change upon vaporization. The residual specific volume at dew point was calculated utilizing a molecular weight of *n*-decane of 142.276 and a value of the universal gas constant of R = 10.73147(p.s.i.)(cu. ft.)/(lb.-mole)(° R).

Values of the volumetric correction factor used in the reduction of the calorimetric measurements have been included in Table II. The slight deviation of this factor from unity serves to illustrate the small effect of uncertainties in the slope of the vapor pressure curve upon the reported values of the latent heat of vaporization. The latent heats of vaporization recorded in Table II are depicted graphically in Figure 1. Values reported by Rossini (*6*) at 77° and at 345° F. have been included for comparison.

In order to permit a more meaningful comparison of the precision of the experimental data and the agreement with the values recorded by Rossini (*6*), residual techniques have been employed. For present purposes the residual latent heat of vaporization of *n*-decane was established from:

$$l = l - (166.667 - 0.166667\,t) \qquad (4)$$

There is shown in Figure 2 values of the residual latent heat of vaporization of *n*-decane along with the values reported by Rossini (*6*). The standard error of estimate of the current latent heat of vaporization measurements from the smooth curves shown in Figures 1 and 2 is 0.30 B.t.u. per pound.

Table III records the smooth values of the latent heat of vaporization as a function of temperature. The internal energy change upon vaporization and the specific volume at dew point are recorded in a part of Table III.

Table III. Critically Chosen Values of Some Properties of *n*-Decane

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.
100	578	144.60	152.40
110	434	143.10	151.04
120	329	141.62	149.70
130	251	140.12	148.34
140	193	138.61	146.96
150	149.1[a]	137.11	145.59[a]
160	116.4	135.60	144.21
170	91.5	134.07	142.82
180	72.6	132.56	141.43
190	57.9	131.05	140.04
200	46.5	129.54	138.64
210	37.5	128.03	137.25
220	30.5	126.52	135.84
230	25.0	125.00	134.43
240	20.6	123.49	133.02
250	17.1	121.98	131.60
260	14.3	120.47	130.18
270	12.0	118.96	128.76
280	10.2	117.44	127.33
290	8.6	115.91	125.89
310	6.4	112.88	123.03
320	5.5	111.36	121.58
330	4.8	109.83	120.15
340	4.2	108.30	118.70

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

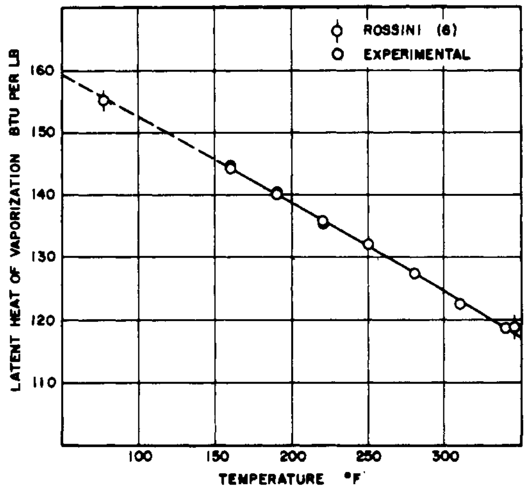

Figure 1. Effect of temperature on latent heat of vaporization for *n*-decane

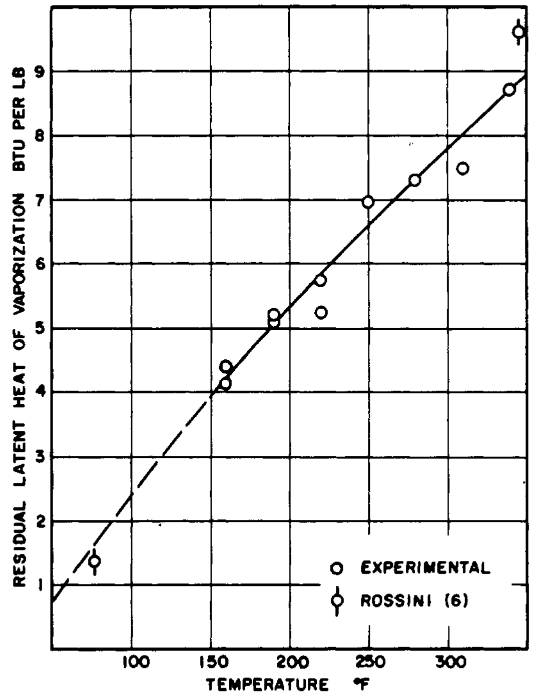

Figure 2. Residual latent heat of vaporization for *n*-decane

Values of the compressibility factor for the dew-point gas as a function of vapor pressure are shown in Figure 3. It is apparent that even at a vapor pressure of 13 p.s.i.a., corresponding to a temperature of 340° F., the dew-point gas of *n*-decane deviates only approximately 6.3% from the behavior of a perfect gas. At 160° F. additional uncertainty exists in evaluation of the slope of the vapor pressure–temperature relation. The standard error of estimate of the experimental values of the specific volume of the dew-point gas reported in Table II from the smooth curves drawn in Figure 3 is 0.27 cubic foot per pound, or 0.0025 when expressed in terms of the compressibility factor. This standard error corresponds to an uncertainty of approximately 0.26%.

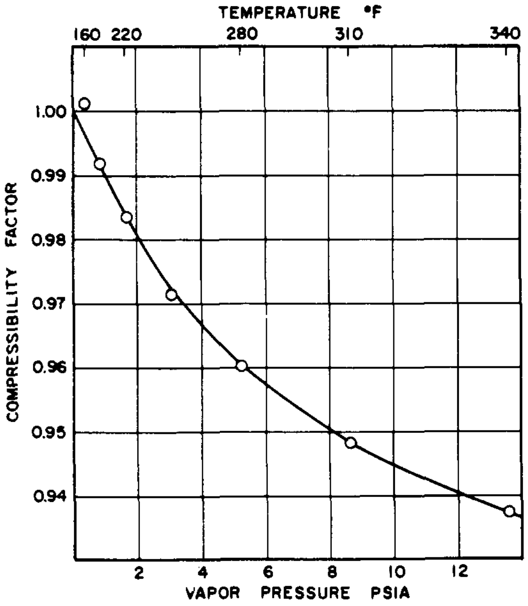

Figure 3. Compressibility factor for the dew-point gas

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NOMENCLATURE

d = differential operator
H = enthalpy, B.t.u./lb.
l = latent heat of vaporization, B.t.u./lb.
l = residual latent heat of vaporization, B.t.u./lb.
m = weight of material, lb.
P'' = vapor pressure, p.s.i.a.
$[Q]$ = heat added per unit weight of material withdrawn under idealized conditions, B.t.u./lb.
$Q^*_{1,2}$ = net energy added to calorimeter under ideal conditions, B.t.u.
T = thermodynamic temperature, ° R.
t = temperature, ° F.
V = specific volume, cu. ft./lb.

Subscripts

g = gas phase
l = liquid phase
P = pressure
T = temperature
1 = initial state
2 = final state

LITERATURE CITED

(1) McKay, R.A., Sage, B.H., Am. Doc. Inst., Washington, D. C., Doc. No. **6072**, (1959).
(2) McKay, R.A., Sage, B.H., J. CHEM. ENG. DATA **5**, 21 (1960).
(3) Osborne, N.S., Stimson, H.F., Fiock, E.F., *Natl. Bur. Std. J. Res.* 4, 411 (1930).
(4) Osborne, N.S., Stimson, H.F., Ginnings, D.C., *Ibid.*, **23**, 197 (1939).
(5) Reamer, H.H., Olds. R.H., Sage, B.H., Lacey, W.N., *Ind. Eng. Chem.* **34**, 1526 (1942).
(6) Rossini, F.D., others, "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds," Carnegie Press, Pittsburgh, Pa., 1953.
(7) Sage, B.H., Hough, E.W., *Anal. Chem.* **22**, 1304 (1950).
(8) Willingham, C.B., Taylor, W.J., Pignocco, J. Rossini, F.D., *J. Res. Natl. Bur. Std.* **35**, 219 (1945).
(9) Young, S., *Proc. Roy. Irish Acad.* **B38**, 65 (1928).

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Vapor Liquid Equilibrium at Atmospheric Pressure: The Ternary System Benzene–Ethanol–*n*-Hexane

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IN THIS STUDY vapor-liquid equilibrium data at atmospheric pressure for the ternary system benzene–ethanol-*n*-hexane were determined. This is the fourth ternary system investigated involving the compounds benzene, ethanol, *n*-hexane, and methylcyclohexane. The other three ternary systems were studied by Sinor and Weber (*14*), Belknap and Weber (*1*), and Kaes and Weber (*7*). Quaternary data have also been obtained in the previous investigations. The six binary systems which can be made with these four compounds have been investigated (*5, 10, 11, 12, 14, 15*).

The ternary system in the present study showed large deviations from ideal liquid phase behavior, although no ternary azeotrope was found. Also, as a part of this investigation, an attempt was made to predict the ternary equilibrium data from binary vapor-liquid equilibrium data by the method proposed by Black (*2, 3*).

EXPERIMENTAL

Purity of Compounds. The benzene and *n*-hexane used were pure grade materials of a minimum of 99 mole % purity (Phillips Petroleum Co.). The ethyl alcohol (U. S. Industrial Chemical Co.) and the hydrocarbons were not

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