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LITERATURE CITED

(1) Baron, J.D., Roof, J.G., Wells, F.W., J. CHEM. ENG. DATA 4, 283 (1959).
(2) Barua, A.K., Ross, J., Afzal, M., Project SQUID Tech. Rept. **BRN-10-P**, 1964.
(3) Bicher, L.B., Jr., Katz, D.L., *Ind. Eng. Chem.* **35**, 754 (1943).
(4) Carmichael, L.T., Berry, Virginia, Sage, B.H., J. CHEM. ENG. DATA **10**, 57 (1965).
(5) Carmichael, L.T., Sage, B.H., *Ibid.*, **8**, 612 (1963).
(6) Carr, N.L., *Ill. Inst. of Tech. Bull.* **23**, 1953.
(7) Comings, E.W., Mayland, B.J., Egly, R.S., *Univ. Illinois Bull., Eng. Exp. Sta., Bull. Ser.* **354**, 42, No. 15 (1944).
(8) Dolan, J.P., Ellington, R.T., Lee, A.L., J. CHEM. ENG. DATA **9**, 484 (1964).
(9) Dolan, J.P., Starling, K.E., Lee, A.L., Eakin, B.E., Ellington, R.T., *Ibid.*, **8**, 396 (1963).
(10) Kestin, J., Leidenfrost, W., "The Effect of Moderate Pressures on the Viscosity of Five Gases," Bulletin, Brown Univ., Providence, R. I.
(11) Lipkin, M.R., Davison, J.A., Kurtz, S.S., Jr., *Ind. Eng. Chem.* **34**, 976 (1942).
(12) Reamer, H.H., Cokelet, G., Sage, B.H., *Anal. Chem.* **31**, 1422 (1959).
(13) Ross, J.F., Brown, G.M., *Ind. Eng. Chem.* **49**, 2026 (1957).
(14) Sage, B.H., Lacey, W.N., *Trans, AIME* **127**, 118 (1938).
(15) Sage, B.H., Yale, W.D., Lacey, W.N., *Ind. Eng. Chem.* **31**, 223 (1939).
(16) Starling, K.E., Eakin, B.E., Dolan, J.P., Ellington, R.T., "Progress in International Research and Thermodynamic and Transport Properties," Second Symposium on Thermophysical Properties, Princeton University, Princeton, N. J., January 1962.
(17) Swift, G.W., Lohrenz, J., Kurata, F., *A.I.Ch.E.J.* **6**, 415 (1960).
(18) Titani, T., *Bull. Chem. Soc. Japan* **5**, 98 (1930).

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Latent Heat of Vaporization of Propane

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Calorimetric measurements of the latent heat of vaporization of propane were made in the temperature interval between 100° and 135° F. A critical review of the available calorimetric and volumetric data was made and an analytical expression developed by regression analysis, to describe the latent heat of vaporization for propane from 0° F. to the critical state with a standard error of estimate of 1.5 B.t.u. per pound.

THE latent heat of vaporization of propane has been the subject of a number of investigations. The early work of Dana *et al.* (*3*) was followed by some additional calorimetric measurements of the latent heat of vaporization of this hydrocarbon (*6*). The volumetric behavior of the compound and the vapor pressure have been studied by several investigators (*1*, *2*, *5*, *8*, *9*). There existed discrepancies of the order of 5 B.t.u. per pound between the latent heat of vaporization as estimated at 80° F. from the two calorimetric investigations (*3*, *6*), and from the more recent volumetric measurements (*1*, *2*, *5*) and the calorimetric data at a temperature of 100° F.

As a result of this discrepancy, calorimetric measurements were made of the latent heat of vaporization of propane. The technique and equipment employed have been described (*4*, *7*) and differ materially from the apparatus used earlier (*6*). The temperatures were measured with a platinum resistance thermometer which was compared recently with the indications of a similar instrument calibrated by the National Bureau of Standards. The temperature within the calorimeter was known within 0.01° F. of the international platinum scale. Temperature differences were established within 0.002° F. The experimental results are set forth in Table I. The measurements were not carried above 135° F. because the large volumetric corrections necessary in the calorimetric measurements made use of the Clapeyron equation based upon volumetric and vapor pressure measurements a preferable approach. The calorimeter is not arranged to permit measurements below 100° F. Direct comparison of the present calorimetric measurements with the data mentioned earlier is presented in Figure 1. In this figure, where data were obtained at nearly the same temperature, a single average value was depicted.

The following analytical expression was used to describe the latent heat of vaporization of propane in the temperature interval between 40° and 206.26° F.:

$$l = A(T_c - T)^{1/3} + B(T_c - T)^{2/3} + C(T_c - T) \quad (1)$$

The application of least square regression methods yielded the following coefficients: $A = 21.771$; $B = 1.8935$; and $C = -0.10836$, with a standard deviation, σ, of 1.5 B.t.u. per pound from the experimental values depicted in Figure 1. The critical temperature employed was 665.95° R., based on Beattie's (*2*) measurements.

To illustrate the quantitative nature of the disagreement of the several sets of data, residual values of the latent heat of vaporization have been calculated, using Equation 1 as a reference value. The residual latent heat of vaporization is defined as

$$l = l_r - l_c \quad (2)$$

and is shown as a function of temperature for each of the experimental points employed in obtaining the points shown in Figure 2. The range of temperatures, the standard error of estimate, and average error are reported in Table II for each set of data from the values obtained from Equation 1.

As can be seen from Figure 2, the data of Dana *et al.* (*3*) yield values of at least 5 B.t.u. per pound above the current data when extrapolated to 100° F. The earlier

Table I. Experimental Results for Latent Heat of Vaporization of Propane

Temperature, ° F.	Pressure, p.s.i.a.	Energy Added: Electrically, B.t.u.	Energy Added: By Agitation, B.t.u.	Energy Added: By Conduction & Radiation, B.t.u.	Weight of Material Withdrawn, Lb.	Super Heat of Liquid, ° F.	dP''/dT, p.s.i./° F.	Specific Volume Bubble Point, Cu. Ft./Lb.	Volumetric Term,[a] B.t.u./Lb.	Latent Heat of Vaporization, B.t.u./Lb.
100	188.7	3.8687	0.0680	−0.0010	0.027627	0.06	2.4378	0.03390	8.560	133.96
100	188.7	3.2311	0.0664	−0.0105	0.023286	0.09	2.4378	0.03390	8.560	132.68
100	188.7	2.7045	0.0529	−0.0032	0.019465	0.06	2.4378	0.03390	8.560	133.00
100	188.7	3.1647	0.0647	−0.0073	0.022758	0.07	2.4378	0.03390	8.560	133.09
120	242.7	4.0332	0.0472	−0.0037	0.030399	0.07	2.9483	0.03547	11.220	122.95
120	242.7	4.7240	0.0579	0.0053	0.035754	0.06	2.9483	0.03547	11.220	122.74
130	273.5	3.1396	0.0471	−0.0006	0.024587	0.05	3.2215	0.03637	12.788	116.85
130	273.5	3.3003	0.0536	0.0000	0.025834	0.06	3.2215	0.03637	12.788	117.09
130	273.5	3.4455	0.0512	−0.0012	0.026955	0.04	3.2215	0.03637	12.788	116.93
135	289.9	3.2296	0.0438	0.0062	0.025749	0.06	3.3640	0.03686	13.644	113.79
135	289.9	3.8423	0.0521	0.0031	0.030766	0.06	3.3640	0.03686	13.644	113.10
135	289.9	5.3429	0.0705	−0.0079	0.042737	0.07	3.3640	0.03686	13.644	112.91
135	289.9	3.7124	0.0530	0.0041	0.029658	0.06	3.3640	0.03686	13.644	113.52
135	289.9	3.6679	0.0897	0.0130	0.029750	0.04	3.3640	0.03686	13.644	113.14

[a] $V_b T(dP''/dT)$.

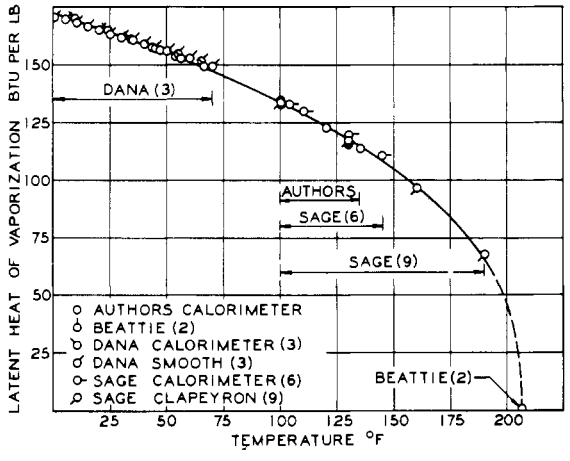

Figure 1. Latent heat of vaporization for propane

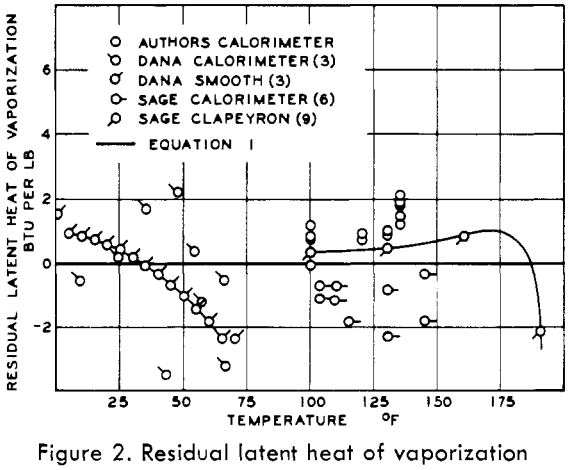

Figure 2. Residual latent heat of vaporization

calorimetric measurements of Sage (*6*) are lower than those extrapolated from the data of Dana but are higher by at least 2 B.t.u. per pound than the current calorimetric data. The volumetric measurements of Sage *et al.* (*9*) utilizing the Clapeyron equation give average agreement within 0.35 B.t.u. per pound with the current calorimetric data, in the temperature interval between 100° and 130° F. However, the agreement is less satisfactory at 135° F.

Table II. Comparison of Results from Several Investigators

Source	Number of Points: Used	Number of Points: Rejected[a]	Temp., ° F.: Min.	Temp., ° F.: Max.	Deviation, B.t.u./Lb.: Average[b]	Deviation, B.t.u./Lb.: Standard[c]
Authors	14	0	100	135	1.12	1.23
Dana (*3*)[d]	15	0	0	70	1.07	1.26
Sage (*6*)	16	7	103	167	1.43	1.53
Sage (*9*)[e]	4	0	100	190	0.98	1.21
Over-all	49	7	0	190	1.16	1.45

[a] Data points rejected when deviation of experimental values exceeds 2σ.

[b] Average deviation defined by:

$$s = \sum_{1}^{N} | l_r - l_e | /N.$$

[c] Standard deviation defined by:

$$\sigma = \left[\sum_{1}^{N} (l_r - l_e)^2/N \right]^{1/2}.$$

[d] Smoothed.

[e] Volumetric data from (*9*).

Table III presents values of the vapor pressure, the slope of the vapor pressure curve, and the specific volume of the coexisting gas and liquid phases as a function of temperature, based upon the volumetric and phase measurements of Sage *et al.* (*5, 9*) and Beattie (*1*) at a temperature above 135° F. Also included are values of the latent heat of vaporization. At temperatures below 135° and above 70° F., the current and the earlier (*6*) calorimetric data were employed to establish the latent heat of vaporization, and to evaluate the specific volume of the coexisting gas phase by use of the Clapeyron equation. At temperatures above 135° F., the Clapeyron equation was applied to the volumetric data of Sage *et al.* (*5, 9*) and Beattie (*1, 2*) to yield the appropriate values of the latent heat of vaporization. At temperatures below 70° F., the data of Dana *et al.* (*3*) were employed.

Table III. Critically Chosen Values of Some Properties of Propane

Temp., °F.	Vapor Pressure, p.s.i.a.	dP''/dT, P.S.I./°F.	Specific Volume, Cu. Ft./Lb. Dew point	Specific Volume, Cu. Ft./Lb. Bubble point	Latent Heat of Vaporization, B.t.u./Lb.
40	79.0	1.288	1.3627	0.03055	158.7
50	92.8	1.451	1.1638	0.03100	155.0
60	107.8	1.626	0.9983	0.03150	151.2
70	125.0	1.814	0.8596	0.03202	147.2
80	144.1	2.016	0.7428	0.03261	143.0
90	165.3	2.231	0.6437	0.03322	138.5
100	188.7	2.461	0.5592	0.03388	133.9
110	214.5	2.705	0.4868	0.03465	128.9
120	242.7	2.964	0.4244	0.03547	123.6
130	273.5	3.238	0.3702	0.03638	118.0
140	307.3	3.527	0.3230	0.03740	111.8
150	344.0	3.832	0.2814	0.03855	105.0
160	383.8	4.153	0.2446	0.03994	97.4
170	426.9	4.490	0.2115	0.04177	88.8
180	473.6	4.843	0.1811	0.04411	78.6
190	524.8	5.213	0.1514	0.04683	65.6

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NOMENCLATURE

- A, B, C = coefficients for Equation 1
- d = differential operator
- l = latent heat of vaporization, B.t.u./lb.
- l = residual latent heat of vaporization, B.t.u./lb.
- N = number of points
- P'' = vapor pressure, p.s.i.a.
- s = average deviation expressed in B.t.u./lb. and defined in Table II
- T = absolute temperature, ° R.
- V = specific volume, cu.ft./lb.
- σ = standard deviation expressed in B.t.u./lb. and defined in Table II
- Σ = summation operator

Subscripts

- b = bubble point
- c = critical
- d = dew point
- e = experimental
- r = reference

LITERATURE CITED

(1) Beattie, J. A., Kay, W. C., Kaminsky, J., *J. Am. Chem. Soc.* **59,** 1589 (1937).
(2) Beattie, J. A., Poffenberger, Noland, Hadlock, Canfield, *J. Chem. Phys.* **3,** 96 (1935).
(3) Dana, L. I., Jenkins, A. C., Burdick, J. N., Timm, R. C., *Refrig. Eng.* **12,** 387 (1926).
(4) McKay, R. A., Sage, B. H., J. CHEM. ENG. DATA **5,** 21 (1960).
(5) Reamer, H. H., Sage, B. H., Lacey, W. N., *Ind. Eng. Chem.* **41,** 482 (1949).
(6) Sage, B. H., Evans, H. D., Lacey, W. N., *Ibid.*, **31,** 763 (1939).
(7) Sage, B. H., Hough, E. W., *Anal. Chem.* **22,** 1304 (1950).
(8) Sage, B. H., Schaafsma, J. G., Lacey, W. N., *Ind. Eng. Chem.* **26,** 1218 (1934).
(9) Sage, B. H., Lacey, W. N., "Thermodynamic Properties of the Lighter Paraffin Hydrocarbons and Nitrogen," American Petroleum Institute, New York, 1950.

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Partial Volumetric Behavior in Binary Hydrocarbon Systems Propane and *n*-Decane in the Liquid Phase of the Propane–*n*-Decane System

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The partial molal volumes of propane and *n*-decane have been established for the volumetric behavior of the propane–*n*-decane system at pressures up to 10,000 p.s.i.a. in the temperature interval between 40° and 460° F. The evaluation of the partial volumes was carried out by conventional graphical methods and by numerical techniques involving the use of orthogonal polynomials. The agreement between the two methods is considered satisfactory.

INFORMATION concerning the partial molal volumes of the components of binary systems is of assistance in evaluating their thermodynamic properties and in the determination of heat and work for changes in state. Furthermore, the partial molal volumes, hereafter called partial volumes, are important in the evaluation of molecular transport under conditions where the requisite diffusion coefficients are available (*6*). The volumetric and phase behavior of the propane–*n*-decane system (*8*) has recently been established at pressures up to 10,000 p.s.i.a. in the temperature interval between 40° and 460° F. Utilizing well-established graphical methods and newly developed analytical techniques, the partial molal volumes of propane and *n*-decane were established from the above-mentioned experimental data throughout the indicated range of temperatures and pressures.

The partial volume may be defined (*4*) as

$$\overline{V}_k = \left(\frac{\partial V}{\partial m_k}\right)_{T, P, m_i} \quad (1)$$