Table V. Heat of Solution of $H_5IO_6(s)$

Millimoles H_5IO_6 in Ampoule	Moles H_2O	Total Energy Change	ΔH_s, Kcal./Mole
3.988	27.5	42.9 cal.	10.8
3.522	27.5	38.5	10.9
3.835	27.5	36.1	9.41
3.083	27.5	34.6	11.2
2.256	27.5	22.6	10.0
1.867	27.5	18.8	10.0
2.095	27.5	20.6	9.85
1.149	27.5	12.6	10.9
1.282	27.5	12.4	9.95
1.212	27.5	13.0	10.8

Av. $\Delta H_s = 10.4 \pm 0.6$ kcal./mole $H_5IO_6(s)$.

Combining the average ΔH_1 (-128.8 ± 0.3 kcal./mole) from Table I with appropriate heats of formation and dilution corrections from Table III, gives ΔH_f° of H_5IO_6(aq.) = -175.9 kcal./mole.

Similarly, the average ΔH_2 (-32.4 ± 0.8 kcal./mole) from Table II yields $\Delta H_f^\circ = -177.2$ kcal./mole for H_5IO_6(aq.). The agreement between these two independently determined values is good and their mean gives ΔH_f° of H_5IO_6(aq.) = -176.5 kcal./mole with an estimated over-all uncertainty of ± 1.2 kcal./mole. ΔH_f° of $H_5IO_6(s)$ is -186.9 ± 1.5 kcal./mole and was obtained by combining ΔH_f° of H_5IO_6(aq.) with the average heat of solution from Table V.

Circular 500 (*3*) lists the heats of formation of H_5IO_6(aq.) and $H_5IO_6(s)$ as -183.0 and -184.4 kcal./mole, respectively. These values are based on Thomsen's heats of reduction of $0.23M$ H_5IO_6 with $SnCl_4^{-2}$ in acid solution (*6*). Since no heats of dilution were reported we believe that our values are more reliable.

LITERATURE CITED

(1) Kolthoff, I.M., Elving, E.B., "Treatise on Analytical Chemistry," Part 2, Vol. **7**, pp. 374-375, Interscience, John Wiley, New York, 1961.

(2) Latimer, W.M., "Oxidation Potentials", pp. 66, 2nd ed., Prentice Hall, Englewood Cliffs, N.J., 1952.

(3) Natl. Bur. Std. (U. S.) Circ. **500**, 1952. Reprinted July 1961.

(4) Somsen, G., Coops, J., Tolk, M.W., *Recueil* **82**, 231 (1963).

(5) Stern, J.H., Passchier, A.A., J. CHEM. ENG. DATA **7**, 73 (1962).

(6) Thomsen, J., "Thermochemische Untersuchungen", p. 164, Vol. **II**, Barth, Leipzig, 1882.

(7) Wu, C., Birky, M.M., Hepler, L.G., *J. Phys. Chem.* **67**, 1202 (1963).

RECEIVED for review April 28, 1964. Accepted June 29, 1964.

Volumetric and Latent Heat of Vaporization Measurements for *trans*-2-Butene

JOHN HUISMAN and B. H. SAGE
Chemical Engineering Laboratory, California Institute of Technology, Pasadena, Calif.

The specific volumes of the liquid and dense phases of *trans*-2-butene were measured at pressures up to 5000 p.s.i. in the temperature interval between 40° and 400° F. The latent heat of vaporization was determined from calorimetric measurements at temperatures between 100° and 250° F. The results are presented in graphical and tabular form together with comparisons with earlier published data.

THE THERMODYNAMIC properties of *trans*-2-butene have not been studied in great detail. Lamb and Roper (*8*) measured the vapor pressure of this compound at temperatures between −91° and 49° F., while Kistiakowsky (*7*) reported values at temperatures from −108° to 76° F. Guttman and Pitzer (*4*) measured the vapor pressure of *trans*-2-butene at temperatures between −96° and 34° F. and also determined the latent heat of vaporization of this compound at a temperature in the vicinity of 34° F. The specific weight of the bubble-point liquid has been reported (*1*). The available experimental information did not seem sufficient to establish with certainty the volumetric behavior in the liquid phase nor the latent heat of vaporization of this compound. For this reason, measurements were made of the volumetric behavior of the liquid phase at pressures up to 5000 p.s.i. in the temperature interval between 40° and 400° F. and of the latent heat of vaporization at temperatures between 100° and 250° F.

MATERIALS

The *trans*-2-butene employed for both the volumetric and calorimetric measurements was obtained from the Phillips Petroleum Co. and was reported to contain less than 0.2 mole % of impurity. After appropriate deaeration, the sample showed from a special set of measurements less than 0.25 p.s.i. variation in vapor pressure with change in quality from 0.1 to 0.9 at 160° F. This set of measurements was not employed in evaluating the actual vapor pressure of *trans*-2-butene reported here.

VOLUMETRIC MEASUREMENTS

Utilizing available pressure-volume-temperature equipment, the volumetric behavior of *trans*-2-butene in the liquid phase was established. In principle, the apparatus involved a stainless steel pressure vessel within which a sample of known weight was confined over mercury. The effective volume of the system was varied by the introduction or withdrawal of mercury, and the resulting equilibrium pressure was measured. The attainment of physical equilibrium was hastened by the use of a mechanical agitator. The temperature of the vessel was known within 0.05° F. relative to the international platinum scale. Pressures were determined by means of a balance (*13*) with an uncertainty of 0.1 p.s.i. or 0.03%, whichever was the larger measure of uncertainty. The volumes occupied by the hydrocarbon system were known within 0.25% throughout the entire range of pressures and temperatures covered by this investigation. The weight of the hydrocarbon employed was determined by gravimetric methods, and the sample was introduced into the pressure-volume-temperature equipment by conventional weighing bomb techniques (*13*). A detailed description of this equipment and the methods employed is available (*13*).

The results of the experimental measurements at eight temperatures between 40° and 400° F. are set forth in Table I. The corresponding measurements of vapor pressure at these temperatures constitute Table II. The experimental volumetric measurements are portrayed graphically in Figure I. The standard error of estimate of the experimental data from the smooth curves was 1.3×10^{-5} cu. ft. per pound. The vapor pressure of *trans*-2-butene may be described approximately by

$$\log P_r'' = 5.62209 - \left(\frac{2206.093}{T}\right) \tag{1}$$

Utilizing this as a reference, the residual vapor pressure may be defined as

$$P'' = P_r'' - P'' \tag{2}$$

The residual vapor pressure is shown as a function of temperature in Figure 2. Included also are the API 44(*1*) critically chosen values and those reported by other investigators (*3, 4, 7, 8*). The standard error of estimate (*6*) of the current data from the smooth curve shown in Figure 2 was 0.06 p.s.i. The data of API 44 (*1*) and Guttman and Pitzer (*4*) yielded a standard error of estimate of 0.02, while those reported by Kistiakowsky and coworkers (*7*) and Lamb and Roper (*8*) indicated a standard error of 0.03 and 0.04 p.s.i.,

Table I. Experimental Volumetric Measurements[a]

Pressure, P.S.I.A.	Volume, Cu. Ft./Lb.	Pressure, P.S.I.A.	Volume, Cu. Ft./Lb.	Pressure, P.S.I.A.	Volume, Cu. Ft./Lb.
40° F.		77° F.		100° F.	
58.8	0.025722	113.8	0.026733	140.4	0.027460
152.9	0.025672	182.0	0.026682	752.0	0.027073
997.7	0.025361	919.9	0.026328	1858.1	0.026510
1994.8	0.025043	1396.8	0.026098	2874.0	0.026083
3637.3	0.024575	2021.6	0.025973	3846.5	0.025809
4749.0	0.024408	3508.7	0.025378	4660.7	0.025564
		4727.0	0.025087		
160° F.		220° F.		280° F.	
138.5	0.029754	283.6	0.033052	456.1	0.039726
247.6	0.029629	401.2	0.032724	486.2	0.039246
1046.0	0.028808	948.4	0.031545	621.7	0.037767
2178.1	0.027961	2076.0	0.030035	936.2	0.035811
3596.3	0.027215	3454.7	0.028905	2150.3	0.032515
4790.5	0.026738	4756.4	0.028170	3698.2	0.030561
				4783.7	0.029691
340° F.		400° F.			
672.8	0.101536	874.6	0.100753		
673.7	0.101177	874.8	0.100741		
717.8	0.076430	998.8	0.076949		
808.9	0.052705	1247.5	0.055121		
1075.4	0.043034	1846.9	0.043018		
1895.3	0.036817	2393.4	0.037326		
2974.7	0.033880	3951.1	0.034784		
4113.5	0.032162	4850.6	0.033358		
4912.6	0.031309				

[a] Sample weight 0.276521 lb.

Table II. Experimental Vapor Pressure Measurements

Pressure, P.S.I.A.	Quality	Pressure, P.S.I.A.	Quality	Pressure, P.S.I.A.	Quality
40° F. (16.83)[a]		77° F. (33.93)		100° F. (49.88)	
16.96	0.0003	34.10	0.0007	50.11	0.0081
16.94	0.0028	34.09	0.0052	50.03	0.0315
16.91	0.0114	34.05	0.0226	50.00	0.0380
16.90	0.0138	34.03	0.0265	50.13	0.0004
				50.14[b]	0.0004
				50.01[b]	0.0435
160° F. (117.89)		220° F. (239.25)		280° F. (436.18)	
118.45	0.0036	239.61	0.006	436.62	0.015
118.35	0.0186	239.51	0.030	436.58	0.104
118.37	0.0736	239.30	0.152	436.26	0.361
118.19	0.0865	239.51	0.190	436.28	0.452
		239.58	0.006	436.68	0.015

[a] Chosen value of vapor pressure taken at a quality of 0.5 for all temperatures shown. [b] Second set of measurements with a different loading of the equipment made at 100° F.

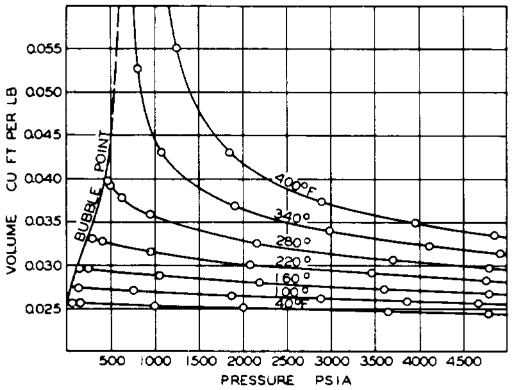

Figure 1. Specific volume of liquid phase

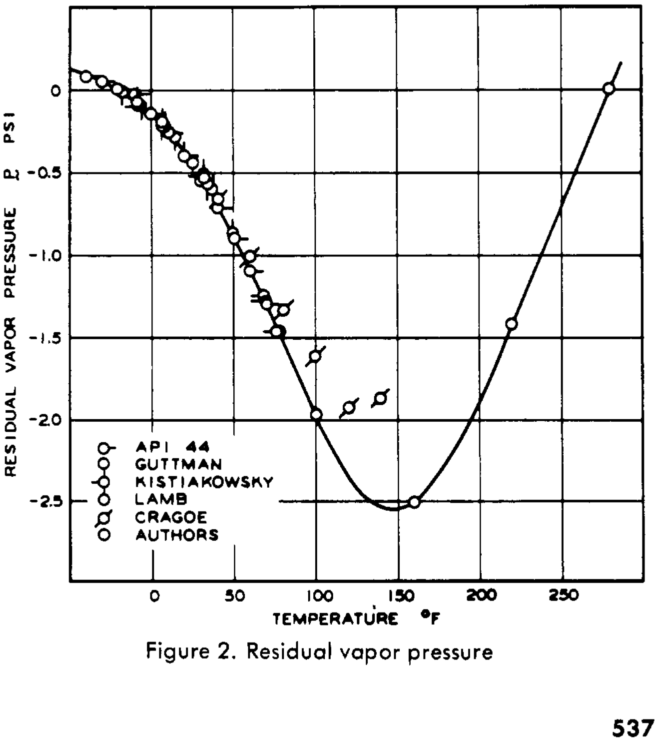

Figure 2. Residual vapor pressure

respectively. The data of Cragoe (*3*) deviated from the present measurements at temperatures above 80° F. From the data reported in Table I and Table II, taking into account the vapor pressure measurements of other investigators (*1, 4, 7, 8*), the specific volume of *trans*-2-butene in the liquid and dense phases and critically chosen values of the vapor pressure are set forth in Table III.

LATENT HEAT OF VAPORIZATION MEASUREMENTS

The latent heat of vaporization of *trans*-2-butene was determined by calorimetric techniques at temperatures between 100° and 250° F. In principle, the equipment consists of an isochoric vessel within which the hydrocarbon was confined. An electric heater added energy at a known rate. Physical and thermal equilibrium was approached by means of a mechanical agitator. The gas phase was withdrawn from the calorimeter at a fixed rate and collected in a weighing bomb. From a knowledge of the electrical energy added, and the weight of hydrocarbon removed, together with the necessary volumetric corrections, the latent heat of vaporization was evaluated (*9, 10*). The details of the equipment employed and the methods utilized are available (*10, 12*).

As the temperature is increased, the magnitude of the volumetric correction becomes greater. As a result, the use of such calorimetric techniques for the evaluation of the enthalpy change upon vaporization becomes less accurate as the critical state is approached. For this reason, no effort was made to carry the measurements above 250° F., although the equipment will permit measurements at temperatures as high 340° F.

The experimental measurements associated with the latent heat of vaporization of *trans*-2-butene are set forth in Table IV. The pertinent, experimentally measured quantities and the associated corrections have been included. The volumetric correction (*2*) was established from the specific volume of the bubble-point liquid, the temperature, and the slope of the vapor pressure curve. The latent heat of vaporization, as measured under idealized (*2*), isobaric, and isothermal conditions, is related to the measured thermal quantities by

$$l = (H_g - H_l)_T = [Q]_{T,P} - V_l T(dP''/dT) \qquad (3)$$

The magnitude of the volumetric correction term, V_l $T(dP''/dT)$, is set forth in Figure 3 and is recorded in

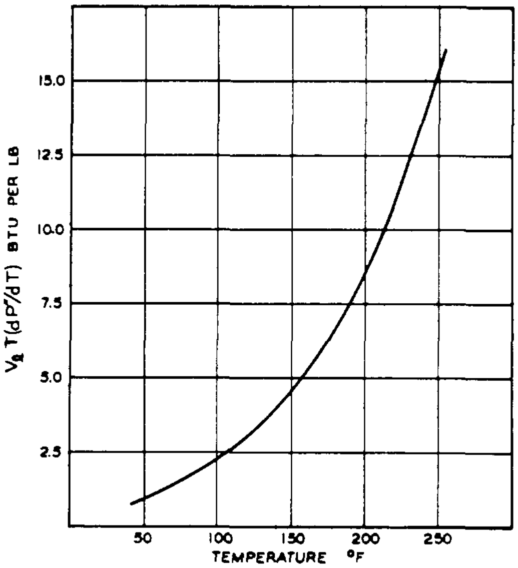

Figure 3. Volumetric correction term

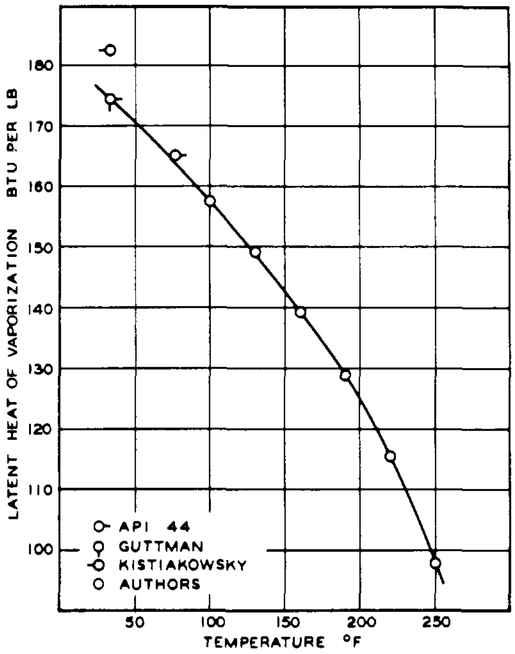

Figure 4. Latent heat of vaporization

Table III. Specific Volumes in the Liquid Phase

Pressure P.S.I.A.	Temperature, ° F. 40	100	160	220	280	340	400
Vapor Pressure	16.8[a]	49.9	117.9	239.3	436.2		
Bubble Point	0.02573	0.02748	0.02977	0.03317	0.04004		
200	0.02567[b]	0.02739	0.02968	...	...	...	...
400	0.02560	0.02728	0.02946	0.03274	...	...	...
600	0.02552	0.02716	0.02924	0.03225	0.03800	...	...
800	0.02545	0.02704	0.02904	0.03183	0.03653	0.05340	...
1000	0.02538	0.02693	0.02885	0.03146	0.03554	0.04432	0.07630
1250	0.02529	0.02679	0.02863	0.03106	0.03460	0.04093	0.05500
1500	0.02520	0.02666	0.02843	0.03070	0.03388	0.03894	0.04790
1750	0.02512	0.02654	0.02824	0.03039	0.03329	0.03750	0.04415
2000	0.02504	0.02642	0.02807	0.03012	0.03279	0.03642	0.04175
2250	0.02496	0.02632	0.02791	0.02987	0.03234	0.03560	0.04001
2500	0.02488	0.02621	0.02776	0.02964	0.03194	0.03493	0.03880
2750	0.02481	0.02612	0.02762	0.02944	0.03158	0.03435	0.03782
3000	0.02474	0.02603	0.02749	0.02924	0.03127	0.03384	0.03700
3500	0.02462	0.02586	0.02726	0.02888	0.03073	0.03299	0.03570
4000	0.02451	0.02572	0.02705	0.02855	0.03028	0.03230	0.03470
4500	0.02442	0.02559	0.02685	0.02826	0.02990	0.03174	0.03387
5000	0.02436	0.02547	0.02666	0.02800	0.02954	0.03123	0.03316

[a] Vapor pressure expressed in pounds per square inch absolute. [b] Volumes expressed in cubic foot per pound.

Table IV. Experimental Results for Latent Heat of Vaporization

Identification	Temperature, °F.	Pressure, 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 Liquid, °F.	dP''/dT P.S.I./°R.	Compressibility Factor	Specific Volume: Dew point, cu. ft./lb.	Specific Volume: Bubble point, cu. ft./lb.	Volumetric Term, B.t.u./Lb.	Latent Heat of Vaporization, B.t.u./Lb.
413	100	49.90	4.4327	0.1497	-0.0003	0.028689	0.05	0.7986	0.9002	1.931	0.02748	2.27	157.46
414	100	49.90	4.1283	0.0568	-0.0005	0.026178	0.10	0.7986	0.9001	1.933	0.02748	2.27	157.62
411	130	78.52	4.8075	0.1045	0.0005	0.032187	0.09	1.1204	0.8695	1.249	0.02852	3.49	149.17
416	160	117.89	7.2003	0.0750	-0.0002	0.050362	0.10	1.5196	0.8247	0.8292	0.02977	5.19	139.31
417	160	117.89	6.1960	0.1167	-0.0003	0.043663	0.06	1.5196	0.8253	0.8298	0.02977	5.19	139.41
419	190	170.56	4.5620	0.0920	0.0006	0.034121	0.05	2.0108	0.7745	0.5643	0.03125	7.56	128.87
426	190	170.56	6.0161	0.0593	-0.0046	0.044491	0.10	2.0108	0.7749	0.5646	0.03125	7.56	128.93
427	190	170.56	3.6487	0.0361	-0.0027	0.026971	0.10	2.0108	0.7752	0.5648	0.03125	7.56	128.99
420	220	239.32	3.5367	0.0283	0.0169	0.028369	0.06	2.5916	0.7131	0.3874	0.03317	10.81	115.48
421	220	239.32	2.4867	0.0273	-0.0014	0.019919	0.04	2.5916	0.7123	0.3870	0.03317	10.81	115.35
423	250	326.95	5.4756	0.0344	-0.0038	0.048709	0.04	3.2620	0.6356	0.2639	0.03575	15.32	97.74
424	250	326.95	1.6344	0.0833	0.0063	0.015261	0.00	3.2620	0.6351	0.2637	0.03575	15.32	97.65

a part of Table IV. The estimated uncertainties of measurement, associated with the investigation of the latent heat of vaporization, are set forth in Table V. The greatest uncertainty lies in the evaluation of the energy added by agitation, followed by the determination of the volumetric correction term.

The latent heat of vaporization which is recorded in a part of Table IV is portrayed graphically in Figure 4, along with the measurements of Guttman and Pitzer (*4*) and Kistiakowsky (*7*), as well as the API 44 (*1*) critically chosen values. The latent heat of vaporization of *trans*-2-butene may be approximated by

$$l_r = 185 - 0.35t \qquad (4)$$

The residual latent heat of vaporization, utilizing Equation 4 as a reference, may be expressed as

$$l = l - l_r \qquad (5)$$

Figure 5 shows the residual latent heat of vaporization as a function of temperature including the current measurements, the available, critically chosen values (*1*), and the measured values of Guttman and Pitzer (*4*) and of Kistiakowsky (*7*). The standard error of estimate of the current experimental data from the smooth curve shown in Figure 5 was 0.13 B.t.u. per pound. The average error of the values at a single temperature reported by Guttman and Pitzer (*4*) was 0.1 B.t.u. per pound.

Since no volumetric measurements in the gas phase were known to the authors, the Clapeyron equation in the following form was employed to evaluate the specific volume of the dew-point gas:

$$V_g = \frac{[Q]_{T,P}}{T(dP''/dT)} \qquad (6)$$

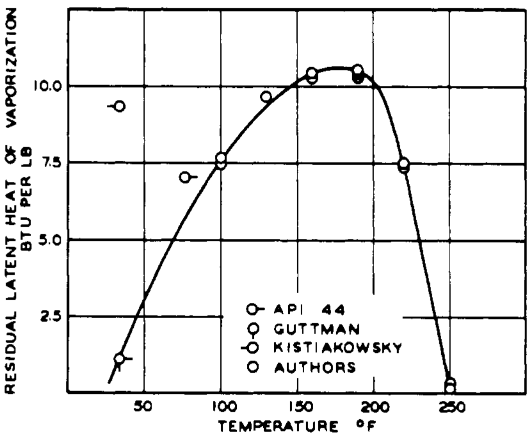

Figure 5. Residual latent heat of vaporization

Table V. Estimated Uncertainties of Measurement

Quantity	Probable Uncertainty, %
Energy added electrically	0.03
Energy added by agitation	0.10
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	0.08
Superheat of liquid	0.01

Likewise, the compressibility factor of the dew-point gas may be established from

$$Z = \frac{P'' V_g}{bT} \tag{7}$$

This factor is shown for the dew-point gas as a function of temperature in Figure 6. The dashed portion of the curve is based on an equation of state of the virial type evaluated by Roper (*11*). Good agreement between the present values, based in part on calorimetric measurements, and the values established from an equation of state by Roper is apparent. In many ways, the use of the Clapeyron equation is the most satisfactory way of determining the volumetric behavior of the dew-point gas at reduced temperatures, since direct measurements are fraught with uncertainties associated with adsorption.

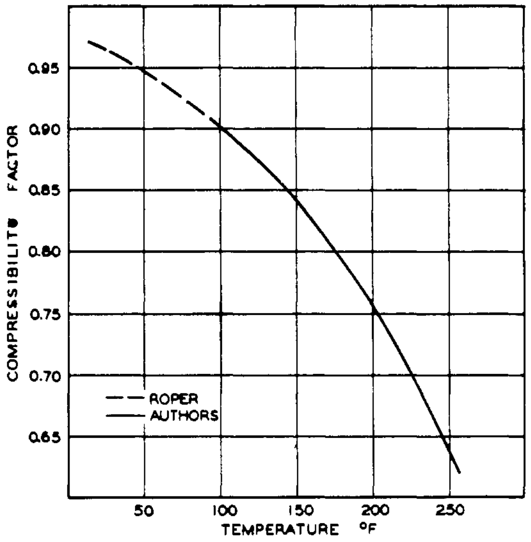

Figure 6. Compressibility factor for dew-point gas

Table VI. Critically Chosen Values of some Properties of *trans*-2-Butene

Temp., °F	Vapor Pressure, P.S.I.A.	Specific Volume Bubble point, cu. ft./lb.	Specific Volume Dew point, cu. ft./lb.	Internal Energy Change upon Vaporization, B.t.u./Lb.	Latent Heat of Vaporization, B.t.u./Lb.
40	16.80	0.02573	5.430	156.05	172.85
50	20.55	0.02600	4.495	153.50	170.50
60	24.90	0.02627	3.753	150.91	168.08
70	29.94	0.02656	3.151	148.27	165.58
80	35.75	0.02685	2.664	145.56	163.00
90	42.39	0.02716	2.263	142.76	160.30
100	49.90	0.02748	1.936	139.89	157.52
110	58.38	0.02780	1.664	137.01	154.68
120	67.89	0.02816	1.437	134.06	151.76
130	78.52	0.02852	1.246	131.11	148.79
140	90.32	0.02892	1.085	128.09	145.74
150	103.4	0.02933	0.9475	125.03	142.60
160	117.9	0.02977	0.8300	121.91	139.37
170	133.8	0.03022	0.7290	188.73	136.03
180	151.4	0.03072	0.6411	115.46	132.56
190	170.6	0.03125	0.5645	112.14	128.97
200	191.6	0.03182	0.4976	108.66	125.18
210	214.5	0.03245	0.4390	104.71	120.84
220	239.3	0.03317	0.3873	99.75	115.43
230	266.4	0.03390	0.3415	94.61	109.77
240	295.5	0.03477	0.3005	89.32	103.85
250	327.0	0.03575	0.2638	83.90	97.70

From the current measurements, coupled with the available data at lower temperatures (*1*, *11*), a set of critically chosen values of the properties of the bubble-point liquid and the dew-point gas are presented in Table VI. In this table, the vapor pressure is recorded, along with the specific volume of the bubble-point liquid and the dew-point gas, and the changes in internal energy and enthalpy associated with vaporization for even values of temperature between 40° and 250° F.

It is estimated that the over-all uncertainty of measurement of the specific volume of the dew-point gas is approximately 0.35%, while the internal energy change upon vaporization is known within 0.4% and the enthalpy change change upon vaporization within 0.5%.

ACKNOWLEDGMENT

The authors acknowledge the support of the Standard Oil Co. of California which provided the fellowship for the senior author during the period this experimental work was being done. Virginia Berry assisted in the preparation of the experimental measurements in a form suitable for publication and B. Lawson Miller assisted with the preparation of the manuscript.

NOMENCLATURE

b = gas constant, (p.s.i)(cu. ft.)/(lb.)(° R.)
d = differential operator
H = enthalpy, B.t.u./lb.
l = latent heat of vaporization,B.t.u./lb.
$\boldsymbol{l}$ = residual latent heat of vaporization, B.t.u.
P'' = vapor pressure, p.s.i.a.
$\boldsymbol{P}''$ = residual 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.
Z = compressibility factor

Subscripts

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

LITERATURE CITED

(1) Am. Petroleum Inst., Research Project 44, Petroleum Research Laboratory, Carnegie Institute of Technology, "Selected Values of Properties of Hydrocarbons and Related Compounds."
(2) Couch, H. T., Kozicki, William, Sage, B. H., J. Chem. Eng. Data **8**, 346 (1963).
(3) Cragoe, C. S., *Natl. Bur. Std., Letter Circ.* **LC-736**, Wash-
(4) Guttman, Lester, Pitzer, K. S., *J. Am. Chem. Soc.* **67**, 324 (1945).
(5) Hackmuth, K. H., Hanson, G. H., Smith, M. L., *Trans. Am. Inst. Chem. Engrs.* **42**, 975 (1946).
(6) Huisman, John, Sage, B. H., J. Chem. Eng. Data **9**, 223 (1964).
(7) Kistiakowsky, G. B., Ruhoff, J. R., Smith, H. A., Vaughan, W. E., *J. Am. Chem. Soc.* **57**, 876 (1935).
(8) Lamb, A. B., Roper, E. E., *Ibid.*, **62**, 806 (1940).
(9) McKay, R.A., Sage, B.H., Am. Doc. Inst., Washington, D. C., Doc. No. **6072** (1959).
(10) McKay, R. A., Sage, B. H., J. Chem. Eng. Data **5**, 21 (1960).
(11) Roper, E. E., *J. Phys. Chem.* **44**, 835 (1940).
(12) Sage, B. H., Hough, E. W., *Anal. Chem.* **22**, 1304 (1950).
(13) Sage, B. H., Lacey, W. N., *Trans. AIME* **136**, 136 (1940).
(14) Smith, C. H., Thodos, George, *A.I.Ch.E. J.* **6**, 569 (1960).

Received for review April 29, 1964. Accepted August 14, 1964.