[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

The Vapor Pressure, Orthobaric Liquid Density, and Critical Constants of 1-Butene

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In continuation of a program of study of certain thermodynamic properties of hydrocarbons[1] we measured during 1941 the vapor pressure, orthobaric liquid density, and critical constants of 1-butene. The bomb with a glass liner was used.[1]

The vapor pressure of 1-butene has been measured from −78 to −4° by Coffin and Maass,[2] from −57 to 0° by Lamb and Roper,[3] from −74 to −7° by Aston and co-workers,[4] and from 38° to the critical point by Olds, Sage and Lacey,[5] who also determined the orthobaric liquid and vapor densities over this range, and the critical constants.

The 1-butene used in the present investigation was furnished by the Linde Air Products Company through the courtesy of Dr. J. M. Gaines, Jr. The sample was transferred to the system used for removal of permanent gases, cooled with liquid nitrogen, evacuated until about one-tenth of the sample had been evaporated, distilled into a second receiver, and the last tenth discarded. This operation was repeated seven times. During the first three cycles decreasingly small amounts of a white solid were observed when the sample was cooled, but this solid had completely disappeared by the fourth cycle. However, the increase in vapor pressure of the sample with decreasing vapor volume and the isotherms in the critical region indicate that the 1-butene was not so pure as were the other hydrocarbons we have studied.

In Table I are given the measured vapor pressures and orthobaric liquid densities. The increase of vapor pressure with decrease in vapor volume indicates the presence of a moderate amount of an impurity, which does not, however, seem to be a permanent gas. Although plots of pressure against vapor volume at constant temperature are concave upward, they are not hyperbolic. Thus at 50° the pressure rose 0.004 atm. for a variation of vapor volume from 5.2 to 0.08 ml.; at 75° there was a rise of 0.004 atm. for a variation of 3.9 to 0.03 ml.; and at 100° a rise of 0.035 atm. for a variation of 22 to 0.02 ml. Extrapolation of the pressure *vs.* vapor volume curves to large volumes gave pressures essentially the same, within a few thousands of an atmosphere, as those measured at the largest volume. The latter are the values recorded in Table I. In Table II the observed pressures are compared with those computed from the equation

$$\log p(\text{atm.}) = 4.34677 - 1156.15/T \qquad (1)$$
$$T = t°\text{C. (Int.)} + 273.16. \quad 30° < t° < 125°$$

which is of the type used for the other hydrocarbons.

In Table III pressures computed for −75 to 0° from the equation of Lamb and Roper[3] (covering the range −78 to +1°) together with our measured vapor pressures are compared with those computed from the least square equation through the two sets of measurements

$$\log p(\text{atm.}) = 5.196066 - 1298.722/T - 0.00124829\,T \qquad (2)$$
$$T = t°\text{C.} + 273.16. \quad -75° < t° < 125°$$

The values of the ratios p(obsd.)/p(calcd.) are plotted in Fig. 1. The smoothness of the plot indicates that our vapor pressures piece on to those of Lamb and Roper very satisfactorily; in fact their equation extrapolated to 30° computes 3.414 atm. in comparison with our measured value, 3.410 atm. In Table III and Fig. 1 are also given the representation of the measurements of Olds, Sage and Lacey.[5] The lowest temperature point is from their Table I and the others from their smoothed values given in their Table III. Except in the neighborhood of 50 to 75° their pressures and ours are in excellent agreement and the deviations of their pressures from ours are both positive and negative.

TABLE I

VAPOR PRESSURE AND ORTHOBARIC LIQUID DENSITY OF 1-BUTENE

Temp., °C. (Int.)	Largest and smallest vapor volumes, ml.		Increase in vapor pressure, atm.	Vapor pressure, normal atm.	Orthobaric liquid density, g./ml.
30	111	42	0.008	3.410	
50	97	0.08	.029	5.889	0.561
75	98	0.03	.047	10.613	.523
100	102	0.02	.058	17.675	.477
125	78	2	.069	27.784	.411

TABLE II

COMPARISON OF CALCULATED WITH OBSERVED VAPOR PRESSURE OF 1-BUTENE

Temp., °C. (Int.)	Observed vapor pressure normal, atm.	Obsd. − calcd. pressure atm.
30	3.410	−0.003
50	5.889	+ .012
75	10.613	− .005
100	17.675	− .047
125	27.784	+ .048

Aston and co-workers[4] measured the vapor pressure of 1-butene from −78 to −70° and repre-

(1) For the last report on this work see J. A. Beattie, D. G. Edwards, and Stanley Marple, Jr., *J. Chem. Phys.*, **17**, 576 (1949), the apparatus and general method of procedure are described by J. A. Beattie, *Proc. Amer. Acad. Arts and Sci.*, **69**, 389 (1934).

(2) C. C. Coffin and O. Maass, THIS JOURNAL, **50**, 1427 (1928).

(3) A. B. Lamb and E. E. Roper, *ibid.*, **62**, 806 (1940).

(4) J. G. Aston, H. L. Fink, A. B. Bestul, E. L. Pace and G. J. Szasz, *ibid.*, **68**, 52 (1946).

(5) R. H. Olds, B. H. Sage and W. N. Lacey, *Ind. Eng. Chem.*, **38**, 301 (1946).

TABLE III

COMPARISON OF THE CALCULATED VAPOR PRESSURES OF 1-BUTENE WITH THOSE OBSERVED BY LAMB AND ROPER, BY OLDS, SAGE AND LACEY, AND BY THE PRESENT AUTHORS

$\log p(\text{calcd.}) = 5.196066 - 1298.722/T - 0.00124829T$, $T = t°\text{C.} + 273.16$; $-75° > t° > 125°$

Temp., °C.	Observed vapor pressure, normal atm.	p(obsd.)/p(cald.)
Measurements of Lamb and Roper[c]		
−75	0.0246	0.9919
−50	0.1260	1.0056
−25	0.4540	1.0096
0	1.2702	1.0075
Measurements of the present authors		
30	3.410	0.9980
50	5.889	0.9912
75	10.613	0.9877
100	17.675	0.9942
125	27.784	1.0152
146.4[a]	39.70	1.0517
Measurements of Olds, Sage and Lacey[d]		
37.78	4.253	0.9944
55.94	6.805	0.9859
73.33	10.207	0.9853
86.67	13.609	0.9913
98.00	17.011	0.9933
107.67	20.414	0.9988
116.11	23.816	1.0070
123.78	27.218	1.0142
147.22[b]	40.01	1.0478

[a] Critical point according to present authors. [b] Critical point according to Olds, Sage and Lacey. [c] From the equation of Lamb and Roper, Ref. 3. [d] Ref. 5. The first point is from their Table I; the others from their Table III in which the temperature is listed to the nearest 0.1°F. for vapor pressures at intervals of 50 pounds per square inch.

TABLE IV

COMPARISON OF CALCULATED VAPOR PRESSURES OF 1-BUTENE WITH THOSE OBSERVED BY ASTON AND CO-WORKERS, AND BY THE PRESENT AUTHORS

$\log p(\text{calcd.}) = 5.475462 - 1343.516/T - 0.00167515T$, $T = t°\text{C.} + 273.16$; $-75° > t° > 125°$

Temp., °C.	Observed vapor pressure, normal atm.	p(obsd.)/p(calcd.)
Measurements of Aston, Fink, Bestul, Pace and Szasz[b]		
−75	0.0227	0.9827
−50	0.1222	1.0133
−25	0.4516	1.0208
0	1.2663	1.0071
Measurements by the present authors		
30	3.410	0.9927
50	5.889	0.9848
75	10.613	0.9829
100	17.675	0.9940
125	27.784	1.0224
146.4[a]	39.70	1.0675

[a] Critical point. [b] From the equation of Aston, etc., Ref. 4. The 0° point is an extrapolation of 7° above their highest measured point.

sented them by a four constant equation. Their pressures are uniformly lower than those of Lamb and Roper by about 1 to 3 mm., and they suggest that Lamb and Roper had air in their 1-butene.

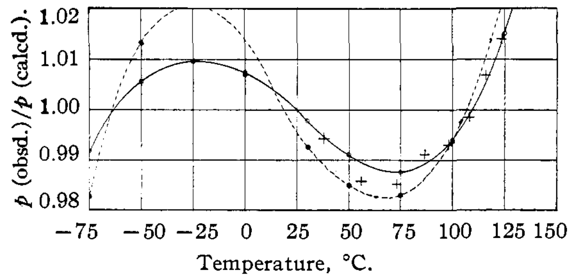

Fig. 1.—Representation of the vapor pressure of 1-butene by a three-constant equation. The open circles and unbroken line refer to Eq. 2 through the results of Lamb and Roper, and of the present authors. The crosses are the values of Olds, Sage and Lacey referred to the same equation. The solid circles and dotted line refer to Eq. 3 through the results of Aston and co-workers, and of the present authors.

Aston's equation extrapolated to 30° computes a vapor pressure of 3.332 atm. Aston's equation was used to compute vapor pressures from −75 to 0° (an extrapolation of 7°). In Table IV these pressures and ours for 30 to 125° are compared with those computed from the least square equation through the combined set

$$\log p(\text{atm.}) = 5.475462 - 1343.516/T - 0.00167515T \quad (3)$$

The ratios p(obsd.)/p(calcd.) are plotted in Fig. 1 as the solid circles connected by the dotted line. It will be noticed that the deviations of each set of points are larger than those of Table III. It seems that our measurements piece on to those of Lamb and Roper better than to those of Aston and co-workers.

The orthobaric liquid volumes given in Table I were obtained by noticing the break on the liquid side in a plot of pressure against volume at each temperature. The uncertainty is 0.002 g. per ml. Our densities are on the average 1.3% higher than those of Olds, Sage and Lacey.[5]

The isotherms of 1-butene in the critical region are given in Table V and plotted in Fig. 2. From the plot we find: $t_c = 146.4 \pm 0.3$°C. (Int.), $p_c = 39.7 \pm 0.3$ normal atm., $v_c = 0.241$ liters per mole (4.30 ml. per g.), $d_c = 4.15$ moles per liter (0.233 g. per ml.). The uncertainty in the critical volume and density is 5%. Olds, Sage and Lacey[5] give 147.2° (297°F.), 40.0 atm., 0.240 liter per mole. The agreement is quite satisfactory.

The large uncertainties in the critical constants must be allowed because of a moderate amount of impurity in the sample as evidenced by an increase of vapor pressure with a decrease in vapor volume at constant temperature and by the slope of the isotherms in the two phase region in the neighbor-

TABLE V

ISOTHERMS OF 1-BUTENE (C_4H_8) IN THE CRITICAL REGION, MOLECULAR WEIGHT, 56.0616

Temp., °C. (Int.) Density moles/liter	Volume liters/mole	146.100	146.150	146.200	146.240	146.280	146.300	146.300[a]	146.320	146.340	143.360	146.400
		Pressure, normal atmospheres										
5.125	0.1951	39.620		39.697			39.781					39.860
4.826	.2072	39.531		39.604			39.677					39.750
4.687	.2134		39.552									
4.557	.2194	39.518	39.548	39.581	39.605	39.637	39.656					39.719
4.434	.2255	39.512	39.541	39.579	39.602	39.629	39.650		39.659	39.672	39.685	
4.317	.2316	39.511	39.542	39.575	39.598	39.626	39.643		39.655	39.668	39.681	39.710
4.262	.2346					39.625		39.640	39.654			
4.207	.2377		39.540	39.573	39.598	39.623	39.641		39.653	39.664	39.677	
4.154	.2407							39.637	39.650	39.662		
4.102	.2438	39.509	39.538	39.571	39.595	39.622	39.637		39.649	39.662	39.675	39.702
4.051	.2469							39.633	39.647	39.660	39.671	
4.002	.2499		39.536	39.567	39.594	39.619	39.636	39.634	39.645	39.658	39.670	39.697
3.952	.2530							39.632	39.643	39.656	39.668	
3.907	.2560	39.503	39.533	39.566	39.590	39.615	39.632		39.643	39.653	39.666	
3.860	.2591					39.614		39.627		39.652		
3.815	.2621	39.501	39.529	39.563	39.588	39.612	39.628		39.627	39.649	39.661	39.686
3.728	.2682	39.498	39.525	39.556	39.583	38.606			39.629	39.642	39.653	
3.644	.2744	39.493	39.519	39.547	39.572	39.596	39.612			39.632	39.644	39.669
3.564	.2806		39.508									
3.489	.2866	39.470		39.527			39.583					39.640
3.346	.2989	39.431		39.485			39.541					39.596

[a] Check run.

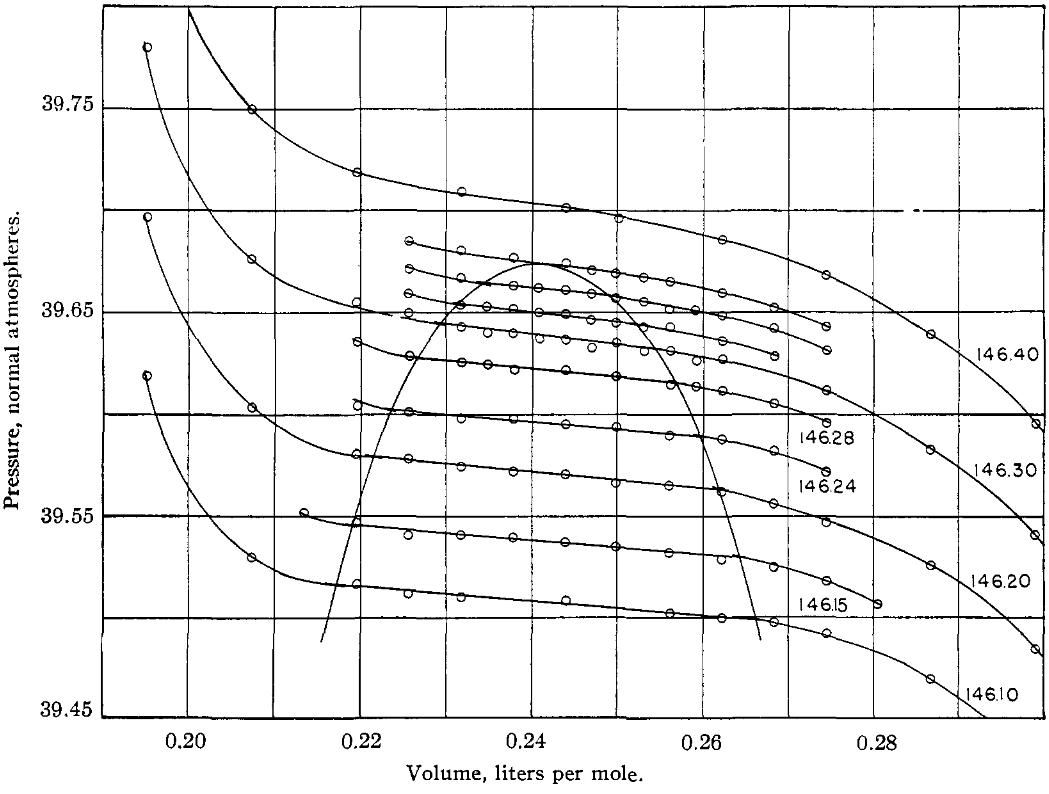

Fig. 2.—Isotherms of 1-butene in the critical region: the isotherms immediately above 146.30° are 146.32, 146.34 and 146.36°. The critical constants are t_c = 146.4 ± 0.03 °C. (Int.), p_c = 39.7 ± 0.3 normal atm., v_c = 0.241 liter per mole (4.30 ml. per g.); d_c = 4.15 moles per liter (0.233 g. per ml.) with an uncertainty of 5% in v_c and d_c.

hood of the critical point, see Fig. 2. A consideration of these effects and a comparison of the work of Lamb and Roper with that of Aston and coworkers indicate clearly that the purity of the sample and not the experimental technique of measurement of pressures, temperatures, volumes, and masses is the limiting element in the accuracy of the final results in the type of experimental work considered here.

Summary

The vapor pressure and orthobaric liquid density of 1-butene has been measured in the range 30–125°. The pressures are represented fairly well by the equation

$$\log p(\text{atm.}) = 4.34677 - (1156.15/T),\ T = t°\text{C. (Int.)} + 273.16.$$

The combined measurements of Lamb and Roper and of the present investigation are represented quite well by the equation

$$\log p(\text{atm.}) = 5.196066 - 1298.722/T - 0.00124829T,\ (T = t°\text{C.} + 273.16 \text{ and } -75° < t° < 125°)$$

The measured critical constants of 1-butene are: $t_c = 146.4 \pm 0.3$°C. (Int.), $p_c = 39.7 \pm 0.3$ normal atm., $v_c = 0.241$ liter per mole (4.30 ml. per g.), $d_c = 4.15$ moles per liter (0.233 g. per ml.), with an uncertainty of 5% in the critical volume and density.

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Some Physical Properties of Diborane, Pentaborane and Aluminum Borohydride

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Various boron hydrides and borohydrides have been studied with regards to methods of synthesis, storage stability, methods of handling, etc. Pertinent physical properties of some of these compounds had been determined previously; *e. g.*, vapor pressure,[1] vapor density,[2] gaseous heat capacity,[3] liquid density,[4,5] melting point,[4] boiling point,[4] surface tension,[5] critical constants,[6] heat of formation[7] and heat of hydrolysis[8] of diborane; melting point,[9] boiling point[9] and vapor pressure[4,9] of dihydropentaborane; vapor pressure of decaborane[10]; heat of formation of B_2O_3[7,8,11]; vapor pressures, melting points, and boiling points of lithium borohydride, beryllium borohydride and aluminum borohydride.[12]

In this study the pressure–volume–temperature diagram of diborane (B_2H_6) has been obtained. An equation relating vapor pressure and temperature for diborane is presented. Density *versus* temperature has been measured for pentaborane (B_5H_9) and aluminum borohydride ($Al(BH_4)_3$), and equations for these relations are given. Viscosities and surface tensions of diborane, pentaborane and aluminum borohydride have been measured, and equations for the calculations of these values at any given temperature have been derived.

Pressure–Volume–Temperature for Diborane.—Measurements of diborane vapor pressure, liquid and gas (saturated) density and liquid compressibility were accomplished in the apparatus of Fig. 1. The system was assembled with no mercury in the capillary. With needle valve 1 closed, the capillary was evacuated and baked out. Then mercury was distilled from the storage bulb into the capillary until there was enough to bring the level slightly above valve 1 during subsequent measurements. (This would permit measurements under constant volume conditions by simply closing valve 1.) The mercury was adjusted to the proper position by letting atmospheric pressure into the vacuum line and reducing the pressure in the manifold through valve 2. Next the mercury was frozen in place with a liquid nitrogen bath, a known amount of diborane was condensed in the capillary over the mercury, and the capillary was sealed off near the top of the calibrated portion. (The method of using this calibration was to add the volumes of 1 cm. increments, since the diameter of the tube was non-uniform. The volume of the irregularly shaped seal was determined after the apparatus was dismantled.) The liquid nitrogen bath was then removed and a clear glass dewar was placed around the capillary. The dewar contained acetone and was cooled with Dry Ice to whatever temperature was desired. Temperatures were read to 0.1° by means of an iron–constantan thermocouple. Lengths were read with a cathetometer.

Diborane, Vapor Pressure.—To read vapor pressure, valve 2 was closed and the pressure in the manifold raised with nitrogen through valve 3

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(12) Schlesinger, Sanderson, Burg and Brown, *ibid.*, **62**, 3421 ff. (1940).