amination this was found to be a mixture of two substances which we were able to separate mechanically. The major portion was a deep yellow product, well crystallized and melting at 124°. The second substance began to blacken at 150° in the capillary tube and then melted at 186°. This compound proved to be easily soluble in water and could be freed from the compound melting at 124° by washing with this solvent. Of the purified compound melting at 124° we obtained 2.0 g. and of the higher melting compound 0.3 g. This experiment was repeated several times but without increasing the yield of the compound melting at 186°. The compound melting at 124° is easily purified by crystallization from methyl alcohol, while the 186° product is purified best by dissolving in cold water and then precipitating by dilution with alcohol. Both compounds evolved ammonia when dissolved in cold alkali, and hydrogen sulfide is liberated on acidifying the alkaline solution.

Anal. (Compound melting at 186°, 5-thio-2-desoxyhydantoin.) Calcd. for $C_3H_6N_2S$: N, 27.46. Found: N, 27.48, 27.45. (Compound melting at 124°, iminodiacetothioamide.) Calcd. for $C_4H_9N_3S_2$: N, 25.74. Found: N, 25.51, 25.54.

Summary

1. In our study of the chemical behavior of hydrogen sulfide toward nitriles of amino acids, we have thus far succeeded in revealing the following three characteristic types of reaction. (*a*) Formation of a dithiopiperazine as is illustrated in the action of hydrogen sulfide on aminoacetonitrile. (*b*) Molecular condensation with formation of an imino nitrile as is illustrated in the action of hydrogen sulfide on α-aminopropionitrile, giving the corresponding imino compound with loss of ammonia. (*c*) Formation of a thiodesoxyhydantoin as is illustrated in the action of hydrogen sulfide on amino-*iso*butyronitrile.

2. From the present evidence it is impossible to predict the course of the reaction which will take place when a given nitrile in this series of compounds is exposed to the action of hydrogen sulfide.

NEW HAVEN, CONNECTICUT

[CONTRIBUTION FROM THE PHYSICAL CHEMICAL LABORATORY OF McGILL UNIVERSITY]

THE PREPARATION AND PHYSICAL PROPERTIES OF α-, β- AND γ-BUTYLENE AND NORMAL AND ISOBUTANE

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Introduction

A number of the physical properties of hydrocarbons containing two and three carbon atoms have been accurately determined in this Laboratory.[1] The present paper describes an extension of this work to compounds of 4 carbon atoms, namely, the three butylenes and the two butanes. The preparation of these compounds is described and their boiling points, melting points and critical temperatures are tabulated. The vapor pressures, densities and surface tensions were determined over a wide

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[1] Maass and Wright, THIS JOURNAL, **43**, 1093 (1921).

range of temperature. Great stress was laid upon the purity of the compounds and the accuracy of the measurements, since small differences in physical properties were to be expected in the case of the isomeric substances. No measurements were made in cases where reliable data were found to exist in the literature. The data obtained are discussed from the point of view of the effect of molecular attraction and constitution upon physical properties.

Preparation and Purification of the Hydrocarbons

α-Butylene was prepared by the action of an excess of alcoholic potash on *n*-butyl iodide, the evolved gas being collected over water in a gasometer. As it was found that the butylenes polymerized rapidly in the presence of phosphorus pentoxide, this substance could not be used as a drying agent. The following is a description of the method employed for the drying and purification of these compounds.

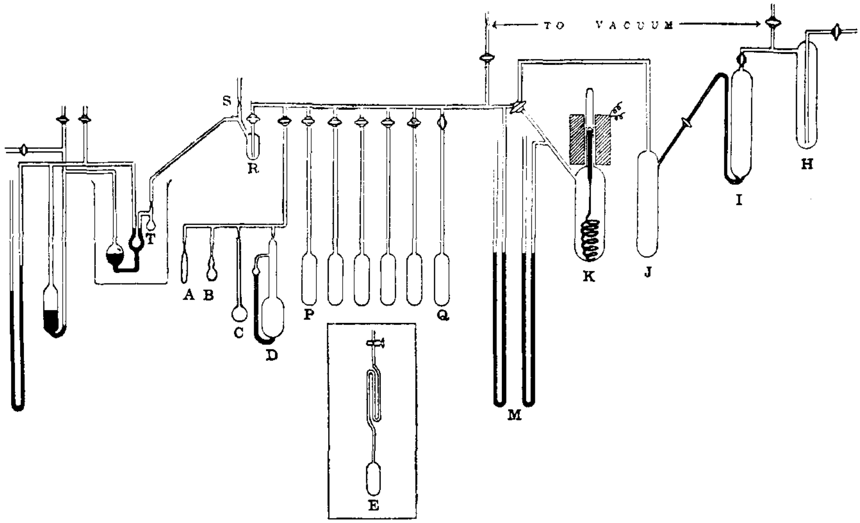

Fig. 1.

The butylene was condensed in H (Fig. 1) by means of carbon dioxide and ether and the system was evacuated. It was then distilled into I and the tap above it was closed. By opening the tap on the capillary between I and J and warming the upper part of I with the hand, the liquid was forced over into J, which was also surrounded with carbon dioxide and ether. In this way the liquid butylene was separated at −78° from the water which remained frozen to the sides of I. This was found to be more effective than fractionation in removing water. From J it was distilled to K for fractionation. The receivers (bulbs P to Q) were kept at −78°. The liquid in K was kept at −55 to 60° by means of an ether-bath cooled with carbon dioxide and stirred with a current of dry air. The liquid being fractionated was kept vigorously agitated by a magnetic stirrer. Under these conditions distillation proceeded slowly and a very satisfactory fractionation was obtained. By means of the manometers, M, the vapor pressures of any fraction or of the residue in K could be determined. Fractions of like vapor pressures were combined in K and refractionated. The heads and tails of each fractionation were rejected. The form of the receivers as shown at E was found to be very convenient. Their flexibility made it possible to agitate the contents when determining the vapor pressure of the fractions and enabled as many as three bulbs to be kept in the one Dewar flask for storage. The final constant boiling middle fraction was distilled into the critical temperature bulb, the melting point bulb, the dilatometer and the surface tension tube (A, B, C and D), which were then sealed off.

For identification purposes and as a test of the purity of the butylenes, the dibromide of the final middle fraction was made and its boiling point determined. A few drops of bromine were introduced into R through the tube S. R was cooled in ice and the butylene passed through until the bromine was decolorized. The tap on R was then closed. S was sealed off and the system was evacuated. A sufficient quantity of the dibromide was distilled into T, which was sealed off at the constriction just above the bulb. The vapor pressure curve of the dibromide was then determined in a manner described elsewhere.[2]

The product of the potassium hydroxide-*n*-butyl iodide reaction consisted of practically pure α-butylene boiling over a range of 0.2° at $-6°$. Several fractionations failed to isolate a higher or a lower boiling fraction. The final middle fraction taken as the pure compound boiled at $-6.1°$. The boiling point of the dibromobutane prepared from this fraction was 166°. (I. C. T. gives 166° as the boiling point of 1,2-dibromobutane).

β-**Butylene** was prepared by the method described by King.[3] The vapor of *n*-butyl alcohol was passed over lump pumice impregnated with glacial phosphoric acid. Dehydration proceeded rapidly at 250–280°. The product as indicated by the fractionation of a considerable quantity of the dibromide and of the condensed olefin itself was 85 to 90% β-butylene, the remainder being α-butylene. Some experiments on the dehydration of *n*-butyl alcohol by alumina at 250° gave a mixture of α- and β-butylene, the α-isomer predominating. It is worth mentioning that this is in agreement with the conclusion reached from some recent work on the dibromobutanes prepared in the same way.[4] The final middle fraction of the product from the phosphoric acid dehydration boiled at 1.0° and gave a dibromobutane boiling at 158°. These values are in good agreement with those in the literature for β-butylene and 2,3-dibromobutane.

γ-**Butylene** was prepared by the dehydration of *iso*butyl alcohol by alumina at 250 to 300° as described elsewhere.[5]

n-**Butane** was prepared by the hydrogenation of α- and β-butylene over a nickel catalyst. Small-mesh pumice was impregnated with nickel hydroxide precipitated from nickel nitrate (+1% of silver nitrate) solution with sodium hydroxide. The pumice with the adhering hydroxide was washed free of soluble salts, dried at 100° and reduced in the catalyst tube with hydrogen at 300°. The butylenes were hydrogenated at 150–200° and the butane was purified by slowly passing it a number of times through bromine, potassium hydroxide, sulfuric acid and phosphorus pentoxide. The product was then condensed and fractionated as described above.

*Iso***butane** was prepared in the same way by the hydrogenation of γ-butylene. These butane preparations afford a check on the purity of the butylenes. α-Butylene prepared from the iodide gave pure *n*-butane. A compound with identical properties was obtained when the products of the dehydration of *n*-butyl alcohol by alumina and phosphoric acid (a mixture of α- and β-butylenes) were hydrogenated in the same way.

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[2] Sutherland and Maass, *Trans. Roy. Soc.* (*Canada*), **20,** 499 (1926).

[3] King, *J. Chem. Soc.*, **115,** 1401 (1920).

[4] Lépingle, *Bull. soc. chim.*, **39,** 741 (1926).

[5] Coffin and Maass, *Trans. Roy. Soc.* (*Canada*), **21,** 33 (1927).

No γ-butylene is therefore formed in these preparations from *n*-butyl alcohol. That pure *iso*butylene is formed by the dehydration of *iso*butyl alcohol with alumina was proved by the fact that this olefin was hydrogenated to pure *iso*butane.

Determination of Physical Properties

Temperatures below —30° were measured with a platinum resistance thermometer calibrated at the ice, carbon dioxide and oxygen points.

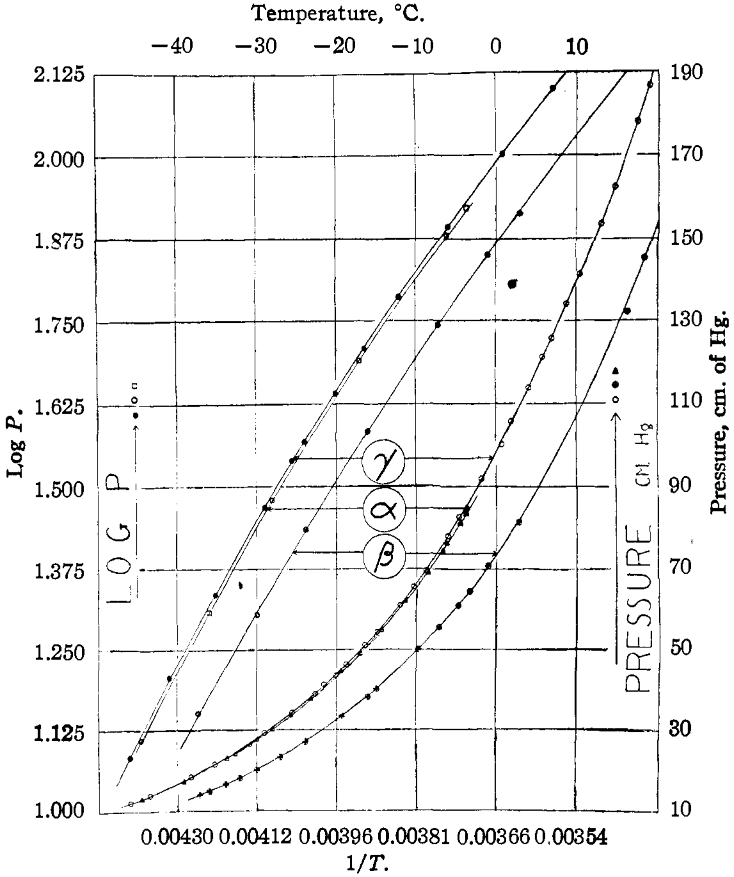
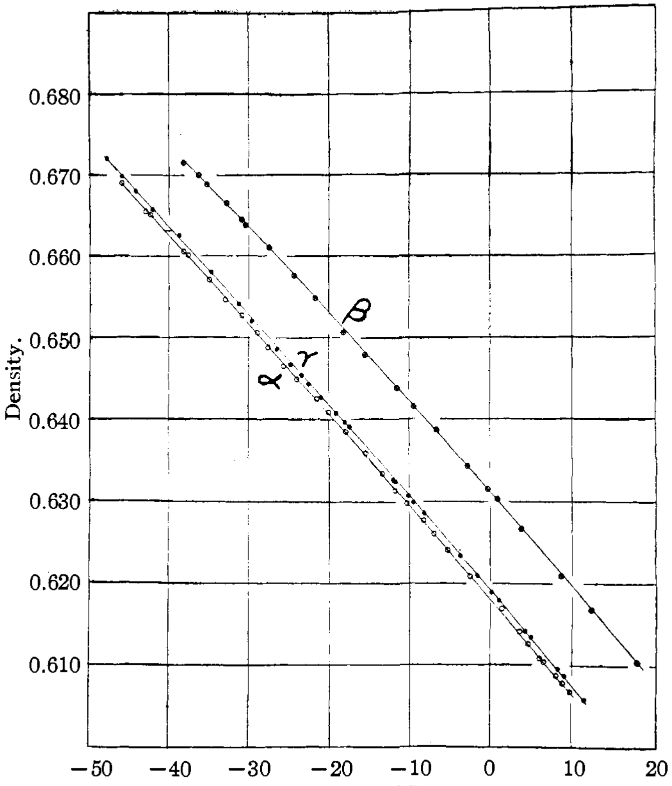


Fig. 2.

Intermediate temperatures were calculated by means of the Callendar–Barnes formula. The calibrations were checked from time to time. This thermometer agreed to within 0.1° with a standard mercury thermometer over the range 0 to 36°, so that all temperature measurements are probably correct to within at least 0.2°. Temperatures above −30° were measured with standard mercury thermometers graduated in tenths.

The constant temperature baths and the methods of determining density, surface tension, vapor pressures, melting points and critical



α = α-Butylene; β = β-butylene; γ = γ-butylene.

Fig. 3.

TABLE I

VAPOR PRESSURES OF α- AND β-BUTYLENE

α-Butylene				β-Butylene			
Temp., °C.	Press., cm. Hg	Temp., °C.	Press., cm. Hg	Temp., °C.	Press., cm. Hg	Temp., °C.	Press., cm. Hg
−3.7	83.37	−28.0	30.29	20.4	155	−23.8	27.22
−4.4	81.14	−29.9	27.69	18.3	145	−27.0	23.33
−6.1	76.02	−32.6	24.22	16.2	132	−30.0	20.14
−6.7	74.02	−33.7	23.00	2.9	81.4	−32.1	18.15
−8.5	69.13	−39.2	17.53	−1.0	70.74	−33.9	16.57
−11.3	62.17	−44.6	13.08	−3.3	64.46	−36.0	14.92
−14.3	54.96	−52.3	8.33	−4.7	60.98	−37.2	14.07
−17.0	49.13	−57.1	6.20	−7.1	55.52	−40.2	11.88
−19.4	44.51	−60.1	5.05	−9.7	49.97	−47.1	7.96
−23.1	37.77	−77.5	2.35	−14.9	40.27	−53.8	5.33
−25.6	33.80			−16.0	38.32	−60.1	3.53
				−19.2	33.47	−66.8	2.19
				−22.3	32.50		

temperatures were in the main those described by Maass and Wright.[1] The surface tension tube, of the type recommended by Richards, was carefully calibrated with dry ether and a mercury thread. Readings were made through a telescope and the tube was kept vertical by means of plumb bobs. As a great many readings were taken, the temperature range being covered at least twice for each substance, the values given in the table are those picked from the smooth temperature surface tension curve at 5° intervals. The weight of the substance in the vapor state and the expansion of the glass of the dilatometer were taken into account in the density determinations, for which an accuracy of one part in 2000 is claimed. All fractionations and measurements were made in the ab-

TABLE II

DENSITIES OF α- AND β-BUTYLENE AND NORMAL AND *Iso*BUTANE

α-Butylene		β-Butylene		*n*-Butane		*Iso*butane	
Temp., °C.	Density	Temp., °C.	Density	Temp., °C.	Density	Temp., °C.	Density
9.8	0.6067	17.8	0.6105	32.5	0.5644	25.3	0.5530
8.9	.6077	14.3	.6146	29.3	.5681	20.2	.5591
8.1	.6088	12.3	.6169	26.5	.5715	12.5	.5682
6.6	.6105	8.6	.6210	23.3	.5753	11.7	.5691
6.1	.6109	5.9	.6216	18.8	.5805	8.5	.5729
4.7	.6127	3.8	.6267	15.5	.5844	4.3	.5787
3.6	.6142	1.7	.6289	13.7	.5865	0.7	.5821
1.9	.6158	0.9	.6303	8.5	.5928	−1.3	.5845
−0.5	.6170	−0.3	.6315	1.3	.5998	−2.7	.5857
−1.4	.6189	−2.8	.6345	−0.8	.6020	−5.5	.5893
−2.5	.6209	−4.2	.6355	−3.5	.6048	−6.2	.5899
−4.1	.6229	−6.6	.6387	−6.7	.6081	−8.5	.5924
−5.2	.6241	−9.4	.6416	−10.5	.6121	−11.2	.5957
−6.9	.6261	−11.5	.6439	−14.4	.6159	−13.6	.5980
−8.2	.6277	−13.0	.6454	−19.0	.6207	−15.8	.6005
−10.3	.6298	−15.5	.6480	−24.6	.6265	−20.7	.6055
−11.8	.6314	−18.2	.6507	−30.2	.6318	−27.8	.6131
−13.4	.6334	−21.8	.6549	−32.8	.6346		
−15.4	.6359	−24.4	.6576	−34.4	.6362		
−17.9	.6385	−27.5	.6611				
−20.0	.6409	−30.4	.6638				
−21.5	.6426	−32.8	.6666				
−24.0	.6450	−35.3	.6689				
−25.7	.6466	−36.3	.6700				
−27.6	.6489	−38.2	.6715				
−29.0	.6507	−42.4	.6746				
−30.9	.6528						
−33.0	.6547						
−35.0	.6571						
−38.2	.6606						
−42.4	.6651						
−43.0	.6655						
−46.0	.6690						

sence of air and moisture and glass sealed connections were used throughout. All temperatures and pressures are corrected to standard conditions.

Vapor pressures are given in Table I, densities in Table II and surface tensions in Table III. The comparison of the isomers is best brought out by the graphs, Figs. 2 to 6, to which the values of γ-butylene previously published have been added. Figs. 4 and 6 show the variation of molecular surface energy with the temperature.

TABLE III

SURFACE TENSIONS OF α- AND β-BUTYLENE AND NORMAL AND *ISO*BUTANE

α-Butylene		β-Butylene	*n*-Butane		*Iso*butane	
Temp., °C.	γ, dynes	γ, dynes	Temp., °C.	γ, dynes	Temp., °C.	γ, dynes
20	12.60	13.51	29.7	11.28	23.3	9.80
15	13.21	14.16	26.0	11.67	19.1	10.51
10	13.85	14.82	18.7	12.58	12.4	11.39
5	14.49	15.49	10.1	13.64	9.8	11.61
0	15.14	16.15	0.5	14.88	4.5	12.31
−5	15.81	16.74	−2.4	15.21	−1.0	12.30
−10	16.46	17.42	−4.5	15.43	−8.5	13.81
−15	17.14	18.01	−7.8	15.77	−11.0	14.01
−20	17.82	18.70	−10.4	16.01	−15.0	14.80
−25	18.50	19.30	−15.0	16.72	−19.0	15.07
−30	19.20	20.00	−17.8	16.95	−24.4	15.96
−35	19.80	20.61	−28.1	18.21	−30.0	16.55
−40	20.50	21.22	−36.1	19.22	−36.3	17.30
−45	21.13	21.84				
−50	21.85	22.57				
−55	22.48					

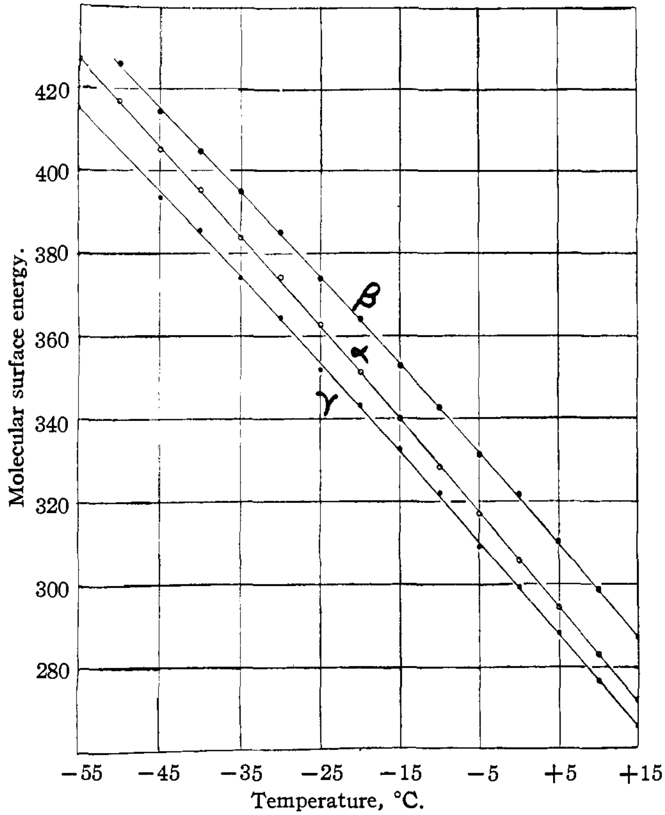
The physical properties of the butylenes and butanes together with those previously obtained by Maass and Wright for the two and three carbon compounds are compared in the following three tables. The melting points and critical temperatures of the butanes were taken from the literature.

TABLE IV

PHYSICAL PROPERTIES

Compound	M. p.	B. p.	Critical temp. Obs.	Critical temp. Calcd.	*Tb/Tc*
Ethane	−172.0	−88.3	35.0	34.6	0.60
Propane	−189.9	−44.5	95.6	91.6	.62
n-Butane	−135	−0.5	153.2	147.0	.64
*Iso*butane	−145	−10.2	133.7	129.5	.64
Ethylene	−169.4	−103.9	9.9	5.9	.60
Propylene	−185.2	−47.0	92.1	91.3	.62
α-Butylene	<−190	−6.1	144	145	.64
β-Butylene	−127	1.0	155	156	.64
γ-Butylene	−146.8	−6.6	143.5	147	.64

The alternating melting point in the normal paraffin series is seen in the low melting point of propane as compared to ethane and normal butane. The olefins, with the rather surprising exception of α-butylene, have higher melting points than the corresponding paraffins. α-Butylene was not frozen, although kept for many hours with frequent agitation in the neighborhood of −210°. The liquid becomes very viscous but not glassy at this temperature,[6] and may be supercooled, but it is probable that its melting point is considerably below that of normal butane. The rule that the *iso* compound melts at a higher temperature than its straight chain isomer does not hold in the case of the butanes. The butylenes, however, follow this rule as well as that which states that the most symmetrical isomer has the highest melting point.



α = α-Butylene; β = β-butylene; γ = γ-butylene.

Fig. 4.

The *iso* compound in both cases is the more volatile, in agreement with the general rule. It is of interest to note that the ratio Tb/Tc has exactly the same value for all of the compounds containing the same number of

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[6] This substance, which is easily prepared pure, should make an excellent thermometric liquid for low temperature work.

carbon atoms. The critical temperature determined experimentally and the value calculated from surface tension data agree very well considering the relatively low temperatures at which the surface tensions were determined. The average value calculated differs by only −1.7° from that found.

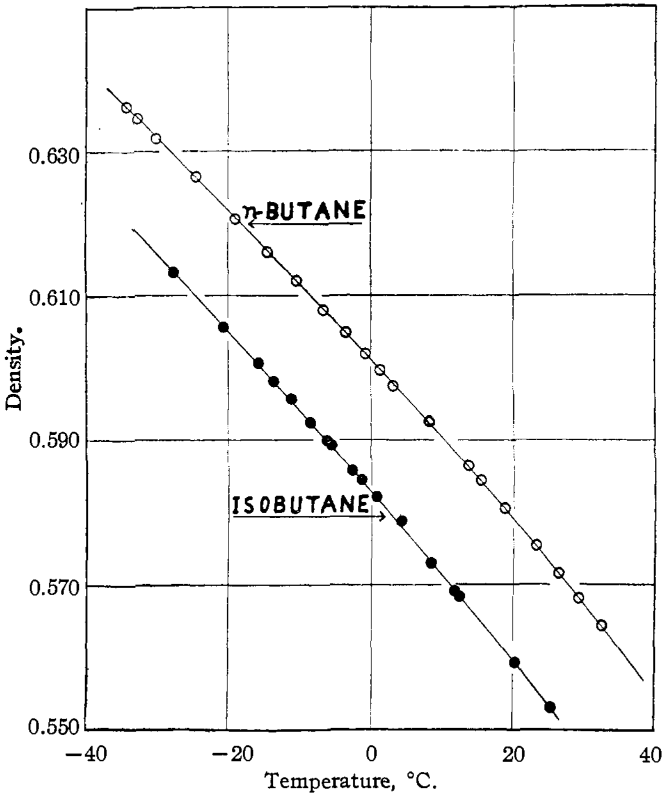

Fig. 5.

TABLE V

PHYSICAL PROPERTIES

Compound	Latent heat	Ramsay and Shields constant	Trouton's constant	Surface tension at the b. p.	Total surface energy
Ethane	3880	1.98	21.0	16.05	45.7
Propane	4700	2.15	20.6	15.63	50.3
n-Butane	5597	2.21	20.5	14.90	47.8
*Iso*butane	5480	2.23	20.8	14.10	47.2
Ethylene	3510	2.14	20.8	16.50	47.7
Propylene	4600	2.12	19.0	16.70	49.7
α-Butylene	5400	2:21	20.2	15.95	51.1
β-Butylene	5400	2.14	19.7	16.78	51.2
γ-Butylene	5200	2.15	19.7	15.72	49.8

The values for the Ramsay and Shields constant and for Trouton's constant show that all these liquids distinctly belong to the non-associated type. The molecular latent heats given were calculated from the vapor pressure data.

The surface tensions at the boiling point and the total surface energies show that unsaturation increases these properties. One would expect this from the greater polarity induced by the unsaturation. β-Butylene, the symmetrical compound, has a distinctly higher surface tension than either of its isomers. This is to be expected as is also the fact that the two *iso* compounds have lower surface tensions than their normal isomers. The total surface energies show no marked regularity and it is probable that only after the six-carbon compound will the constant value for the series be reached.

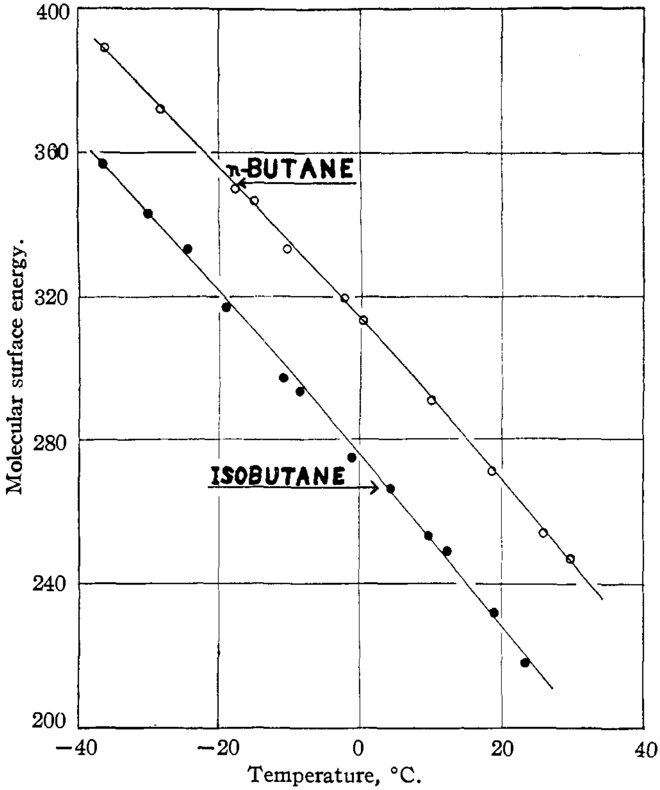

Fig. 6.

A comparison of the molecular volumes determined experimentally with those calculated on the basis of Kopp and Le Bas[7] shows that espe-

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[7] Le Bas, monograph, "The Molecular Volumes of Liquid Chemical Compounds," Longmans, Green and Co., 1915.

TABLE VI

PHYSICAL PROPERTIES

Compound	Molecular volume at the b. p. Found	Calcd. Kopp	Calcd. Le Bas	Molecular volume at the m. p. Found	Calcd.
Ethane	54.9	55	51.6	32.8	41.6
Propane	75.0	77	73.7	41.3	59.4
n-Butane	96.3	99	95.9	76.0	77.2
*Iso*butane	97.6	99	95.9	78.1	77.2
Ethylene	49.1	45.5	44.2	32.4	35.6
Propylene	69.0	67.5	66.3	38.7	53.4
α-Butylene	89.5	89.5	87.8	..	71.2
β-Butylene	88.9	89.5	87.8	72.5	71.2
γ-Butylene	89.3	89.5	87.8	71.6	71.2

cially for the two- and three-carbon compounds, Kopp's values are in far better agreement. It is to be expected that Le Bas' values for the higher members should approach more nearly those of Kopp because he uses the same value for the CH_2 group. In the calculation of Kopp's values for the olefins, 1.5 units were added for unsaturation. This evidently was not enough for the first members. It is quite evident that Le Bas' contention that unsaturation does not cause an increase of volume cannot be maintained.

The values found by extrapolation for the molecular volume at the melting point and those calculated with Le Bas' figures are given in the last two columns of the above table. The four carbon compounds show fair agreement between the observed and calculated values but the others differ widely. The alternation emphasized by Le Bas is a simple consequence of the alternation of the melting points. The temperature coefficient of the density for the four carbon compounds is 0.0011 as compared to 0.0033 for the three and 0.0044 for the two carbon compounds.

Acknowledgment is made of a Bursary granted to one of us by the Research Council of Canada.

Summary

A number of the physical properties of the three butylenes and the two butanes have been accurately determined over a wide range of temperature. These quantities, together with those previously obtained for ethane and ethylene and propane and propylene, are discussed.

MONTREAL, CANADA