

2. Measurements of equivalent conductance of various acids and of sodium chloride have been made and negligible differences between the direct current values and the values by Kohlrausch's method are found except for solutions over 0.5 *N* in sulfuric and hydrochloric acids.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF MCGILL UNIVERSITY.]
SOME PHYSICAL PROPERTIES OF HYDROCARBONS CONTAINING TWO AND THREE CARBON ATOMS.

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Introduction.—As some of the simpler hydrocarbons had been prepared in the pure state for an investigation on molecular compound formation and as the surface tensions, previously measured by one of us¹ are not exact in the light of Richards'² recent work, it has been considered worth while to measure their physical properties. The interest lies principally in the fact that the particular compounds investigated, ethane, ethylene, acetylene, propane, propylene and allylene, are the first members of homologous series of which the physical properties of the higher members only are well known. The effect on these properties of passing from saturation to various degrees of unsaturation is brought out by this investigation. Densities and surface tensions have been measured over a wide temperature range and the melting points determined in every case. With compounds where doubt existed as to the true boiling point, vapor-pressure and critical-temperature determinations have been made.

Preparation of Hydrocarbons.—Ethane and propane were prepared by the action of the zinc-copper couple on ethyl iodide and propyl iodide, respectively; ethylene and propylene by the catalytic influence of aluminum oxide on the corresponding purified alcohols at a temperature of 350°; and acetylene by the action of water on calcium carbide. An especially pure sample of allylene was available for this work. It had been prepared for a previous investigation by the action of methyl iodide on sodium acetylide in liquid ammonia; reference to this method of preparation, which was first used by Lebeau and Picon,³ has been made in greater detail in another paper.⁴

Purification of Hydrocarbons.—The hydrocarbons were collected by displacement of water in large gasometers and subjected to a very careful purification. Ethane and propane were passed through spirals cooled to -78°, then a number of times over the zinc-copper couple moistened with alcohol at 50° until free from iodide, then through conc. silver nitrate and conc. alkali solutions, finally dried by phosphorus pentoxide, and condensed.

The ethylene and propylene, saturated with water vapor, when dried by phosphorus pentoxide and condensed was still found to contain a considerable amount of impurity. After boiling off the ethylene from a large amount of distillate a sufficient

¹ McIntosh and Maass, *THIS JOURNAL*, **36**, 737 (1914).

² T. W. Richards and L. B. Coombs, *ibid.*, **37**, 1656 (1915).

³ Lebeau and Picon, *Compt. rend.*, **156**, 1077 (1913).

⁴ To be published later.

quantity of liquid impurity remained with a boiling point of from 10° to 20° to allow a molecular-weight determination to be made. The freezing-point method was used with benzene as solvent. The molecular weight was practically constant at various concentrations and approximated to a compound of the formula $(C_2H_4)_3$. The darkened appearance of the phosphorus pentoxide in the tube gave the indication that it might have given rise to the polymer. Ethylene when in the gaseous state and dry is apparently without action on phosphorus pentoxide. Care was taken to remove by an adequate number of distillations the possibility of polymerized products in the ethylene and propylene used in this investigation. The acetylene was purified by the ordinary methods.¹

The purity of the final products was determined by density determinations of the gases; for example, the allylene at a pressure of 71.62 cm. of mercury and a temperature of 20° was found to have a density corresponding to a molecular weight of 40.58, and at a pressure of 25.05 cm. and a temperature of 20° it was found to have a molecular weight of 40.24, indicating a molecular weight when under ideal conditions of 40.05, compared to the theoretical molecular weight under the same conditions of 40.0. Finally the pure hydrocarbons were distilled 5 times *in vacuo*, the middle portions being retained in each instance. Glass sealed apparatus, which had been thoroughly dried *in vacuo*, was used throughout. The final condensation was made in the evacuated surface tension, density, etc., apparatus which was then sealed off.

Measurement of Temperature.—The temperatures throughout were measured by use of a platinum resistance thermometer. The thermometer was standardized by the 3 fixed temperatures given by steam, ice-water and solid-carbon-dioxide-ether under atmospheric pressure, the Calendar-Barnes formula being used for the calculations of intermediate temperatures. This was tested out by the boiling point of liquid air of 37.0% oxygen content and the value -188.8° was given by the Barnes-Calendar formula compared to -189.0° as found by Baly. Thus all the temperatures measured were probably correct to 0.2° absolute as a maximum.

Constant-Temperature Baths.—Temperature baths to be constant to 0.1° at any particular temperature were required throughout the range of temperature from 0° to -200° . From 0° to -78° the bath consisted of ether, contained in a Dewar flask stirred by a current of dry air, the temperature being hand-regulated by the addition of small amounts of solid carbon dioxide.² It was found to be advantageous to use instead of pure ether an alcohol-ether solution containing 20% of alcohol. Water is insoluble in pure ether at low temperatures, so that moisture from the atmosphere condensing in the ether-bath rendered the latter opaque. Alcohol-ether solution, on the other hand, dissolves considerable quantities of water even at -80° without becoming viscous as alcohol does at this temperature, so that this bath remains transparent throughout the experiment.

From -78° to -160° the bath consisted of the first distillate from petroleum ether condensed by use of a salt-ice mixture as cooling agent. The temperature of this bath was regulated by the addition of liquid air, as explained diagrammatically in a previous paper.³ Below -160° the petroleum ether became very viscous and generally unsatisfactory.

From -160° to liquid-air temperature the bath consisted of liquid propylene cooled by liquid air, as shown in Fig. 1. The propylene (liquid) P is contained in a large test-tube B held in a vertical position by means of a stiff wire W. A is an unsilvered Dewar flask which contains a quantity of liquid air L. It is held in position as shown

¹ O. Maass and J. Russell, *THIS JOURNAL*, **40**, 1569 (1918).

² O. Maass and D. McIntosh, *ibid.*, **35**, 536 (1913).

³ O. Maass and D. McIntosh, *ibid.*, **36**, 738 (1914).

such that it may be raised or lowered at will. The propylene is cooled by contact with the liquid air and by intermittent raising and lowering of the Dewar flask the temperatures, as read by Thermometer T, can be maintained at any temperature, between -160° and the boiling point of liquid air, to within 0.1° provided the test-tube be of thick glass and the propylene be subjected to vigorous stirring by means of a stiff steel wire. Propylene used for such a bath can be conveniently stored in a gasometer and can be used over and over again, if care is taken to dry it before each condensation.

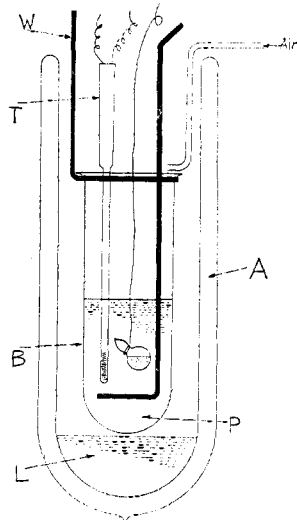


Fig. 1.

From the boiling point of liquid air to -205° the bath consisted of liquid air in a test-tube surrounded by liquid air which could be cooled by boiling under various degrees of reduced pressure. For temperatures below -200° the air-bath must necessarily be closed off from the atmosphere on account of the heat changes caused by the rapid condensation of the air of the room in its vicinity.

Determination of Melting Points of the Hydrocarbons.

For the determination of the melting points of the hydrocarbons glass bulbs were used with volumes of about 2 cc., into which, while evacuated, the hydrocarbons had been distilled.

The bulbs, held by wires, were in turn placed in the temperature bath most suitable, as found by trial and error, and the bulb contents kept thoroughly stirred by vigorous agitation. The liquid hydrocarbon was first frozen and then the bath was allowed to warm up gradually until a temperature was reached such that when maintained for 5 minutes liquid and solid remained in equilibrium. This temperature was taken as the melting point of the compound. The experimental values found for this constant are indicated in Table I.

TABLE I.
MELTING POINTS OF THE HYDROCARBONS.

	$^{\circ}$ C.		$^{\circ}$ C.
Ethane.....	-172.0	Propane.....	-189.9
Ethylene.....	-169.4	Propylene.....	-185.2
Acetylene.....	- 81.8	Allylene.....	-104.7

Mention has been made in the literature that propane and propylene are still liquid at -195° . The bulbs containing these hydrocarbons were first of all placed directly in liquid air boiled under reduced pressure (less than 2 cm. of mercury), our thermometer indicating a temperature of -215° ; under these conditions it was only after several hours that solidification occurred. The bulbs were then transferred to the temperature bath and the melting points found to be -189.9° and -185.2° , respectively, showing that these liquids had supercooled *circa* 25° . It is interesting to note that, after the first solidification, on subsequent freezing the amount of supercooling before a solid appeared was considerably less.

The melting point of the freshly distilled allylene was found to be -104.7° . The melting point of a sample of allylene prepared a year earlier was also determined during the present investigation and found to be the same as that of the freshly dis-

tilled, thus showing that no change, such as polymerization, had occurred although the liquid had been kept for a year at room temperature.

Unsaturation causes a rise in melting point. In the 2- and 3-carbon hydrocarbons, passing from saturation to ethylene linkage causes a rise of 3° to 4°, from ethylene linkage to acetylene linkage causes a rise of 81° to 87°, showing that there is a slight increase in secondary valences in the first case, whereas there is a marked increase in the second case. It is to be noted also that in each of the series the 3-carbon compound has the lowest melting point.

Determination of Vapor Pressures and Critical Temperatures of the Hydrocarbons.

The vapor pressures of the hydrocarbons at various temperatures, especially those above the boiling point, were required in order to apply corrections in measurements of physical constants described further on and those which are not recorded in the literature were measured. The manometer which was used to measure the high pressures (up to 10 atmospheres) consisted of a U-tube closed at one end and half filled with mercury, the free end being connected to a bulb containing the liquid hydrocarbon. The closed portion contained a known mass of air whose volume for different positions of the mercury had been calibrated.

The vapor-pressure curve of allylene was determined, and as this has not been previously measured, the results are recorded below.

TABLE II.
Vapor Pressures of Allylene at Various Temperatures.

Temp. ° C.	Press. in cm. of Hg.
—73.3	7.15
—64.8	11.8
—58.4	17.1
—51.75	24.4
—41.20	40.8
—40.85	42.1
—31.20	64.5
—30.85	66.3
—21.30	99.2
—20.80	101.4
—13.20	136.5

The vapor pressures of ethane are also given below, since the values previously determined by one of us (b. p. —88.3°) were in fair agreement with those of Burrell and Robertson¹ (b. p., —89.5°), but differed from those recently obtained by Cardoso² (b. p. —84.1°).

¹ Burrell and Robertson, *THIS JOURNAL*, **37**, 1893 (1915).

² Cardoso, *J. Chem. Soc.*, **104**, II, 110 (1912).

TABLE III.
Vapor Pressures of Ethane at Various Temperatures.

Temp. ° C.	Press. in cm. of Hg.
—100.8	36.45
—95.5	50.40
—90.6	66.45
—88.4	75.30
—79.7	117.70
—74.1	154.70
—72.7	165.45

These results give a boiling point for ethane of —88.3°.

The vapor pressures of propane and propylene for temperatures above the boiling point are recorded in Table IV and Table V, respectively.

TABLE IV.
Vapor Pressures of Propane at Various
Temperatures Above the Boiling Point.

Temp. ° C.	Press. in cm. of Hg.
—43.4	85.7
—42.9	87.0
—42.3	89.4
—38.4	105.0
—30.85	136.8
—23.1	202.1

TABLE V.
Vapor Pressures of Propylene at Various
Temperatures Above the Boiling Point.

Temp. ° C.	Press. in cm. of Hg.
—37.45	111.0
—34.4	130.7
—27.85	167.1
—15.65	257.0
+0.1	426
+5.75	524
+7.5	552
+10.0	594

Our values for the vapor pressures of ethylene, acetylene, propane and propylene at various temperatures below their boiling points were found to be in fair agreement with those published by Burrell and Robertson.¹ Since the vapor pressures of ethylene and acetylene above the boiling points were only of interest in connection with small corrections required in the calculations from later measurements the values determined by Villard² were used.

Because of the considerable disagreement in the values for the critical temperatures of these hydrocarbons, as given in the literature, these constants were redetermined in the usual way and are included in the following table.

TABLE VI.
Boiling Points and Critical Temperatures of the Hydrocarbons.

	t_B ° C.	t_C ° C.	L (cal.)	$\frac{t_B}{t_C}$	$\frac{L}{t_B}$
Ethane.....	—88.3	35.0	3800	0.60	20.6
Ethylene.....	—103.9	9.9	3510	0.60	20.7
Acetylene.....	—83.6	36.5	5150	0.61
Propane.....	—44.5	95.6	4500	0.62	19.7
Propylene.....	—47.0	92.1	4600	0.62	20.3
Allylene.....	—27.5	127.9	5230	0.61	21.3

¹ *Loc. cit.*

² Villard, *Ann. chim. phys.*, 7, 10,395 (1897).

In Table VI, Col. 1 gives the values of the boiling points (t_B) of the hydrocarbons investigated. They are in fair agreement with those found by Burrell and Robertson. The critical temperatures (t_C) are tabulated in Col. 2. Of these the value for acetylene is taken from a determination by McIntosh¹ and that for ethane from Dewar.² The others determined by the authors differ by 2° or 3° from previously determined values except in the case of ethylene, which differs by only a few tenths of a degree. Col. 3 gives the values for the molecular latent heats of evaporation, all except that for allylene being taken from Burrell and Robertson's results. It is to be noted that the value given for acetylene includes the molecular latent heat of fusion.

Col. 4, $\frac{t_B}{t_C}$, shows that the boiling points are approximately equal fractions of the critical temperatures. The last column shows that Trouton's rule applied to the 2- and 3-carbon hydrocarbons gives values for unassociated liquids, only allylene indicating the existence of some association. The latent heat of fusion for acetylene not being known, the ratio $\frac{L}{t_B}$ could not be calculated.

It is seen that in both the 2- and 3-carbon hydrocarbons those with the ethylene linkage have the lowest boiling point. The ethylene linkage, however, has a small effect on the latent heat of evaporation, whereas the acetylene linkage increases this constant considerably.

Determination of Densities of the Liquid Hydrocarbons.

The densities of the liquid hydrocarbons were measured by the dilatometer method.

The dilatometer consisted of a thick-walled glass bulb sealed to a graduated capillary of uniform bore. The dilatometer was glass sealed to an apparatus consisting of a vacuum pump and a tube containing the pure liquid hydrocarbon. After evacuation the latter was distilled into the dilatometer cooled by liquid air. When a sufficient quantity had been condensed the dilatometer was sealed off just above the capillary.

The height of the meniscus in the capillary was then measured over the desired temperature range, bulb and capillary being completely immersed in one of the temperature baths described above and contained in an unsilvered Dewar flask. The liquid was then allowed to warm up to room temperature and accurately weighed, the bulb having been chosen so as to withstand high pressures. After cooling again by liquid air the tip was broken off, the liquid allowed to evaporate, dry air passed through the bulb and the latter weighed. After making the proper correction for weight of the air, the weight of the hydrocarbon was accurately known. The volume occupied by the liquid was given by the position the meniscus had occupied in the capillary which, together with the bulb, had been accurately calibrated. This volume was corrected for the temperature expansion of the glass. The weight was corrected by taking account of the weight of the vapor above the liquid. An example will illustrate the method of calculation and the accuracy attained.

¹ McIntosh, *J. Phys. Chem.*, **11**, 306 (1907).

² Dewar, *Phil. Mag.*, [5] **18**, 210 (1884).

One mm. of the capillary corresponded to 0.01 cc. so that the volumes could be read to 0.001 cc. In the particular example chosen for illustration of the method used the volume occupied by liquid propylene at -27.5° was found by calibration to be 3.3965 cc. at 20° and the true volume on correcting for the contraction of the glass to -27.5° to be 3.3925 cc. The weight of the bulb and propylene was 26.1093 g., that of the glass and air 24.1255 g., giving, on correcting for the weight of the air, 1.9890 as the weight of the propylene. An error which is made at times by those using this method is in not allowing for that portion of the substance which exists in the vapor state. This error may in some cases, especially above the boiling point, equal a few tenths of 1%. In this particular case the closed space above the liquid had a volume of 0.643 cc., and taking the vapor pressure of propylene as 168 cm. of mercury at this temperature, the weight of the substance in the vapor state is found to be 0.003 g. and the density $1.9860 \div 3.3925 = 0.5854$. The accuracy of the determinations is better than 1 in 2000.

The densities experimentally determined are tabulated below.

TABLE VII.
Densities of the Liquid Hydrocarbons at Various Temperatures.

	Temp. °C.	d _t .		Temp. °C.	d _t .
Ethane.....	-108.2	0.5719	Propane.....	-78.2	0.6238
	-105.8	0.5685		-68.3	0.6124
	-99.7	0.5608		-63.2	0.6063
	-98.2	0.5589		-59.5	0.6022
	-95.3	0.5549		-58.7	0.6013
	-89.05	0.5472		-53.3	0.5957
	-88.1	0.5458		-47.95	0.5892
	-83.1	0.5392		-45.9	0.5869
	-78.8	0.5338		-42.4	0.5831
	-74.0	0.5272	-38.7	0.5783	
			-34.35	0.5735	
Ethylene.....	-108.7	0.5762	-30.1	0.5685	
	-103.7	0.5696	-24.5	0.5615	
	-99.05	0.5630			
	-94.3	0.5559	Propylene.....	-78.2	0.6486
	-89.4	0.5482		-58.5	0.6247
	-84.05	0.5400		-48.5	0.6109
	-74.2	0.5247		-37.45	0.5973
	-69.45	0.5172	-34.4	0.5937	
			-27.85	0.5854	
Acetylene.....	-81.8	0.6181	-15.65	0.5691	
	-80.3	0.6154	0	0.5473	
	-79.15	0.6136	19	0.5183	
	-76.15	0.6093			
	-70.85	0.6009	Allylene.....	-55.3	0.7128
	-66.35	0.5935		-52.0	0.7093
	-62.5	0.5875		-50.85	0.7076
	-56.0	0.5779		-40.35	0.6943
-55.2	0.5763	-32.3		0.6843	
		-25.3	0.6759		
		-19.3	0.6682		
		-12.9	0.6600		

The values of the densities given in Table VII were plotted against temperature on a scale such that 1 mm. corresponded to a change of 0.0001 in density, which made it possible to read directly from the resulting graphs the density at any desired temperature without the necessity of using a mathematical equation for this purpose. Fig. 2 represents a reduced copy of the graphs used.

The densities found for liquid ethane, ethylene and acetylene at the lower temperatures agree within 1% with the determinations of McIntosh¹ and Maass.¹ The densities at the boiling points for some of the 2- and 3-carbon hydrocarbons have been determined by others. Considering the precautions taken and the number of determinations made over a wide temperature range, we believe that our values are the more nearly correct ones. Thus Ladenburg found the density of ethylene at -102.5° to be 0.609, McIntosh and Maass found it to be 0.565 and we found the value 0.5679 at the same temperature.

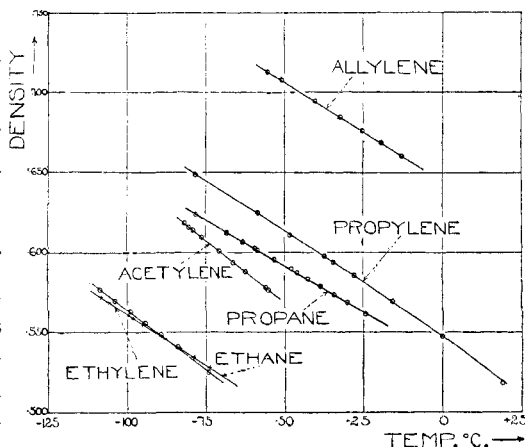


Fig. 2.

Thus Ladenburg found the density of ethylene at -102.5° to be 0.609, McIntosh and Maass found it to be 0.565 and we found the value 0.5679 at the same temperature.

TABLE VIII.

Densities and Molecular Volumes of the Hydrocarbons at the Boiling Point.

	t_B , °C.	d_B .	V_M (exp.).	V_M (calc.).	Differ- ence.	$\frac{\Delta V}{\Delta T}$.
Ethane.....	-88.3	0.5459	54.95	55	...	0.0044
Propane.....	-44.5	0.5853	75.2	77	-1.8	0.0033
Ethylene.....	-103.9	0.5699	49.1	44	+5.1	0.0045
Propylene.....	-47.0	0.6095	68.9	66	+2.9	0.0034
Acetylene.....	-83.6	0.6208	41.9	33	+8.9	0.0046
Allylene.....	-27.5	0.6785	59.0	55	+4.0	0.0027

In Table VIII the first column represents the boiling points of the hydrocarbons, the second column gives the values found for the densities (D_B) at the boiling points, the third gives the molecular volumes (V_M) calculated from the observed densities, the fourth gives the calculated volume (V_M^1) on the basis of $C=2H=11$, the fifth the difference between the experimental and calculated values, and the last ($\Delta V/\Delta T$) the temperature coefficients of the specific volume at the boiling point.

As is seen, experimental and calculated values for ethane agree abso-

¹ *Loc. cit.*

lutely, whereas the value observed for propane is smaller by 1.8 units. Le Bas¹ has already pointed out that the difference between the experimental and calculated values of the saturated hydrocarbons increases till hexane is reached and then decreases, that is, the 5- and 6-carbon chain molecules occupy a relatively smaller volume than those of greater and shorter lengths. Le Bas denies the increase of volume due to unsaturation by assigning the value of 3.70 to hydrogen and 14.8 to carbon. Now even when these values are used in the cases of ethylene, propylene and acetylene the experimental results are larger by 4.7, 2.3, 4.9 units, respectively. In the unsaturated series it seems probable that here also lengthening the carbon chain causes a decrease in volume of the molecule, thus masking the increase due to unsaturation. After the 6-carbon chain has been passed, from the analogy to the saturated hydrocarbons the unsaturation should again give rise to an increase in volume; and this is the case, for the experimental value of octylene is 177.6, therefore 1.6 units higher than the calculated value. If the 6-carbon chain compound shows a relative decrease in volume one would expect a similar decrease and to a greater extent in benzene thus effectively masking the increase due to unsaturation. It seems probable from our results that unsaturation is accompanied by an increase in volume which may in some cases be masked by another influence.

The values of the temperature coefficients of the specific volumes ($\Delta V/\Delta T$) at the boiling points as given in the last column of the table are, of course, dependent on the critical temperatures of the hydrocarbons. This makes possible the calculation of the specific volumes of any of the hydrocarbons at any temperature, provided the specific volume at any one temperature is known and the specific volumes for one of the other hydrocarbons is known at all temperatures. This was one of the deductions made by van der Waals from his equation of corresponding states, namely, that $(V_1 - V_2)/V_2 = (v_1 - v_2)/v_2$, where V_1 and V_2 are the specific volumes of one liquid, and v_1 and v_2 are the specific volumes of another liquid where V_1 , v_1 and V_2 , v_2 are measured at the same corresponding temperatures. As a test the propylene was chosen as the standard, the experimental value for the specific volume of the hydrocarbons taken at one temperature and the specific volume calculated at another temperature 30° higher. This value was then compared to that actually found by experiment. The following table shows the agreement between the calculated and experimental values, the greatest discrepancy being only 0.3% in the case of propane and in all other cases being within the experimental error of 0.1%.

¹ Le Bas, monograph "The Molecular Volumes of Liquid Chemical Compounds," Longmans, Green and Co., 1915.

TABLE IX.

Data on the Agreement between Experimental and Calculated Values for Specific Volumes.

	Temp. and sp. vol. of liquid hydrocarbon.		Corresponding temps. and sp. vol. of liquid propylene.		Calc.	Exptl.	Diff.
	° C.		° C.				
Ethane	-105	1.761	-73.9	1.554
	-75	...	-38.3	1.671	1.893	1.892	+0.001
Ethylene.....	-110	1.730	-62.7	1.589
	-80	...	-23.9	1.724	1.877	1.874	+0.003
Acetylene.....	-83	1.613	-48.8	1.634
	-53	...	-13.5	1.767	1.744	1.746	-0.002
Propane.....	-60	1.659	-62.0	1.591
	-30	...	-32.3	1.692	1.764	1.759	+0.005
Allylene.....	-53	1.408	-72.7	1.558
	-23	...	-45.4	1.646	1.487	1.486	+0.001

Determination of Surface Tensions of the Hydrocarbons.

The apparatus used for the measurement of surface tensions was essentially that designed by Richards¹ with the following slight modifications necessitated by the nature of the liquids under investigation.

The capillary and the lower portion of the wide tube were etched by graduated marks on their surfaces so that the height of the liquid could be read directly. The whole apparatus, after an adequate amount of the hydrocarbon had been distilled into it in the manner previously described, was sealed off at a point above the union of the capillary to the exit of the larger tube. The size of the apparatus made it possible to immerse it completely in the requisite temperature bath at the time of measurement. The inside diameter of the larger tube was 3.1 cm. which is 0.7 cm. smaller than that required to be equivalent to an unrestricted flat surface. The apparatus was calibrated not only by obtaining the diameter of the capillary by means of mercury but also by a liquid whose surface tension had been accurately determined.²

The capillary was shown to have a uniform radius throughout its length of 0.0276 cm. by measurement of the lengths and corresponding weights of mercury. Taking Richards' value of 28.9 as the surface tension of pure benzene and calibrating the capillary by measurement of the surface tension of benzene, the radius was calculated to be 0.0272 cm. This last value was used as giving the true value of the radius for the experimental conditions. To test this out the surface tension of ethyl ether was measured, this liquid being chosen because its surface tension is of the same order of magnitude as those of the hydrocarbons. The value of 17.0 dynes was found at 20° as compared to the accepted value 17.1 dynes, hence the values of the surface tensions tabulated below may be taken as being correct to within 0.5% of the absolute values.

In Table X, Col. 1 gives the temperature (t), at which the measurements were taken, Col. 2 the height (h) of the meniscus above the surface of the liquid in the wide tube, Col. 3 the density (d_l) of the liquid, Col. 4 the density (d_g) of the gas as calculated from the vapor pressures and

¹ Richards, THIS JOURNAL, 37, 1656 (1915).

² Richards, *loc. cit.*

TABLE X.
Surface Tensions and Molecular Surface Energies of the Hydrocarbons at Various Temperatures.

	$^{\circ}\text{C.}$	$h.$	$d_l.$	$d_g.$	$d_l - d_g.$	$\gamma.$	$\gamma(V_M)^{2/3}.$
Ethane.....	-108.2	2.51	0.5718	0.0006	0.5712	19.17	268.6
	-105.8	2.49	0.5688	0.0008	0.5680	18.90	265.9
	-105.1	2.47	0.5679	0.0008	0.5671	18.73	263.6
	-99.7	2.40	0.5608	0.0011	0.5597	17.95	254.9
	-98.2	2.38	0.5589	0.0012	0.5577	17.74	252.5
	-95.3	2.31	0.5552	0.0014	0.5538	17.10	244.4
	-89.05	2.23	0.5469	0.0019	0.5450	16.25	234.5
	-88.1	2.20	0.5457	0.0020	0.5437	16.00	231.3
	-83.1	2.12	0.5391	0.0025	0.5366	15.22	221.8
	-78.8	2.04	0.5334	0.0030	0.5304	14.48	212.5
	-74.0	1.96	0.5271	0.0037	0.5234	13.73	203.1
	Ethylene....	-112.4	2.33	0.5822	0.0011	0.5811	18.10
-108.9		2.28	0.5765	0.0014	0.5751	17.54	233.4
-104.9		2.19	0.5712	0.0018	0.5694	16.67	223.4
-104.1		2.18	0.5701	0.0019	0.5682	16.57	222.2
-97.15		2.04	0.5601	0.0026	0.5575	15.22	206.5
-92.75		1.96	0.5534	0.0032	0.5502	14.44	197.4
-88.3		1.88	0.5465	0.0040	0.5425	13.66	188.5
Acetylene...		-81.8	2.34	0.6180	0.0020	0.6160	19.28
	-80.3	2.31	0.6156	0.0021	0.6135	18.92	229.9
	-79.15	2.29	0.6138	0.0022	0.6116	18.76	228.0
	-76.15	2.23	0.6091	0.0025	0.6066	18.09	221.0
	-70.85	2.15	0.6008	0.0031	0.5967	17.16	211.4
	-66.35	2.06	0.5937	0.0037	0.5900	16.30	202.6
	-62.5	1.98	0.5877	0.0044	0.5833	15.45	193.4
	-56.0	1.87	0.5775	0.0057	0.5718	14.31	181.1
Propane.....	-71.0	2.39	0.6155	0.0010	0.6145	19.63	338.3
	-68.0	2.36	0.6121	0.0011	0.6110	19.28	333.2
	-66.1	2.32	0.6099	0.0012	0.6087	18.89	324.8
	-63.5	2.29	0.6069	0.0013	0.6056	18.55	322.5
	-59.55	2.22	0.6024	0.0014	0.6010	17.84	311.8
	-53.7	2.13	0.5958	0.0018	0.5940	16.96	298.6
	-49.1	2.08	0.5905	0.0021	0.5884	16.34	289.3
	-46.1	2.02	0.5871	0.0024	0.5847	15.81	280.9
	-43.9	1.99	0.5846	0.0026	0.5820	15.50	276.3
	-39.1	1.94	0.5790	0.0030	0.5760	14.95	268.3
	Propylene...	-62.0	2.26	0.6285	0.0011	0.6274	18.93
-57.8		2.20	0.6233	0.0014	0.6219	18.30	303.0
-54.8		2.16	0.6194	0.0016	0.6178	17.85	296.8
-51.5		2.12	0.6151	0.0019	0.6132	17.39	290.5
-49.5		2.08	0.6126	0.0020	0.6106	17.03	285.2
-48.1		2.06	0.6108	0.0021	0.6087	16.82	282.3
-45.0		2.03	0.6069	0.0024	0.6045	16.46	277.4
-41.6		1.97	0.6026	0.0026	0.6000	15.82	267.9
-36.5		1.90	0.5963	0.0034	0.5929	15.11	257.8
-29.6		1.82	0.5876	0.0043	0.5833	14.21	244.7
-22.9		1.71	0.5787	0.0053	0.5734	13.17	229.1

TABLE X (continued).

	t , °C.	h .	d_l .	d_g .	$d_l - d_g$.	γ .	$\gamma(V_M)^{2/3}$.
Allylene.....	-52.6	2.38	0.7098	0.0007	0.7091	22.61	332.4
	-49.6	2.32	0.7060	0.0008	0.7052	21.93	323.1
	-43.85	2.24	0.6988	0.0010	0.6978	20.95	311.2
	-41.1	2.19	0.6953	0.0011	0.6942	20.38	303.8
	-33.1	2.13	0.6854	0.0016	0.6838	19.48	293.1
	-28.8	2.07	0.6801	0.0019	0.6782	18.78	284.1
	-23.5	1.99	0.6735	0.0023	0.6712	17.86	272.0
	-21.7	1.96	0.6712	0.0025	0.6687	17.54	270.8
	-15.8	1.92	0.6637	0.0031	0.6606	16.97	260.9

temperatures, Col. 6 the surface tensions (γ) calculated from the expression

$$\gamma = 1/2 gr (d_l - d_g) (h + 1/3 r)$$

and the last column the molecular surface energies $\gamma(V_M)^{2/3}$.

The variations of surface tensions with the temperature is shown in Fig. 3 and the variation of molecular surface energies with the temperature in Fig. 4.

The surface tensions of acetylene have been previously measured by one of us.¹ In the method used a capillary was immersed directly in the center of a tube about 1.5 cm. in diameter. The values obtained on this account would be too low and this is found to be the case on comparison of the results. The densities for the liquid, as found in the previous investigation, were too low at the higher temperatures, hence the temperature coefficients of the surface tension as found by use of them is also incorrect.

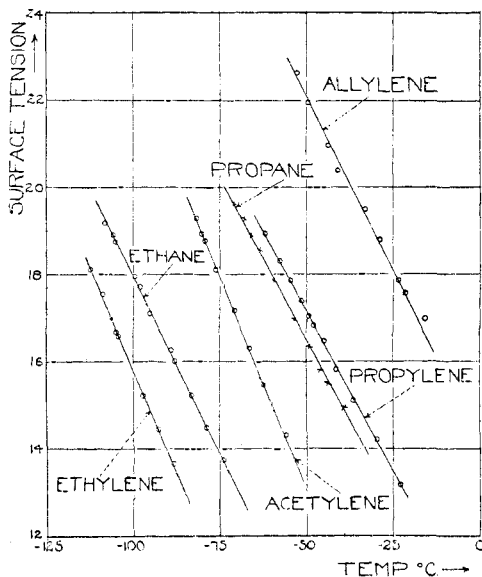


Fig. 3.

In Table XI, Col. 1 gives the surface tensions ($\gamma\beta$) at the boiling points. It is seen that the change from saturation to ethylene linkage is accompanied by a small increase whereas the change to the acetylene linkage shows a marked increase. Col. 3 gives the total surface energy where the values are of interest from the point of view of the predictions of Langmuir² and Harkins.³

¹ Maass and McIntosh, THIS JOURNAL, 36, 737 (1914).

² Langmuir, *ibid.*, 39, 1848 (1917).

³ Harkins, *ibid.*, 39, 541 (1917).

TABLE XI.
Surface Tensions at the Boiling Point, Temperature Coefficients of Surface Tensions, etc.,
of the Hydrocarbons.

	γ_B .	$\frac{d\gamma}{dt}$.	$\gamma + T \frac{d\gamma}{dt}$.	$\gamma(V_M)_B \%$.	K.	t_C calculated. °C.	t_C observed. °C.
Ethane.....	16.05	0.1606	45.7	231.5	1.98	34.6	35.0
Ethylene.....	16.50	0.1845	47.7	222.1	2.14	5.9	9.9
Acetylene.....	19.58	0.1927	56.0	237.0	2.02	39.7	36.5
Propane.....	15.63	0.1520	50.3	279.7	2.15	91.6	95.6
Propylene.....	16.70	0.1462	49.7	280.4	2.12	91.3	92.1
Allylene.....	18.57	0.1545	53.6	280.5	1.96	121.6	127.9

The values for the paraffins are to lie between 46 and 48, which is borne out by ethane 45.7. The value for propane of 50.3 is slightly too high. If this value is the correct one this may be due to the same cause as that which gives too low a value for the molecular volume of propane. A determination of the values for the next few members will establish whether

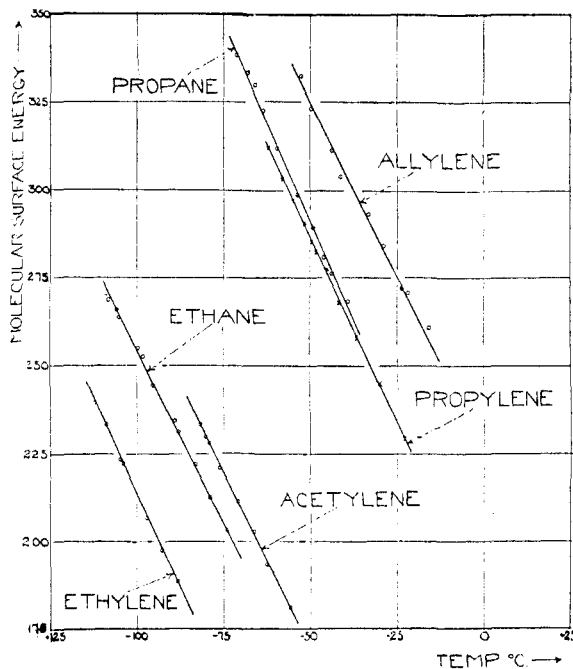


Fig. 4.

this is so. The change from ethane to ethylene, as was to be expected, shows a slight increase¹ in molecular surface energy. The increase in length from 2 to 3 carbons is again accompanied by a slight increase, smaller than in the case of the saturated hydrocarbons, because here the influence of the ethylene bond, from the point of view of the orientation theory, is diminished, that is, propane and propylene have nearly the same value. This is most marked when the acetylene compounds are examined. The acetylene linkage causes a large increase in total surface energy (45.7 ethane to 56.0 acetylene, a difference of 10.3) so that the addition of a methyl group should considerably diminish this difference and this is found to be the case, for the difference between propane and

¹ Harkins, THIS JOURNAL, 42, 708 (1920).

allylene is only 3.3. The ethylene linkage causes a slight increase in the total surface energy whereas the more strongly polar acetylene linkage causes a considerable increase. Lengthening of the carbon chain with consequent orientation of the molecules diminishes the effect of the polar groups on the total surface energy.

Considerable doubt has been thrown on the exact significance of the constant "K" in the Ramsay and Shields equation

$$\gamma(V_M)^{2/3} = K (t_c - t - 6),$$

where K is 2.12 for unassociated liquids. Col. 4, in Table XI, gives the values for the molecular surface energies $\gamma(V_M)_B^{2/3}$ at the boiling point, Col. 5, the values for K and the last two columns the critical temperatures (t_c) calculated from the above equation and the critical temperatures (t_c') observed. Ramsay found that the addition of a CH_2 group increases the constant K and this increase is noticeable when the values for ethane and propane are compared. When acetylene and allylene are compared, it is seen that there is a decrease, so that if a decrease in the constant is indicative of association the allylene molecules are associated to a certain extent. It will be remembered that the value given by Trouton's rule when applied to allylene gave the same indication. In another investigation¹ it has been shown that allylene has a greater tendency for molecular compound formation than acetylene.

A comparison of the observed and calculated values for the critical temperatures shows a very good agreement except again in the case of allylene.

Summary.

Some physical constants of ethane, ethylene, acetylene, propane, propylene and allylene have been determined and the experimental methods described, including descriptions of constant-temperature baths in the temperature range from 0° to -200° . Freezing points, boiling points, vapor pressures, critical temperatures, liquid densities and surface tensions have been tabulated. The values have been discussed from the point of view of the agreement between expected and observed results.

MONTREAL, CANADA.

¹ To be published later.