

THE PREPARATION
OF
ALIPHATIC ACETYLENES

DEPOSITED BY THE FACULTY OF
GRADUATE STUDIES AND RESEARCH

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1M8.1932



ACC. NO. UNACC. DATE 1932

THE PREPARATION AND PHYSICAL PROPERTIES
OF
ALIPHATIC ACETYLENES

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Montreal

April 1932

The writer is grateful for this opportunity of expressing his genuine appreciation of the help and advice so liberally given at all times by Dr. O. Maass under whose direction the work was undertaken. To the National Research Council of Canada acknowledgement is made of a Bursary and Studentship during the course of this research.

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Introductory Outline.

The work to be described in this thesis deals with the preparation and investigation of the physical properties of the lower members of an homologous series namely the alkyl acetylenes. In view of the fact that small differences in properties would be observed in the case of isomeric substances and also that the validity of the observations in the case of certain properties depends solely on the purity of the compound investigated new details have been developed in connection with the methods of preparation and special care devoted to the purification of the compounds. The properties investigated are the physical ones of surface tension, boiling point, density etc. This new data is of interest not only in itself but has been obtained especially with a view to the interest attached to it from a theoretical point of view in connection with the interpretation that can be made with regard to the values observed for these physical constants.

Throughout the course of several years a systematic investigation of the paraffin and olefine hydrocarbons has been undertaken in this laboratory. A comprehensive determination of their physical properties has been made and the different values obtained interpreted in terms of their probable molecular forces of attraction.

The continuation of this problem led to extensive experimental work whose object was to ascertain the extent and degree of the tendency for these compounds to undergo molecular compound formation with molecules of another type. A definite correlation was found to exist between their molecular forces of attraction and the tendency toward molecular compound formation which was in turn further correlated very definitely with their manifestations of intra-molecular attraction.

A continuation of this work, going on from the paraffin and olefine series to the acetylenes, is presented in this thesis. The preparation of the acetylenes by a method that will render them sufficiently free from impurities is much more difficult than is the case for the members of the paraffin and olefine series and hence the scope of this investigation was necessarily limited by time to the first problem which is the preparation, purification and correlation of the physical properties of the aliphatic acetylenes.

In order to show the importance attached to this step in the general program of the investigation it is considered worthwhile to show the interpretation that may be put on the data obtained by referring, as an analogy, to the type and scope of a research on the paraffins and olefines made possible when the preparation and measurement of the physical properties had been completed.

A general review is therefore given below of the interpretation put on molecular forces of attraction and the influence they exert on the chemical and physical characteristics of compounds exhibiting such forces.

General Introduction.

At the present time, since there is no absolute method that can give us a quantitative measurement of the relative magnitude of molecular forces of attraction, recourse must be made to investigations that will yield data of a qualitative nature and the results expressed on a relative rather than an absolute scale.

It is well known that one of the best opportunities for the observation of relative differences in molecular forces of attraction between like molecules lies in a comparison of certain physical properties, particularly those associated with a change of state such as melting point, boiling point and critical temperature. A comparative measurement of the attractive forces between unlike molecules is obtained by the extent of molecular compound formation in such systems or by the magnitude of their deviation from the laws of the ideal solution.

Thus it is that a knowledge of the physical properties of the elementary hydrocarbons is essential for an understanding and classification of the forces of attraction that come into play between the molecules and conversely a knowledge and understanding of these forces may enable us to explain some of the abnormalities observed in various properties and may moreover lend itself to a certain amount of prediction.

A general survey of the theories developed by investigators in this work will serve as an introduction and at the same time show further the object and interest attached to an investigation of the physical properties of the elementary hydrocarbons.

Closely associated with the advances that have been made in defining the forces that exist between molecules and between atoms are the names of Langmuir(1) and Harkins(2) who are of the opinion that these forces are fundamentally alike in character and are of the nature of so-called chemical forces.

However, while modern theory tends to eliminate the distinction between physical and chemical forces and tends more and more to regard them as differing in degree rather than kind, it is more convenient to designate such attractive forces that may exist between unlike as well as like molecules as "physical" in order to distinguish it from the specific and highly selective "chemical force" or "chemical affinity" whose results are chemical reaction and formation of chemical compounds.

Since a number of different opinions are held on the exact distinction between the definitions of physical and chemical force it is desirable to say a few words concerning the criteria upon which the usually accepted definitions are based. Chemical force, or what is usually known as chemical affinity, depends definitely on the nature and structure of the matter concerned and its sphere of influence is limited probably to the atomic dimensions of the substance.

On the other hand the idea of physical force is generally conceived as one which is non specific, additive and of unlimited range of action. It's influence on a given mass is independent of other masses and the direction of it's action does not depend on the nature of the masses. Under chemical may be listed those forces which come into play when molecules such as H_2O or CH_4 are formed while under physical those manifested by such properties as melting point, latent heat and surface tension.

As examples of laws governing typically physical forces may be cited Newton's inverse square law for gravitational attraction and Coulomb's law for the attraction or repulsion of electric charges.

Early attempts have been made to explain certain physico-chemical phenomena by considering the force acting between molecules of liquids and gases as an attraction which varies inversely as the square of the distance between molecules but it is now well known that molecular forces of attraction vary as a high inverse power of the distance between the molecules(3). Due to the complicated nature of this problem the exact magnitude of this power cannot be determined but it is probably greater than four. Consequently the force that gives rise to internal pressures of the order of thousands of atmospheres when the molecules are close together may become negligible when the distance between them is but slightly increased. Langmuir has said that these forces between

atoms and molecules involved in the structure of matter are of the same specific nature as chemical forces and since the magnitude of the forces is dependent on the specific nature of the particular atom or molecule no absolute law correlating force and distance for all molecules is possible.

However it is only in extreme cases of examples of both chemical and physical forces that a real distinction between the two is of any value or is even possible since the two forces tend to gradually merge into one another and when an attempt is made to explain which of the forces causes the association of water molecules or that causing the formation of molecular compounds the unsatisfactory nature of such an artificial definition is at once evident.

One of the early theories concerning the mechanism governing the combination of atoms was the dualistic theory of Berzelius who regarded this combination as due to electric charges on each atom. According to this early theory it might happen that a molecule would form in which the respective charges on the atoms constituting it would not exactly neutralize one another. The molecule so endowed with an excess charge of either sign would then have an external field of force and possess the ability to attract other molecules and hold them if these in their turn possessed an excess of the appropriate charge.

The molecule as such has of course no residual positive or negative charge as Berzelius implied in his theory. However

according to the modern point of view the distribution of positive and negative electricity throughout the molecule is such that the centres of gravity of positive and negative electricity do not coincide. This results in an uneven distribution of the positive and negative electricity which leads to practically the same phenomena as Berzelius suggests inasmuch as two molecules of different species may have considerable attraction for one another in a properly orientated position due to this uneven distribution of electricity. To signify these ideas and to express them the terms "residual Affinity" and "secondary Valence" have become widely used.

Analogous conceptions of atomic and molecular attraction, although considerably modified by subsequent discoveries, are held today and are intimately connected with our ideas of valency. The valency of an element may be defined as the number of hydrogen atoms or their equivalent that one of its atoms is capable of holding in chemical combination. In most cases this number is well defined and always approximates an integer as in the case of carbon it is very nearly equal to four. The valence of oxygen is almost two but that the valence of oxygen is not completely saturated with two hydrogen atoms is evidenced by the ability of water to form the unstable hydrates and oxonium compounds. This whole number-four in the case of carbon and two with oxygen has been denoted as the primary valence while the residual force

that remains in some cases, due to incomplete saturation, has been called the secondary valence. Thus the primary valence gives rise to the formation of molecules employing forces that are strong in comparison to the residual forces which however exist in every case and if of sufficient magnitude give rise to more complex molecules.

Our understanding of atomic or valence forces has, of necessity been dependent to a large extent upon the knowledge at hand concerning atomic structure, a study in which amazing progress has been made in the last quarter century. Judging by the shifting sands of modern physical theory it would seem that the chemist, who had become accustomed to visualizing atoms in terms of electrons, had little or nothing on which to rely. It is now considered obsolete, by physicists, to speak of static electrons in the atom. However in spite of these unavoidable difficulties and contradictions in the natural development of the science considerable progress has been made in recent years in the study of atomic structure from both the physical and chemical point of view. A sound theoretical basis for the periodic table based, not on atomic weight but atomic number, having to do with the number and probable arrangement of the electrons in an atom, has been established, vastly increasing the usefulness of the table and developing it to a logical system.

The firm establishment of the number of electrons in any atom lent, as would be expected, a great deal to the progress and development of chemical theory. Berzelius' electro-chemical theory

was brought to the fore in the clear cut idea of "electro valence" and many of the difficulties of the dualistic theory were removed by the useful conception of "covalence" either "normal" or "co-ordinate" resulting in a reasonable explanation for much that was obscure in the physical and chemical behaviour of matter.

Modern theories of valence regard the force between atoms resulting in the formation of molecules, ie. "chemical", as due to the innate tendency of atoms to gain, share or lose electrons while the purely physical attraction is regarded as a secondary result of such a tendency. An atom or molecule can be conceived as a structure of electron orbits or vibrating electrons resulting in a stray field of force whose magnitude depends on the completeness of the screening effect of the outer electrons and the extent of internal neutralization.

Two unlike molecules, having external fields of force of such a nature as to more or less completely neutralize one another, may unite, or if the fields are not sufficiently large, or their mutual neutralization sufficiently complete to give rise to union, still their influence may make itself apparent in the deviation of the mixture from the laws of the ideal solution. In the case of molecules of the same species, although the forces between them may not be of such magnitude as to cause association, they may greatly influence the properties of the liquid and by the comparative study of the physical properties of pure substances it is possible to obtain an insight into the relative attractive forces existing between their molecules.

While the study of the physical properties of the hydrocarbons enables us to form some idea of the relative forces of molecular attraction between like molecules these forces existing between unlike molecules may also be compared by the extent of molecular compound formation in such systems. In this way a study of the properties of mixtures particularly from the point of view of the Phase Rule will throw light on the attractive forces between unlike molecules.

To recapitulate we may add another and third attractive force to the two main types of Valence recognized by modern theory. We then have (1) Electro valence, due to the electrostatic attraction between ions, (2) Covalence, due to the greater stability of certain spatial arrangements of electrons and (3) Molecular attractive force due to the resistance of stray fields about chemical bonds or distorted atoms.

Considerable work on the subject of molecular attraction between unlike molecules has been done in this laboratory from the point of view of molecular compound formation and reaction velocities. A survey of the work along these lines done by Maass and his co-workers will be given. Several types of systems have been investigated and there is distinct evidence of such attractive forces in many cases.

Maass and Morrison⁴ have shown that when methyl ether and hydrogen chloride are mixed in the vapor state there is a molecular compound formed. Compound formation in the liquid

state has proved to be a very fruitful field for study. Investigations have been carried out using hydrocarbons and the halogen hydrides as the two components. Both of these substances are ideal in that the halogen hydrides are highly polar and that by using a series of hydrocarbons great variations in the external fields of force can be obtained. Maass and Russell⁵ have shown that although toluene, ethylbenzene and mesitylene form molecular compounds with hydrogen bromide no such occurrence is noted for benzene. In an analogous manner it was shown that acetylene behaved similar to benzene in this respect while allylene follows the benzene homologues. It is stated that in benzene and acetylene the symmetry of the molecule leaves apparently no secondary valence due to unsaturation by means of which an attraction is exerted on the hydrogen bromide molecules. Such an attraction would exist in the case of the alkyl substituted derivatives.

The subject of molecular compound formation along these lines was investigated more fully by Maass, Boomer and Morrison⁶. The additional systems studied were ortho-, meta-, and paraxylene, propyl-benzene and methylcyclohexane with hydrogen bromide. The conclusion was drawn that the benzene nucleus, whether in benzene or its alkyl substitution products, has an outer field of force with a definite tendency to attract hydrogen bromide molecules. This force, however, can only come into play when the secondary valence is not such as to

attract molecules of it's own species. There is a greater attraction between molecules of the same species if they are symmetrical than there is between those molecules and hydrogen bromide. Whether or not a molecular compound is formed depends on which of the three attractive forces below predominated.

- (1) The force between hydrocarbon and hydrocarbon.
- (2) " " " " " halogen hydride.
- (3) " " " halogen hydride and halogen hydride.

Physical properties such as melting point are a criterion of force (1) and show that there is notable variation with different hydrocarbons. Since hydrogen bromide was present in all systems, whether or not molecular compounds were formed, force (3) is considered small. Force (2) appears to be independent of the hydrocarbon as long as the benzene nucleus is present. Consequently if force (1) is relatively small there is a great likelihood of molecular compound formation taking place.

The fact that unsaturation in such hydrocarbons is the cause of their attraction is strikingly demonstrated. Methylcyclohexane showed no formation of molecular compounds with hydrogen bromide even though it's freezing point is below that of toluene, the corresponding aromatic hydrocarbon.

As a final conclusion it is stated that unsaturation definitely causes molecular compounds to be formed and that failure to form such compounds in spite of unsaturation is due to the relatively great attraction of molecules of the same species for one another.

Turning to the aliphatic hydrocarbons Maass and Wright⁷ investigated their ability to form molecular compounds. Ethylene was found to form no molecular compound with hydrogen bromide while the reverse is true for propylene. This appears to be more evidence in favor of the conclusion of Maass and Russell⁵ who showed that the more symmetrical the molecule may be the less will be its attraction for hydrogen bromide and consequently the greater will be the force of attraction between molecules of its own species.

Considerable correlation of the physical properties of hydrocarbons with their velocities of reaction have been made in this laboratory.

It was noticed by Maass and Russell in their investigations on unsaturation and molecular compound formation that those substances that formed molecular compounds showed signs of chemical reaction on being allowed to stand at room temperatures. No such reaction was found in the case of hydrocarbons which did not form these compounds. Thus, although benzene and acetylene do not react with hydrogen bromide, the substituted benzenes and allylene show definite signs of reaction.

Continuing on the same line Maass and Wright⁸ showed no reaction to take place with ethylene while propylene follows allylene in its behaviour in that it does react and secondary products are formed.

Maass and Siveritz⁹ investigated the reaction velocity between hydrogen chloride and propylene quite thoroughly. One of the most important facts brought out was that propylene and hydrogen chloride do not react in the gaseous state under normal conditions of temperature and pressure. From the point of view of attractive forces between the molecules this is easily understandable since it is to be expected that the influence of these forces upon reaction velocity, while they may be all important in the liquid state where the molecules are within range of their attractive forces, will become a very minor factor in gaseous reactions.

Further correlation of physical properties of hydrocarbons with velocity of reaction was made by Coffin and Maass¹⁰. The three butylene isomers offered such a field for investigation and the velocity of reaction of these isomers with hydrogen chloride was determined. It was found that γ butylene reacted almost instantaneously with hydrogen chloride at -78.5°C . The more symmetrical isomers reacted much more slowly and were proved to be homogeneous in the liquid state. No reaction occurred with α and β butylenes in the gaseous state but with γ butylene a slow heterogeneous reaction took place. From the curves of reaction velocity there was evidence of a secondary reaction similar to the case of propylene.

The results of all these investigations pointed to the importance of molecular attraction in both molecular compound formation and velocity of reaction. The magnitude of such forces is greatest in condensed systems although not entirely absent in the gaseous phase.

In the hydrocarbons of the saturated methane series the primary valencies of carbon and hydrogen neutralize one another to such an extent that the residual forces are very small. However in the unsaturated ethylene and acetylene series the primary valences are not satisfied to the same extent resulting in an increase of the residual valence depending on the structure of the molecule. The compounds, especially the elementary members, offer an excellent opportunity for the study of the fundamental forces that come into play in the molecule.

The work to be described in this thesis had for its object the investigation of the magnitude and nature of the forces existing between like molecules in so far as these forces can be determined by examining their effect on physical properties which kinetic theory tells us are influenced by the attraction of molecular aggregates.

A large number of the physical properties of compounds containing two and three carbon atoms have been determined in this laboratory by Maass and Wright⁸. The four carbon butylenes and butanes were investigated by Coffin and Maass¹⁰. The work to be described below deals with the extension of this investigation to the four carbon hydrocarbons of the acetylene series along with other members of this homologous series.

Beside the interest attached to the homologous relationship existing between these compounds and those containing two and three carbon atoms the fact that structural isomerism makes its appearance lends further significance to the work.

The preparation and purification of methyl, ethyl, propyl and dimethyl acetylene are described. The vapor pressures, densities and surface tensions accurately determined over a range of temperature are described and tabulated together with the melting points and critical temperatures. Constants calculated from these data such as Molecular surface energy, total surface energy, parachor etc. are also included. Great stress was laid on 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. The properties investigated are discussed from the point of view of modern theories of molecular orientation and attraction. Homologous relationships are considered as well as the effect of carbon chain structure on physical properties.

The determination of the physical constants and their interpretation in terms of physical chemical theories was the prime object of the research. This is dependant on establishing the purity of the compounds examined and it is well to emphasize this once more. As a consequence the methods chosen for the preparation of the compounds were based on obtaining purity at the expense of any experimental complications no matter how involved. The methods of preparation were therefore investigated from the point of view of how each step might possibly affect the purity of the product. This in itself may be looked upon as one of the most important features of the work to be described as it undoubtedly was the time consuming element in this investigation. Many subsidiary changes in experimental technique which were found necessary are not described and their existence solely mentioned at this stage to indicate the importance attached to a method of preparation which ensures a product that can be definitely brought to a high state of purity.

The Preparation and Physical Properties of Methyl-, Ethyl-,
Propyl- and Dimethyl-acetylene.

In order that the aliphatic acetylenes to be investigated would be attainable in the highest possible form of purity the method adopted for their preparation was that of direct synthesis from the simple constituents of each compound. This method, with certain modifications, is that used originally by Lebeau and Picon¹¹ and consists in the alkylation of sodium acetylide in liquid ammonia as a reaction medium.

The general procedure was to melt a suitable quantity of sodium in an atmosphere of hydrogen and straining it while molten through a porous plate to remove the oxide adhering to its surface. It was then dissolved by liquid ammonia and acetylene bubbled through the blue solution until disappearance of color indicated the complete formation of sodium acetylide which separated out in the form of white crystals. The alkyl iodide was then added and the reaction allowed to take place after which separation of the desired alkyl acetylene from ammonia was effected through removal of the latter by passing the mixture of gases through scrubbers filled with water and dilute sulphuric acid. The acetylene compound was then collected by conden-

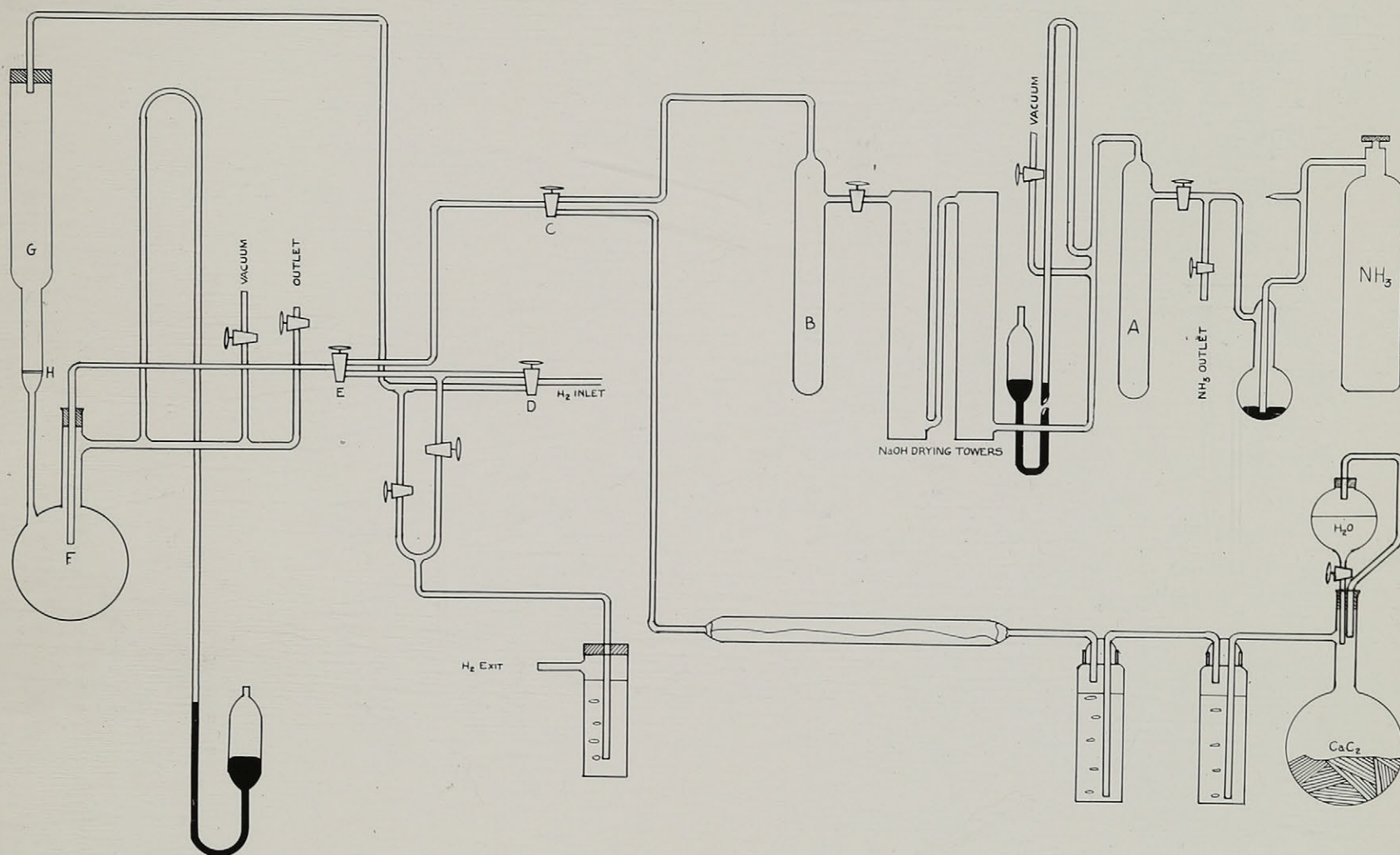


Fig. 1

sation in a tube cooled with a carbon-dioxide ether mixture. This product was subjected to further purification by a system of fractional distillation to be described below.

All reagents, hydrogen, ammonia, acetylene and alkyl iodide were carefully purified and dried before use. An all glass apparatus which eliminated contamination of the reactants from water vapor and oxygen of the air was constructed and is represented diagrammatically in Figure 1.

Most of the air was removed from the apparatus by evacuation and flushing out with hydrogen which was obtained from a Kipp generator and purified by passing it through sodium hydroxide solution, concentrated sulphuric acid and finally over phosphorus pentoxide in order to remove hydrochloric acid and water. Then a suitable amount of sodium was weighed out and dropped into the large pyrex tube (G). The entire apparatus was thoroughly washed out with hydrogen by allowing the gas to flow through the apparatus first in one direction then in the other by manipulation of the stop-cocks (C) and (D). In order that there might be no air in the apparatus due to leaks around the rubber stopper at the top of tube (G) the hydrogen flowing out of the apparatus was allowed to bubble under the pressure of a small height of water in a wash bottle as seen in the diagram. After the hydrogen passed through for about two hours and

no oxygen remained in the apparatus, as was indicated by testing a sample of the emitted gas, tube (G) was heated with a free flame, the stream of hydrogen being directed so that it would force the sodium, when molten, through the perforated plate (H). When the purified sodium was in the bottom of the flask (F) the large tube was sealed off.

The ammonia used was obtained from a cylinder of pure anhydrous ammonia and was further purified by liquifying it in tube (A) which was cooled by a carbon-dioxide ether mixture contained in a dewar flask. The rate of flow of ammonia was first regulated by observing the rate of bubbling through a mercury trap and the extent of condensation followed by a manometer connected to the system. The liquid ammonia in (A) was then purified by allowing some of it to boil off and the middle fraction passed through drying towers of sodium hydroxide to be recondensed in (B). It was then used to dissolve the sodium by condensing it in flask (F). The rate of condensation was followed by a second manometer connected with the system as shown in the diagram. Subsequent experiments showed the ammonia from the cylinder to be anhydrous and of sufficient purity so that it was used to dissolve the sodium directly and was not subjected to fractionation. About three hundred cubic centimeters of liquid ammonia were put in (F) forming an inky-blue solution.

Acetylene from a Prest-O-Lite cylinder was first used but was found to contain a large quantity of acetone and consequently acetylene was prepared and purified as follows.

Water was dropped on pure calcium carbide previously treated with ninety eight percent ethyl alcohol to diminish the intensity of the reaction. The acetylene so generated was passed through wash bottles of sodium hydroxide and chromic acid to remove carbon dioxide and phosphine. It was passed through a phosphorous pentoxide tube to remove water vapor and then allowed to bubble vigorously in to the blue solution so that the sodium acetylide formed would not clog up the tube leading into the ammonia. The end point was given by a change of color from blue to white. Excess acetylene, dissolved in the ammonia, was removed by distilling off some of the ammonia and replacing it with the pure liquid so as not to form too viscous a mixture.

The alkyl iodide was freshly distilled and slightly less than the calculated quantity, based on the amount of sodium put into the flask, was used so as to avoid contaminating the product with a volatile impurity. When this amount of iodide had been added slowly and the reaction mixture shaken from time to time the contents of the flask were allowed to stand to enable the reaction to proceed as nearly as possible to completion.

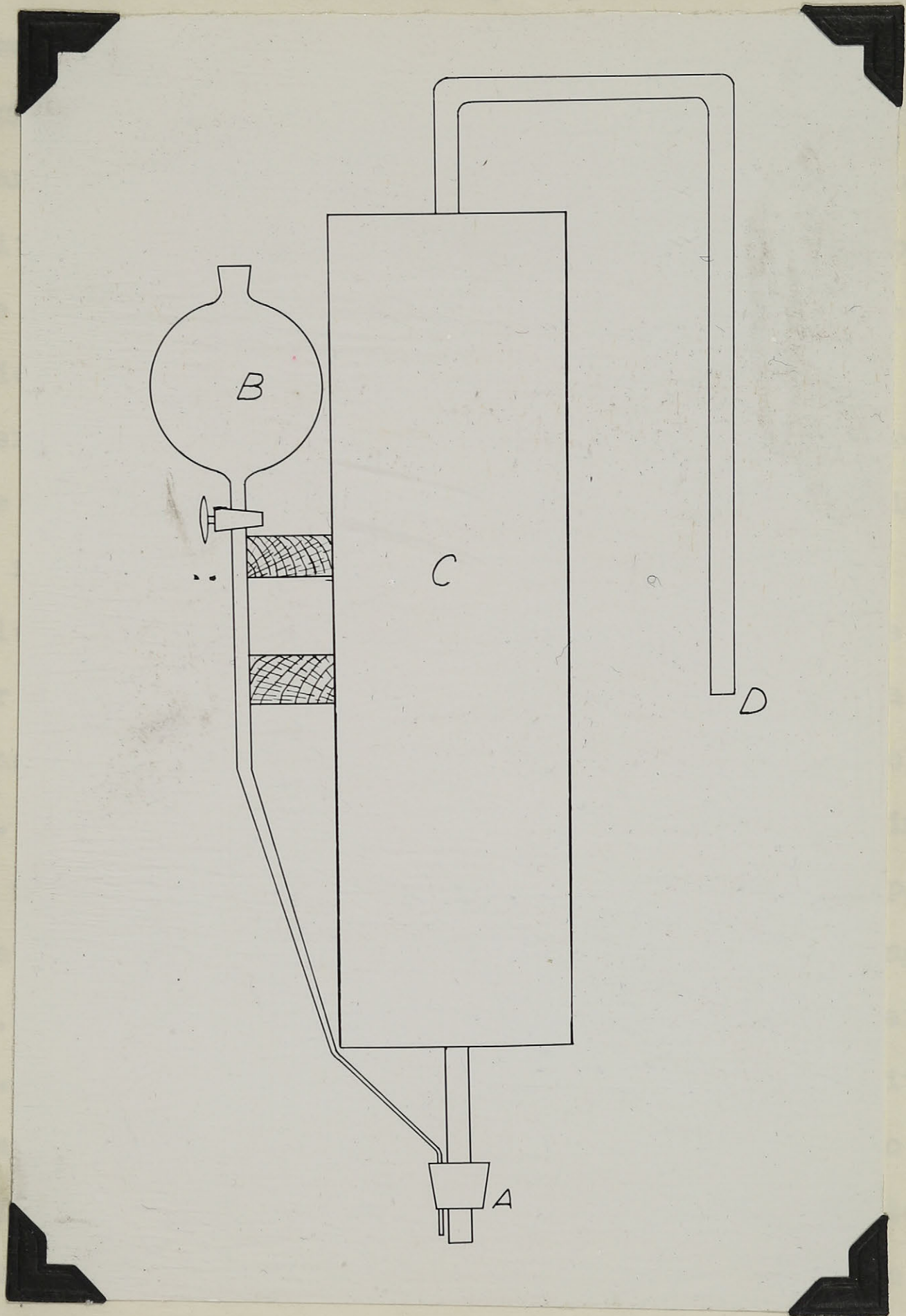


Fig. 2 .

In some of the preliminary experiments where poor yields were obtained, especially in the preparation of ethyl- and propyl-acetylene, since the reaction between the alkyl-iodide and sodium acetylide might be expected to take place with a little more difficulty, the alkyl-iodide was dropped into the liquid ammonia containing the sodium acetylide in suspension while the mixture was being refluxed under atmospheric pressure at the highest possible temperature i.e. the boiling point of liquid ammonia -38°C . For this operation a reflux condenser of the form shown in Figure 2 was employed. A tube (D) of about one centimeter inside diameter bent in the shape of a U was surrounded with a pyrex jacket (C) filled with a carbon-dioxide ether cooling mixture. Tube (D) passed through a rubber stopper fitting tightly in the bottom of (C). Leaks were prevented by pouring in a little mercury which, when frozen by the cooling mixture, completely stopped all leakage around the rubber stopper. Attached to (C) was a dropping funnel for addition of the alkyl iodide. The rubber stopper (A) fitted into the top of flask (F) when the tubes used for the introduction of the ammonia had been removed. Refluxing the reaction mixture in this way in order to facilitate the reaction also served the purpose of removing the excess acetylene, which was dissolved in the ammonia. In order that no water vapor might enter the apparatus during this part of the

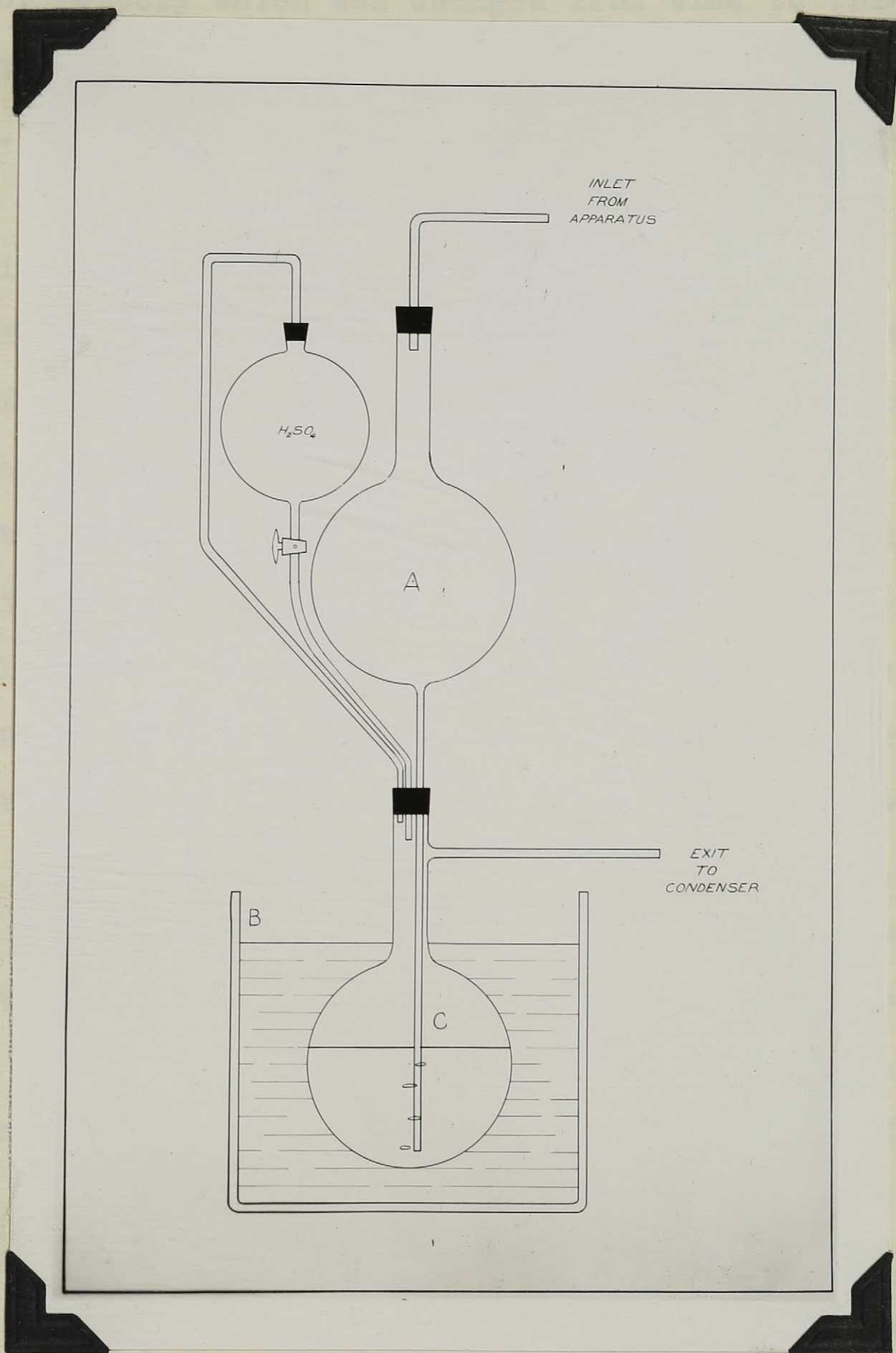


Fig. 3 .

preparation the exit to tube (D) was placed under a small quantity of mercury which was changed from time to time to prevent the possibility of forming too much mercury acetylide. The reaction mixture was refluxed in this way while the alkyl iodide was being added very slowly and the time required was usually two or three hours.

After the reaction was thought to be complete the mixture of ammonia and alkyl acetylene was passed through a scrubbing apparatus as shown in Fig. 3. The gases were boiled off from the reaction flask and passed through a solution in (C) maintained slightly acidic by means of the dropping funnel filled with sulphuric acid. In case the contents of (C) were suddenly sucked back the bulb (A) served to prevent contamination of the reaction mixture with water and acid. The alkyl acetylene, being insoluble in the dilute acid, passed on and was dried by passing it through a calcium chloride tube previous to condensation in a storing tube cooled to -78°C by a carbon-dioxide ether mixture contained in a dewar flask. This more or less crude product was finally subjected to purification by a system of fractional distillation to be described below.

Since special modifications for each compound were found to be necessary for their preparation a description of the preparation of Methyl-, Ethyl-, Propyl- and Dimethyl-acetylene will be given below under separate headings.

Methyl Acetylene.

Methyl acetylene was prepared and its properties studied by Wright and Maass⁷ but since the method of purification used by Coffin and Maass¹⁰ in the investigation of the butylenes and butanes was a marked improvement over the former method where small amounts of material were concerned the preparation of methyl acetylene was undertaken to see if, when purified in this way, the results of Wright and Maass would be confirmed or not.

The preparation of methyl acetylene was carried out in the manner described above. Since this is the first of an homologous series of mono-substituted acetylenes, as would be expected, reaction between the methyl iodide and sodium acetylide took place most easily even at temperatures below the boiling point of liquid ammonia so that in the preparation of this compound it was found to be unnecessary to use the refluxing apparatus for promoting the reaction. The mixture of ammonia and methyl acetylene was passed through a large quantity of water and then through dilute sulphuric acid thus removing the ammonia completely and allowing the methyl acetylene, which is a gas at ordinary temperatures, to be collected by condensation.

Several experiments were made on the preparation of methyl-acetylene to determine what method would produce the maximum yield. Two samples of methyl-acetylene were prepared. The first was obtained without the use of the acid separator and the product in this case was considerably less than that resulting when the mixture of gases was

allowed to pass through the acid solution. Measurements made for vapor pressures and density, to be found in the tables below, on both samples were found to check each other.

Ethyl-acetylene.

Ethyl-acetylene was also prepared twice with slight changes in the method of procedure. In the first preparation it was never in contact with an acid medium which might have polymerized it. In the second preparation where better yields were obtained, by the use of the acid separator, the ethyl-acetylene was in contact with acid both in the separator and also during passage over phosphorus pentoxide for removal of small traces of water. Although propylene polymerizes⁷ on being passed over phosphorous pentoxide ethyl-acetylene does not appear to do so since the vapor pressures and boiling point were found to be the same whether it did or did not come into contact with an acid medium.

The useful information was therefore obtained that no secondary products are formed by passing the ethyl-acetylene through dilute sulphuric acid or, after removal of most of the water by chilling and filtering off the ethyl-acetylene, by passing it over phosphorous pentoxide.

Propyl-acetylene.

In the preparation of propyl-acetylene the method of procedure given above was followed throughout. The mixture was refluxed while the propyl iodide was being added and the propyl-acetylene freed from ammonia by means of the acid separator. Final purification was effected by the method to be described below.

Iso-propyl-acetylene.

Experiments were made in an attempt to synthesize iso-propyl-acetylene by the same method making use of the reaction between sodium acetylide and isopropyl iodide but no product was obtained. The reaction between a branched chain iodide and sodium acetylide does not give the corresponding isopropyl-acetylene but a straight chain ethylenic compound according to the equation:¹²



Since the hydrocarbon could not be prepared in this way for investigation other methods were not thought suitable since they would involve the presence of impurities in the product that would be most difficult if not impossible to remove completely to furnish a sample with the purity required for the density and surface tension measurements.

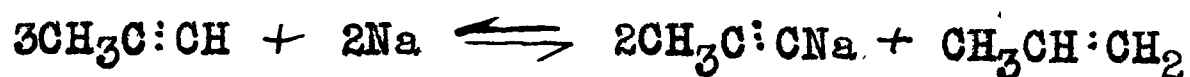
Dimethyl-acetylene.

Dimethyl-acetylene has been prepared by Faworsky¹³ who heated ethyl-acetylene in a sealed tube with alcoholic potash whereby rearrangement of the molecule occurred resulting in the formation of dimethyl-acetylene.

Although this method of preparation was successful it was thought best to develop another method, if possible, in view of the fact that dimethyl-acetylene prepared in this way would contain quantities of alcohol, alkali and ethyl-acetylene which would render purification of the product to the degree desired for the surface tension measurements very difficult.

Consequently the preparation was attempted by methylation of the sodium derivative of methyl-acetylene in a manner analogous to that used in the preparation of the other alkyl acetylenes.

A large quantity of methyl-acetylene was prepared by the usual method and passed into the blue solution of sodium in liquid ammonia until disappearance of the blue color showed complete formation of the sodium-methyl-acetylide. Since Lebeau¹⁴ found this reaction gave one molecule of propylene for every two of sodium derivative formed according to the equation:



this had to be taken into account when calculating the final yield of dimethyl-acetylene desired.

When all the sodium had reacted with the methyl-acetylene the ammonia and propylene were allowed to pass off leaving behind the white solid sodium derivative. Since the mercury and silver derivatives of methyl-acetylene are non explosive¹⁵ it was deemed safe to do this.

Fresh ammonia was condensed in the reaction flask and the solid suspended as usual in the liquid. Methyl-iodide was added and the reaction allowed to proceed without the aid of refluxing. That reaction took place seemed to be indicated by the change in appearance when crystalline sodium iodide settled to the bottom of the flask in the place of the pasty appearance of the sodium methyl-acetylide.

The dimethyl-acetylene was separated from the ammonia in the usual way and purified in the manner to be described below.

When the sample had been purified and the measurements for surface tension and density made it was rather surprisingly found that the value for the parachor, calculated from these measurements, was over four per cent too low. Consequently the surface tension and density were again carefully determined. No difference between these values and those previously obtained was found. This, naturally, caused considerable alarm since it indicated quite strongly that there was a possibility of this compound not being dimethyl-

acetylene at all but possibly some other compound formed perhaps by a rearrangement of the reactants similar to the reaction between isopropyl iodide and sodium acetylide. The next problem was to determine the molecular weight of the product. This was done by the Dumas vapor density method. The apparatus was connected to the fractionating apparatus containing the pure compound and consisted of a large bulb of about 400cc. capacity maintained at a constant temperature by means of a water bath. Attached to the bulb were a manometer and three small glass bulbs connected to the apparatus in such a way that they could be readily sealed off. The method of procedure was to fill the standard volume at known temperature and pressure with a sample of the gas whose molecular weight was to be found. Then, after evacuating the tubing connecting the small bulbs with the standard volume, the gas in the latter was condensed in one of the small bulbs by means of a cooling mixture. The small bulb was then sealed off and weighed. When the weight of the gas was found and various corrections applied the molecular weight was found according to the following equation:

$$P V = \frac{W}{m} R T$$

where :

P	Pressure,	m	Molecular weight.
V	Volume of gas.	R	Gas constant.
w	Weight of gas	T	Absolute temperature.

Three determinations were made at different pressures and the molecular weights so obtained plotted against pressure. The results were extrapolated to zero pressure and it was found that the extrapolated value agreed with the theoretical molecular weight within one per cent.

Now the problem was to determine whether or not the compound was actually an acetylene or some isomer containing a pair of double bonds. The possible isomers are the two butadienes and ethyl-acetylene.

The boiling points of the butadienes are given in the International Critical Tables as 19°C . for the 1.2 butadiene and $-2^{\circ}.6\text{ C}$. for the 1.3 butadiene. The boiling point of ethyl-acetylene has been found to be $8^{\circ}.6\text{ C}$. Since the boiling point of the product thought to be dimethyl-acetylene was found to be $27^{\circ}.1\text{ C}$. and agrees with the value found by other investigators¹⁶, $27^{\circ}.2 - 27^{\circ}.6$, it was not considered likely that the product could be any one of these isomers but as a final check the tetrabrom compound was made and analysed.

Faworsky¹⁷ has prepared dimethyl-acetylene and studied its bromination products. He obtained the fully saturated 2.2.3.3. tetrabrombutane from dimethyl-acetylene and studied its properties. His method of bromination was followed as far as possible.

A few drops of bromine were added to the pure

compound cooled in ice until a permanent bromine color was obtained. According to the above mentioned article 2.2.3.3. tetrabrombutane separated out of the reaction mixture on addition of the equivalent amount of bromine, but in this instance this did not seem to occur. Consequently the reaction mixture was put in a quartz tube and exposed to ultra-violet light. In a very short time white crystals began to appear and after several hours bromination had gone to completion. Considerable difficulty was experienced in handling this compound since either the tetrabrom or the intermediate dibrom exhibited very powerful lacrimatory properties. However the compound was crystallized a number of times from petroleum ether and a sample obtained that was thought to be of sufficient purity to analyse.

Faworsky found the melting point of 2.2.3.3. tetrabrombutane to be 230°C and the melting point found by the author was in the vicinity of 210°C . the discrepancy between this and Faworsky's value being due possibly to a small amount of impurity. That this bromination product could not be obtained from one of the isomers mentioned above can be seen from a list of the properties of the following tetrabrombutanes.¹⁸

1.1.2.2. Tetrabrombutane (from ethyl-acetylene) sublimes at 200°C. without melting.

1.1.4.4. Tetrabrombutane is an oil . B.P. 138-145°C.

1.2.2.3 " is liquid at -17°C.

1.2.3.4. " melts about 118°C.

As a final step in the identification of dimethyl-acetylene this crystalline compound was analysed for bromine. The results of analysis gave 86.6% percent bromine compared to the theoretical 85.5%. This seems to establish fairly well the identity of the compound as dimethyl-acetylene. The values found for it's various physical constants will be found in the tables below.

Purification of the Hydrocarbons.

The crude alkyl acetylene, after having been separated from ammonia, was subjected to final purification as follows.

For the removal of traces of water from the crude product before fractionation the method of drying was that used in the purification of the butylenes and butanes by Goffin¹⁰. Briefly this consists in condensing the hydrocarbon in a tube to the bottom of which is attached a capillary tubing plugged with glass wool and leading to the top of another tube evacuated and cooled to -78°C . When the first tube containing the hydrocarbon is chilled by a cooling mixture the water separates as crystals which adhere to the sides of the tube. After the stop-cock, leading into the evacuated tube, is opened the hydrocarbon is strained through by its own vapor pressure. In this way the liquid hydrocarbon is separated from the water which remains frozen to the sides of the glass tube or is filtered out by the glass wool plug at the opening of the capillary. This method has been found to be much more effective than distillation for removing water.

When the product had been freed from water in this way it was transferred to the fractionating apparatus Fig. 4.

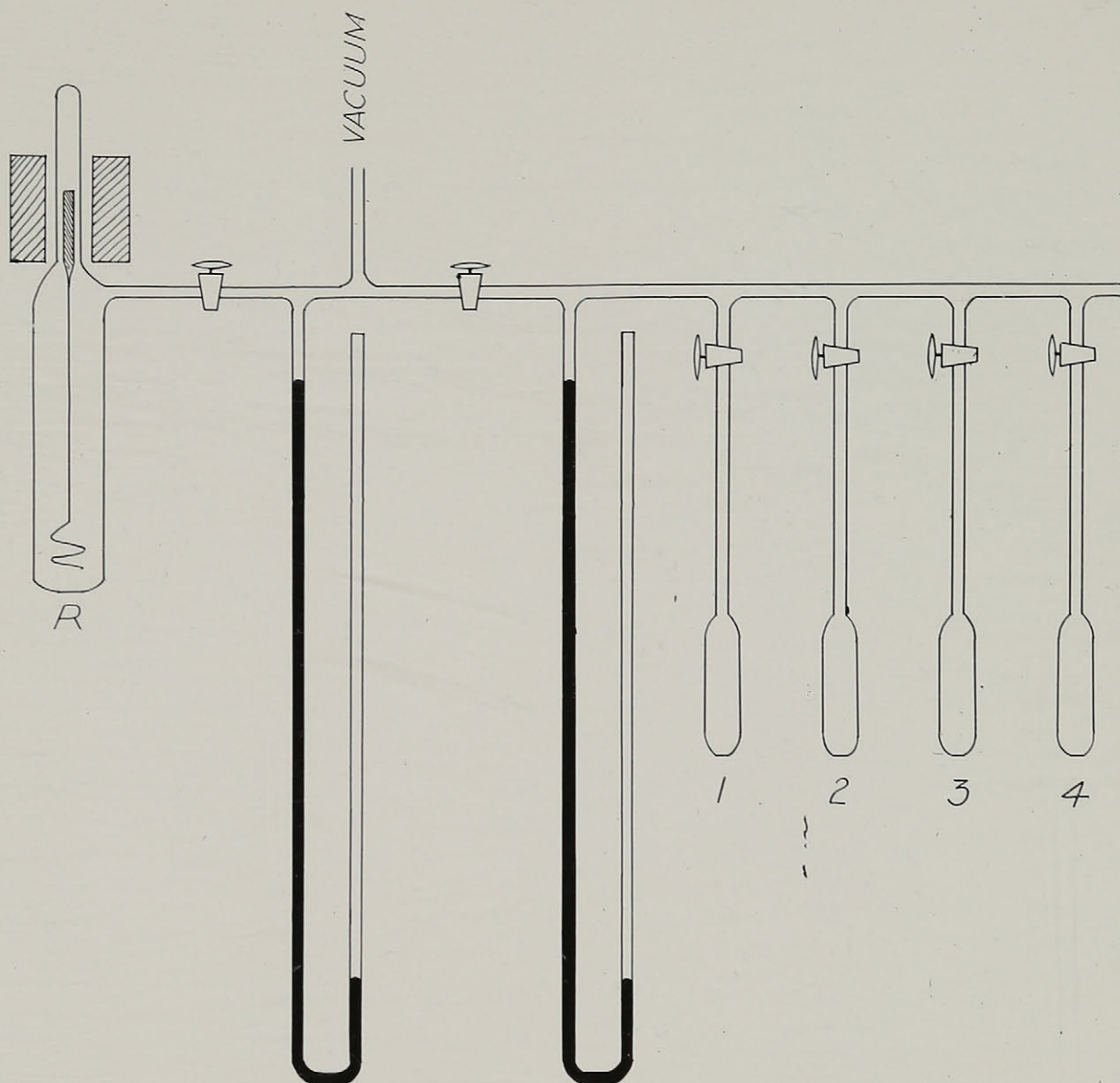


Fig. 4 .

This consisted of a large reservoir (R) equipped with a magnetic stirrer and connected to a system of manometers and receiving bulbs as shown in the diagram. The liquid in (R) was kept at about -50°C . by means of an acetone bath cooled with solid carbon dioxide and stirred vigorously with the magnetic stirrer. The receiving bulb, into which the fraction was being distilled, was cooled to -78°C . with a carbon dioxide ether mixture. Under these conditions distillation proceeded slowly and a very satisfactory fractionation obtained. By means of the manometers vapor pressures of any fraction or of the residue in (R) could be determined. Vapor pressures were measured at appropriately fixed temperatures for each hydrocarbon and were maintained with a carbon dioxide ether bath stirred with a current of dry air bubbles.

Purification of the liquid was accomplished by distilling from a fraction with a low to that with a high vapor pressure. The final heads and tails, consisting of impurities with very high or very low vapor pressures, were rejected. When finally several fractions having the same vapor pressures were obtained they were united and subjected to refractionation. If the same vapor pressures were obtained as before for each fraction the liquid was assumed to be purified and was then used for identification tests after which its physical constants were determined. The hydrocarbons were distilled into the dilatometer, capillarimeter and melting point tube which were then sealed off from the apparatus.

Physical Properties of the Hydrocarbons.

The temperature baths used in the determination of the densities, surface tensions, vapor pressures and melting points consisted of a liquid, suitable for the temperature range under which the observations were being carried out, contained in a transparent dewar flask. All baths were kept vigorously stirred with a current of dry air bubbles and temperatures measured with standard thermometers to an accuracy of one tenth of a degree. It may be noted that all distillations and measurements were made in the absence of air and moisture and glass sealed connections used throughout.

Solid carbon dioxide was used as the cooling agent from $0^{\circ}\text{C}.$ to $-78^{\circ}\text{C}.$ The bath over this temperature range consisted of acetone or ether. For the measurement of properties at lower temperatures high test gasoline was used with liquid air as a cooling agent in a manner to be described later. It was found by previous experimenters that when using ether as a cooling bath it is best to add about twenty per cent alcohol. Water is insoluble in pure ether at low temperatures so that moisture condensing from the atmosphere renders the latter opaque. The alcohol ether solution on the other hand dissolves considerable quantities of water even at $-80^{\circ}\text{C}.$

(i). Density.

The densities of the liquid hydrocarbons over a temperature range suitable for each were measured by the dilatometer method. The dilatometer consisted of a thick walled glass bulb sealed to the end of a capillary tube of uniform bore. After thoroughly evacuating the apparatus the hydrocarbon was distilled into the dilatometer which was sealed onto the fractionating apparatus. When a sufficient quantity had been condensed by cooling with carbon dioxide ether mixture the dilatometer was sealed off just above the capillary.

The volume of the dilatometer for different positions of the meniscus in the capillary was accurately determined by finding the weights of water, at a fixed temperature, that occupied the different positions on the stem. Volumes were determined for three positions of the meniscus and a graph made plotting volume against height of the meniscus. A reference mark etched on the side of the capillary served as a zero mark from which readings were made. All measurements of heights were determined by means of an accurate cathetometer.

After filling the dilatometer with the hydrocarbon under investigation and sealing it off, the height of the meniscus in the capillary was then measured over the desired temperature range, bulb and capillary being entirely immersed

in the temperature bath. The dilatometer was then allowed to come to room temperature and weighed. After cooling again the tip was broken off, the liquid removed, dry air passed through the bulb and the latter weighed. The proper correction was made for the weight of air and the weight of the hydrocarbon was accurately known. The volume occupied by the liquid at various temperatures was given by the position the meniscus occupied in the capillary which, together with the bulb had been accurately calibrated. This volume was further corrected for the coefficient of expansion of the glass.

This method of determining density is very accurate the probable error amounting to less than one part in two thousand. The densities of methyl-, ethyl, propyl- and dimethyl-acetylene over the temperature range suitable for each one are given in Table 1.

The densities of Ethyl- and Methyl-acetylene were determined in duplicate on two samples prepared separately from the start but differing slightly as mentioned above in the method of purification. The results obtained with Preparation 1 are from the sample that had never been in contact with an acid solution or phosphorous pentoxide while those for Preparation 11 are from the sample that was passed through the acid solution and over phosphorous pentoxide. Both sets of data are seen to agree.

Table 1.

Densities of Methyl Acetylene.

Preparation 1.		Preparation 11.	
Temp., °C.	Density	Temp., °C.	Density
-14.4	0.6617	- 0.5	0.6447
-17.5	0.6652	-12.7	0.6582
-22.7	0.6710	-24.2	0.6711
-26.5	0.6759	-33.0	0.6814
-32.5	0.6827	-40.9	0.6911
-36.8	0.6873	-51.9	0.7039
-42.4	0.6936		
-47.4	0.6992		
-53.1	0.7065		
-57.0	0.7109		

Densities of Ethyl Acetylene.

Preparation I		Preparation 11.	
Temp., °C.	Density	Temp., °C.	Density
-28.0	0.7095	-31.3	0.7119
-20.0	0.6997	-23.0	0.7028
-15.0	0.6949	-11.0	0.6899
-10.5	0.6900	- 0.2	0.6784
- 5.0	0.6836	8.9	0.6685
- 0.3	0.6784		
5.6	0.6706		

Densities of Dimethyl Acetylene.

<u>Temp., °C.</u>	<u>Density.</u>
5.0	0.7102
10.0	0.7049
15.0	0.6997
20.0	0.6946
25.0	0.6894
30.0	0.6845

Densities of Propyl Acetylene.

<u>Temp., °C.</u>	<u>Density</u>
5.0	0.7021
10.0	0.7021
15.0	0.6966
20.0	0.6915
25.0	0.6863
30.0	0.6812
35.0	0.6762
40.0	0.6719
45.0	0.6664

A graphical representation of all these results
will be found in Figure 5.

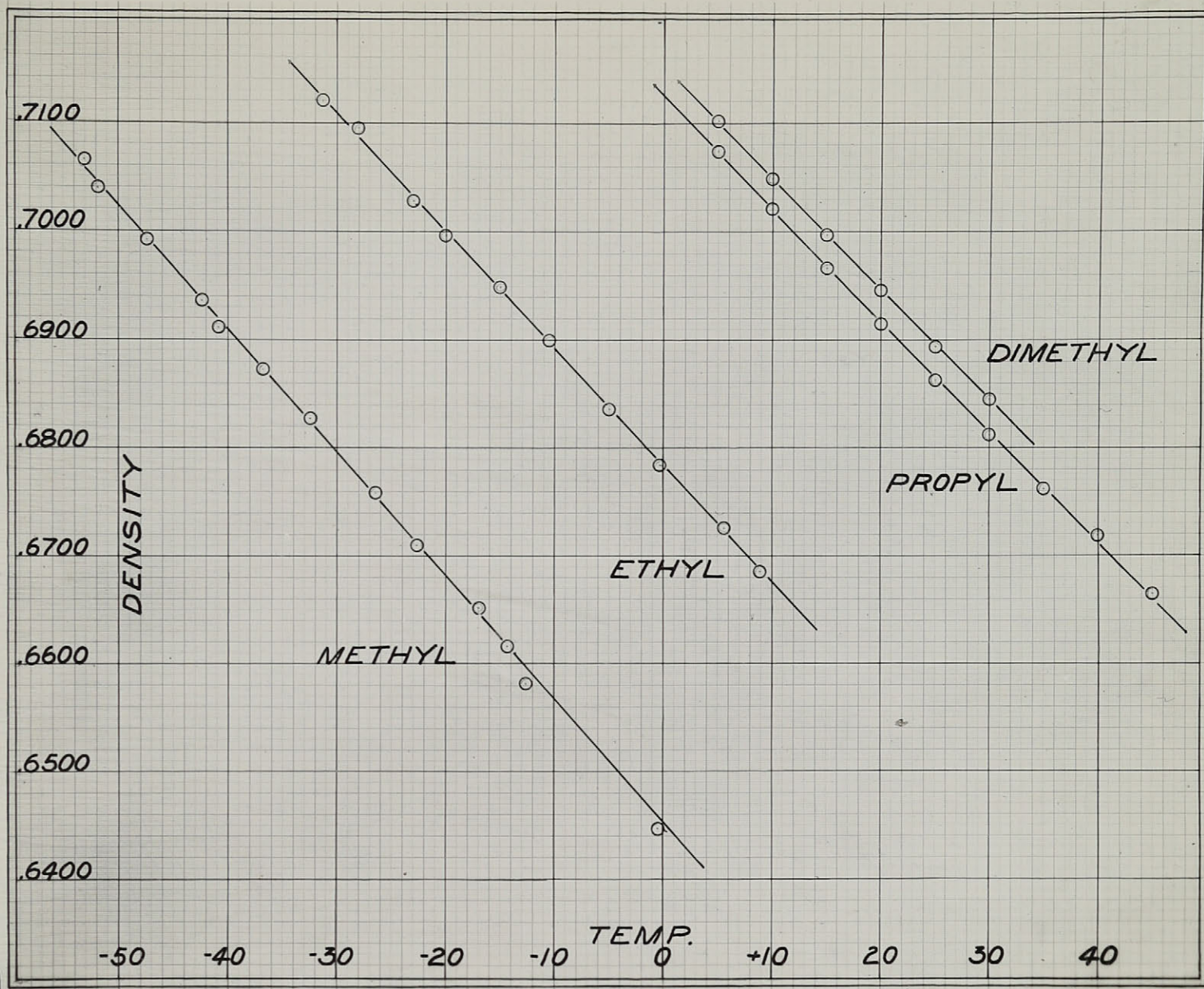


Fig. 5.

The heights observed for the capillary rise were plotted against temperature on a large scale graph. At appropriate temperature intervals the capillary rise was taken from the curve so obtained and these values introduced into the calculations. The expression relating capillary rise, and density is given in the following equation:

$$S = K \cdot \rho \cdot h$$

where:

S = Surface Tension,

K = Constant of the Capillarmeter,

ρ = Density,

h = Capillary rise.

(ii) Surface Tension.

The surface tensions of the hydrocarbons were determined by the capillary rise method using the type of tube recommended by Richards¹⁹ the capillary being attached as a side arm to the tube.

The capillarimeter was filled with the hydrocarbon by distillation and then sealed off from the apparatus. It was entirely immersed in the temperature bath and the capillary rise measured at various temperatures with a cathetometer. Observations over the temperature range were made at least twice for each hydrocarbon and readings made through different parts of the tube to avoid errors due to parallax. The capillarimeter was maintained in a vertical position by lining it up from time to time with a plumb line.

The heights observed for the capillary rise were plotted against temperature on a large scale graph. At appropriate temperature intervals the capillary rise was taken from the curve so obtained and these values introduced into the calculations. The expression relating capillary rise, and density is given in the following equation:

$$S = K \cdot d \cdot h$$

where :

S = Surface Tension.

K = Constant of the Capillarimeter.

d = Density.

h = Capillary rise.

The density was obtained for the necessary temperatures from the curve relating it's variation with temperature.

The remaining factor, K, the constant of the capillarimeter, was obtained by calibrating the capillarimeter with pure ether whose surface tension at 20.0°C. is accurately known. (17.1 dynes). The density of ether is given by the following expression :

$$P_t = P_s + 10^{-3} a (t - t_s) + 10^{-6} b (t - t_s)^2.$$

where:

P_t = Density of ether at t° C.

P_s = Constant .73629

a = " -1.1138

b = " -1.237

t_s = 0^o C.

From this equation the density of ether was found to be 0.7135. The capillary rise for ether was measured and, knowing the density and surface tension for ether at 20.0°C. the constant K for the capillarimeter was obtained.

The surface tensions and molecular surface energies of the hydrocarbons are listed below in Table 2. The surface tensions of all the hydrocarbons were plotted against temperature and are represented for purposes of comparison in Figure 6.

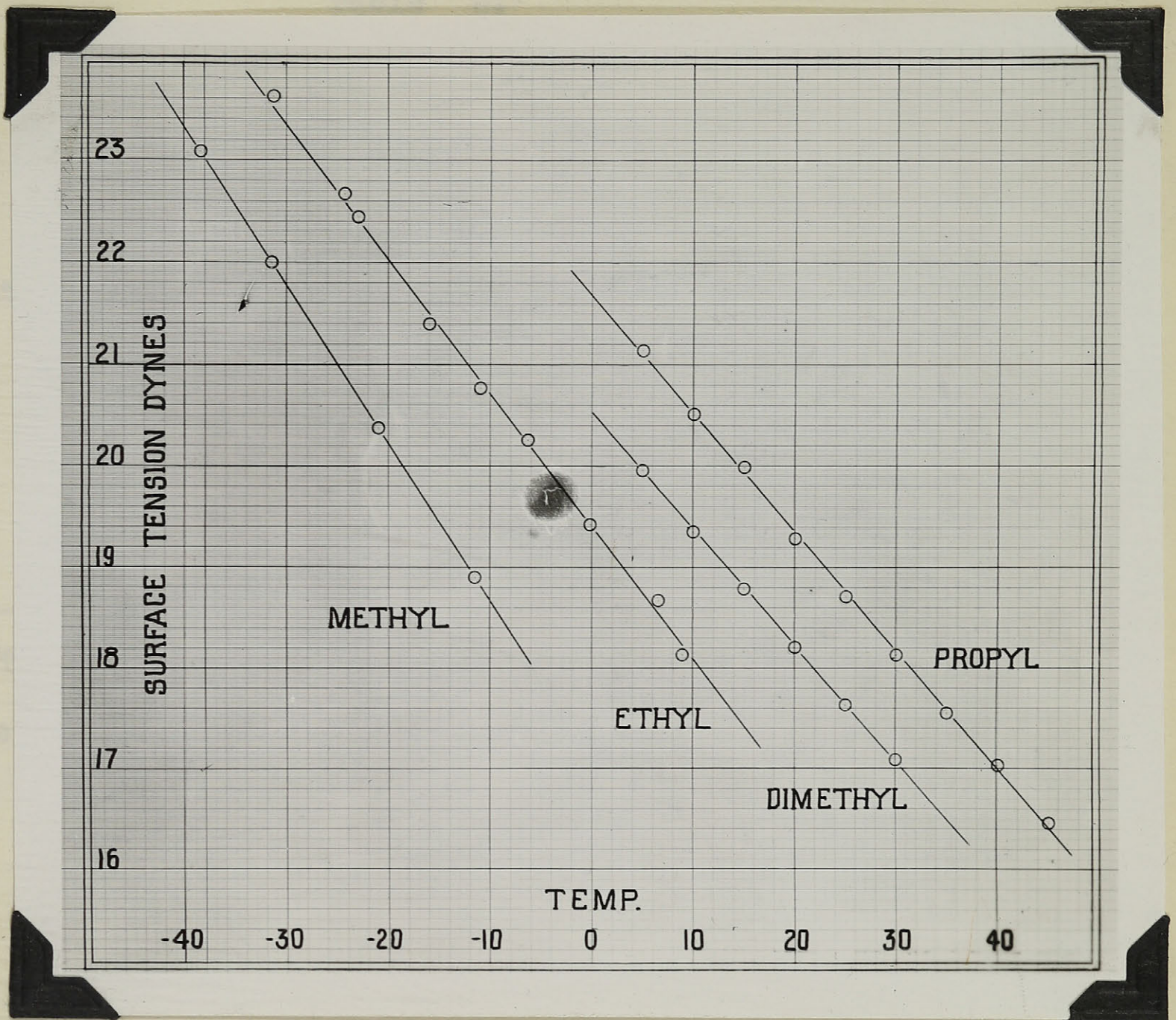


Fig. 6 .

Table 2.

Surface Tension of Methyl Acetylene.

Preparation II.

Temp., °C.	Surface Tension	Molecular Surface Energy
-11.5	18.91 dynes	293.0
-21.0	20.37	312.2
-31.6	22.00	332.8
-38.4	23.08	346.4

The surface tension of methyl-acetylene was found only under those conditions pertaining to Preparation II.

Surface Tension of Ethyl Acetylene.

Preparation I.

Temp., °C.	Surface Tension	Molecular Surface Energy
-26.3	22.65 dynes	407.6
-16.0	21.40	389.3
- 6.3	20.25	372.4
6.5	18.70	348.7

Surface Tension of Ethyl Acetylene.

Preparation II

Temp., ^{OC} C.	Surface Tension	Molecular Surface Energy
-31.3	23.62 dynes	423.2
223.0	22.44	406.1
-11.0	20.77	380.1
- 0.2	19.32	356.9
8.9	18.13	338.8

Surface Tension of Dimethyl Acetylene.

Temp., ^o C.	Surface Tension	Molecular Surface Energy
5.0	19.96	358.3
10.0	19.38	349.2
15.0	18.80	340.8
20.0	18.20	331.9
25.0	17.64	322.9
30.0	17.07	314.0

Surface Tension of Propyl Acetylene.

Temp., ^o C.	Surface Tension	Molecular Surface Energy
5.0	21.14	443.5
10.0	20.51	432.9
15.0	19.89	421.9
20.0	19.28	410.8
25.0	18.71	400.5

Temp., °C.	Surface Tension	Molecular Surface Energy
(Propyl Acetylene Cont'd)		
30.0	18.13	390.1
35.0	17.55	379.8
40.0	17.03	369.7
45.0	16.46	359.2

(iii) Melting Points.

The melting points of the hydrocarbons were determined by the method used by Maass and Wright⁷. Petroleum ether or high test gasoline was used as the bath liquid which was placed in a transparent dewar flask. The bath was cooled by means of liquid air dropped into a pyrex test tube immersed in the gasoline. The liquid air, contained in another dewar flask, was forced into the test tube by air pressure. Efficient stirring of the bath was maintained by a current of dry air bubbles.

The bath was cooled until the hydrocarbon under investigation had solidified. It was then allowed to warm up slowly the temperatures being measured with a pentane thermometer. The temperature taken as the melting point was half way between the temperature at which melting began and that at which the solid just disappeared. In all cases a sharp melting point was observed. The melting points are listed with other properties in Table 4 .

(iv) Vapor Pressures.

Vapor pressures were determined in the fractionating apparatus for those hydrocarbons whose boiling points were below room temperature, care being taken to keep the liquid vigorously agitated in order to prevent superheating. For those compounds having boiling points about or above room temperature an apparatus was devised consisting of a manometer attached to a small bulb into which the hydrocarbon could be distilled. Bulb and manometer were then sealed off from the apparatus and immersed in a bath whose temperature could be regulated. This avoided condensation of the hydrocarbon in the connecting tubing and the manometer.

For low temperatures the bath liquid consisted of a carbon dioxide ether mixture stirred with a current of dry air bubbles and contained in a dewar flask. For the higher temperatures water was used, likewise stirred with air bubbles.

In Table 3 will be found the vapor pressures of the hydrocarbons over a temperature range suitable for each. Vapor pressure curves were obtained from these data and the boiling points of the hydrocarbons taken from these curves which are to be found in Figure 7. The latent heats of evaporation, given in Table 4, were calculated from these curves by means of the Clapeyron equation.

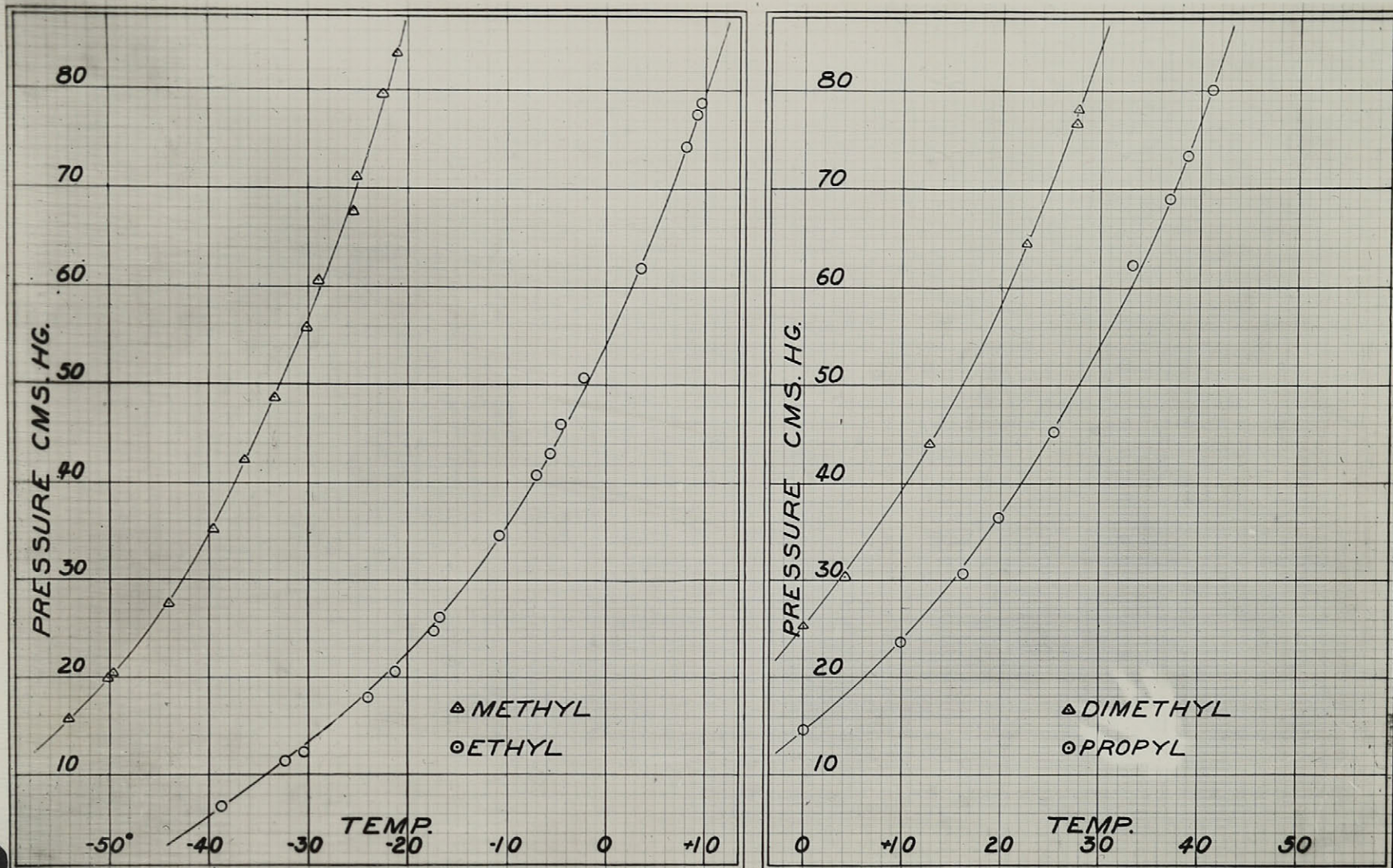


Fig. 7 .

Table 3 .

Vapor Pressures of Methyl Acetylene

Preparation I		Preparation II	
Temp., °C.	Pressure cms. Hg.	Temp., °C.	Cms. Hg.
-54.1	15.88	-50.1	20.03
-49.6	20.46	-39.6	35.18
-44.0	27.64	-30.2	55.90
-36.5	42.17	-25.2	71.15
-33.4	48.74	-22.6	80.01
-28.5	60.80	-21.1	83.80
-25.5	67.80		
-22.5	79.70		

Vapor pressures of Ethyl Acetylene.

Preparation I		Preparation II	
Temp., °C.	Cms. Hg.	Temp., °C.	Cms. Hg.
-38.8	6.80	-32.4	11.46
-30.5	12.38	-24.1	17.93
-21.3	20.67	-17.4	24.81
-16.9	26.18	-11.4	33.57
-10.8	34.60	- 7.0	40.85
- 5.7	43.10	- 4.5	46.03
- 1.3	50.78	8.0	74.42
3.5	61.96	9.5	78.80
9.1	77.66		

Table 3 .

Vapor Pressures.

Dimethyl Acetylene		Propyl Acetylene	
Temp., °C.	Cms. Hg.	Temp., °C.	Cms. Hg.
0.0	25.4	0.0	14.66
4.2	30.4	9.9	23.66
12.7	44.0	16.2	30.66
22.4	64.5	19.8	36.50
27.5	77.0	25.3	45.20
27.7	78.5	33.2	62.30
		37.0	69.00
		38.7	73.40
		41.2	80.10

The boiling points of all the hydrocarbons agree very well with the values given in the literature. The boiling points of Methyl Acetylene obtained by Preparation I and Preparation II agree within 0.1°C. The same result is found for Ethyl Acetylene.

This value for Methyl Acetylene (-23.3°C.) shows fair agreement with that (-23.0°C.) obtained by R.N.Meinert and C.D.Hurd²⁰ but is considerably higher than that found by Maass and Wright⁷. The amount of material available for purification by Maass and Wright was considerably less

and the data given above for Methyl Acetylene may be believed more accurate for this reason.

The boiling point found for Ethyl Acetylene (8.6°C) agrees with the values in the literature²¹ and likewise for Propyl Acetylene²² ($39.7^{\circ}\text{C}.$) and Dimethyl Acetylene²³ ($27.1^{\circ}\text{C}.$).

TABLE 4 .

and the data given above for Methyl Acetylene may be
believed more accurate for this reason.

The boiling point found for Ethyl Acetylene

Compound	1 M.P.	2 B.P.	3 M.L.	4 D _b	5 S _b	6 Tot. S.E.	7 K R.S.	8 <u>M.L.</u> T _b	9 T _c Calc.	10 <u>T_b</u> T _c	11 V _m	12 Par. Obs.	13 Par. Calc.	14 % Diff.
Ethane	-172.0	-88.3	3880	.5469	16.05	45.7	1.98	21.0	34.6	.60	54.9	110.4	112.2	1.6
Propane	-189.9	-44.5	4700	.5853	15.63	50.3	2.15	20.6	91.6	.62	75.0	150.6	151.2	0.4
N-Butane	-135.0	- 0.5	5597	.6014	14.90	47.8	2.21	20.5	147.0	.64	96.3	190.6	190.2	0.2
I-Butane	-145.0	-10.2	5480	.5944	14.10	47.2	2.23	20.8	129.5	.64	97.6	188.8	190.2	0.2
Ethylene	-169.4	-103.9	3510	.5699	1650	47.7	2.14	20.8	5.9	.60	49.1	99.4	101.2	1.8
Propylene	-185.2	-47.0	4600	.6095	16.70	49.7	2.12	19.0	91.3	.62	69.0	139.7	140.2	0.4
✕ Butylene	-190.0	- 6.1	5400	.6250	15.95	51.1	2.21	20.2	145.0	.64	89.5	179.9	179.2	0.4
β Butylene	-127	1.0	5400	.6300	16.78	51.2	2.14	19.7	156.0	.64	88.9	178.7	179.2	0.3
✕ Butylene	-146.8	-6.6	5200	.6268	15.72	49.8	2.15	19.7	147.0	.64	89.3	178.4	179.2	0.4
Acetylene	- 81	-83.6	4273	.6208	19.58	56.0	2.02	22.2	39.7	.61	41.9	88.1	90.4	2.6
Methyl "	-101.5	-23.3	5562	.6698	20.70	59.4	1.99	22.3	121.6	.62	59.7	127.5	129.4	1.5
Ethyl "	-122.5	8 8.6	5983	.6682	18.30	53.5	1.96	21.3	190.5	.61	80.8	167.2	168.6	0.8
Dimethyl Acetylene	- 24.0	27.1	6434	.6873	17.40	51.8	1.75	21.4	215.5	.61	78.6	160.7	168.6	4.6
Propyl Acetylene	- 98.0	39.7	7087	.6718	17.00	53.3	2.12	22.6	220.3	.63	101.3	206.2	207.2	0.5

Discussion.

The constants determined for all the hydrocarbons investigated so far in this laboratory are compiled in Table 4. The two and three carbon compounds were investigated by Wright⁷ and the three butylenes and two butanes by Coffin¹⁰. In the discussion of this table homologous and isomeric relationships will be considered separately as far as possible in order to avoid confusion. The properties considered will, in general, be taken up in the order in which they appear in the table.

The physical properties of the first few members of an homologous series are of particular interest in that the majority of the properties of these compounds show distinct anomalies which cannot be fitted in with the higher members of the series. These peculiarities usually vanish and the series "constants" become constant with the four or five carbon compounds. It is an interesting possibility that the study of the lower and more simple members of a series may throw considerable light on the properties and structure of carbon chains by bringing out various factors that are masked in the higher members by the larger weight of the molecule and the greater length of the chain.

In considering the homologous relationships brought out in the above table it is seen that the well known rule of alternating melting points (column 1) is obeyed in the paraffin series, the compounds ethane and butane, with an even number of carbon atoms each having a higher melting

point than propane with three carbon atoms. This somewhat dubious rule does not hold for the unsaturated olefine and acetylene series and indeed the extremely low melting point of α butylene is a surprising exception to the general rule, obeyed in every other case in the above table, that the melting point of an unsaturated straight chain compound is higher than that of the saturated compound with the same number of carbon atoms. This is seen to be the case for the acetylenes whose melting points are, for compounds containing the same number of carbon atoms, above either the paraffins or olefines.

The variation of melting point due to structural differences in the molecule is strikingly demonstrated in the butylenes and the isomeric acetylenes, dimethyl-acetylene and ethyl-acetylene - all containing four carbon atoms. In considering these compounds it is seen that unsaturation in the acetylenes apparently accounts for their higher melting points. Further more symmetry of the molecule seems to play an important role in governing the melting point. The unsymmetrical butylenes have the lowest while β butylene has the highest melting point of the butylenes. This is also seen to be the case with ethyl-acetylene and dimethyl-acetylene.

The reason why the introduction of a double or triple bond should raise the melting point of a substance is to be looked for in the increased stray field due to unsaturation which thus increases the attraction between the molecules.

The properties observed at higher temperatures such as boiling points, molecular latent heats of evaporation and critical temperatures are, as would be expected, practically uninfluenced by this increased attraction.

These more additive properties boiling point (column 2) and molecular latent heat of evaporation (column 3) vary much more regularly than the markedly constitutive melting points. The critical temperatures (column 9) also conform to this same tendency. These properties in the acetylenes are seen to be consistently higher than for other compounds with the same number of carbon atoms and rise as would be expected with increase of molecular weight. The symmetrical dimethyl-acetylene has a higher boiling point than its isomer ethyl-acetylene.

A consideration of the properties mentioned above leads to a very definite distinction, when compounds having the same number of carbon atoms are compared, between the members of the acetylene series on the one hand, and those of the paraffin and olefine on the other. As stated, the boiling points, molecular latent heats of evaporation, and critical temperatures are distinctly higher for all the acetylenes than for their corresponding compounds in the other two series, although their molecular weights are actually less. Thus it is seen that ethane and propylene have boiling points -88.3°C . and -103.9°C . respectively and that they are below acetylene whose boiling point is -83.6°C .

This tendency is followed throughout by propane, propylene and methyl-acetylene; butane, butylenes and ethyl-acetylene. On comparing the molecular latent heats of evaporation it is seen that the decrease of ethylene under ethane is approximately of the same order of magnitude as the decrease in molecular weight. For acetylene, whose molecular weight is still lower, there is a decided increase in this constant entirely inconsistent with the behaviour of the paraffins and olefines. Likewise this is seen to be the case for the three carbon compounds propane, propylene, allylene and also in the four carbon group, butane, butylenes, dimethyl-acetylene and ethyl-acetylene.

This same apparent anomaly is paralleled in the values for the critical temperatures. In the two carbon compounds acetylene, with the lowest molecular weight, has the highest value for this constant. Similarly in the three and four carbon groups.

Hence, after a comprehensive survey of this data, it is possible to classify the paraffins and olefines together but the acetylenes show a distinct difference from the other two series. This is connected with what will be brought out later on, namely, that the acetylene linkage is of a more definitely pronounced polar character than is the case in the paraffin and olefine series.

The boiling points on the "corresponding" temperature scale (column 10) agree very well among themselves and bring out very well the simple and ideal nature of these liquids.

The Ramsay and Shields constants (column 7) also furnish evidence for the unassociated normal condition of all these substances in the liquid state although the values obtained for the Ramsay and Shields constant in the acetylenes seem to be consistently lower.

The abnormality of the first two members of each series is well brought out by the rapid initial increase of the densities at the boiling point (column 4). The total surface energy (column 6) is seen to increase for the first two members of all series.

This quantity, total surface energy, is of particular value in that it solves the question of the temperature at which the surface tensions of different liquids should be compared. The fact that $\frac{ds}{dT}$ is linear makes U constant in the following equation in which U is the total surface energy and S is the surface tension at the temperature T.

$$U = S + T \frac{dS}{dT}$$

Since $\frac{dS}{dT}$ is strictly linear only at a considerable distance from the critical temperature U will not be constant if calculated from surface tensions measured at too high a temperature. This total surface energy which is thus a constant for any particular liquid is of especial importance in homologous series when considered in the light of modern surface phenomena. The widely accepted views of Langmuir¹

and Harkins² in this respect may be summed up as follows. The molecules at the surface of a liquid are under a differential force due to the molecules beneath them and thus tend to be drawn by this attraction into the body of the liquid. Since this force acts only over a very short distance a long molecule with a polar group at one end e.g. one of the higher fatty acids will tend to orient itself in a direction such that its potential energy is a minimum. In other words the polar group being at the end of the molecule most strongly attracted will penetrate into the liquid leaving the carbon chain normal to the surface. Since the surface energy of a liquid is mainly due to groups possessing stray fields of force, i.e. polar groups, it follows that the farther the polar group penetrates beneath the surface the smaller will be the surface energy. The longer a molecule the farther will its polar group be from the surface so that in ascending an homologous series of such compounds the surface energy should tend to become constant when the surface consists entirely of CH_3CH_2 --- groups. Moreover all homologous series having a CH_3CH_2 --- at one end of the chain should approach the same limiting value.

This constant for the higher paraffins has been found to lie between 46 and 48, values which theoretically should include the surface energies of all members of the series. This is seen to be the case for ethane and the two butanes.

The high value for propane is a distinct anomaly for which at present there seems to be no explanation. (column 6) . The change from paraffins to the corresponding olefines produces ,as would be expected, a small increase in total surface energy. On going from the olefines to the acetylene series the increase is much more marked but seems to become less distinct when the butylenes are compared with the four carbon acetylenes ethyl-acetylene and dimethyl-acetylene.

When considering the property total surface energy in relation to the first few members of an homologous series two classes of compounds may be separately classified. There are first those in which there is no polar group attached to the molecule such as the paraffins and olefines listed above. Secondly there is a large number of compounds, such as the alcohols and fatty acids, which possess a highly polar group attached to one end of the molecule.

As can be seen from the data assembled in Table 4 the total surface energies of those compounds belonging to the first class increase slightly until a more or less limiting value is reached. In the olefine series, where this increase is most marked, the change from ethylene to propylene is greater than from propylene to normal butylene. That this difference should seem smaller with increased length of chain is explained by modern theory as being the

result of the greater orientation in the case of the longer molecule i.e. those having the greater moment.

In compounds of the second type, that is those possessing a polar group on the end of the carbon chain, an entirely different result is observed. Several homologous series of this kind have been investigated such as the alcohols and fatty acids. Hunten and Maass²⁴ studied the variation of total surface energy for the fatty acids and obtained the following results:

Acid	Total Surface Energy
Formic	63.6
Acetic	58.2
Propionic	56.9
Butyric	54.4
Lauric	54.6
Palmitic	54.5
Stearic	54.8

From these data it is seen that for this class of compounds the total surface energy falls off very rapidly as the series is ascended and reaches a normal value for all the higher members of the series. This same result has been found in other homologous series whose members contain a polar group. When the total surface energies of the acetylenes are compared it is seen at once that they follow this

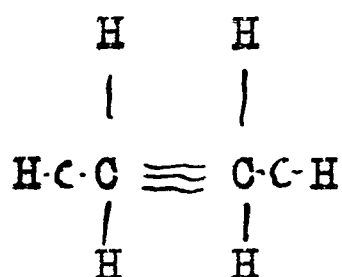
general tendency i.e. to decrease to a normal value with increase of carbon chain. This evidence points to the fact not encountered in the paraffin and olefine series, that the acetylene linkage, a triple bond, exerts a decidedly polar influence on the molecule.

It was pointed out in the general introduction that the more symmetrical a molecule is, the greater is its attraction for molecules of the same species, and consequently the smaller is its attraction for molecules of a different species. Thus it would be expected that dimethyl-acetylene, being the symmetrical isomer to ethyl-acetylene, would have a higher surface tension at the boiling point as is exemplified in the case of the butylenes where the symmetrical (3 butylene has the highest value for this constant, (column 5). This theory is apparently not supported by the data obtained for the acetylenes since it is seen that the value for this constant is less for the symmetrical dimethyl-acetylene than for its unsymmetrical isomer ethyl-acetylene.

It must be remembered, however, that in this particular case the symmetry of the molecule is around a polar group whose polarity is of another order of magnitude than that of the olefine series. Since the property of surface tension is particularly sensitive to this factor it may well be due to this that the symmetrical dimethyl-acetylene

has a smaller surface tension at the boiling point. As will be pointed out more fully later on the polarity and consequently the attractive forces due to the polar group may possibly be partly neutralized in this case by the very fact that the molecule is symmetrical.

The molecule of dimethyl-acetylene may be represented as :



Represented in this way it is seen that the hydrogen atoms overlap and obscure the effect of the highly unsaturated triple bond and, as many of its properties seem to indicate, cause the compound to behave as if it were partially saturated as far as the pronounced unsaturation of an acetylene linkage is concerned.

In consequence of this, in addition to the polarity effect, it would be expected that the surface tension at the boiling point would be smaller, since the molecular forces of attraction would be considerably lessened by the shielding effect of the hydrogen atoms and the strain caused by such a distortion. This is seen to be followed out in all the properties depending on surface tension. A comparison of the surface tensions at the boiling point of dimethyl-acetylene and its isomer ethyl-acetylene shows, as would be expected from this point of view, a lower value for dimethyl-acetylene.

The molecular volume at the boiling point has long been recognised as probably the most additive property of chemical compounds and one which should lend itself readily to calculation and prediction. Among the various relationships connecting molecular volume and structure, that of Kopp²⁵ is probably the most satisfactory and has been most widely used. Although Kopp's apparent insistence on the strictly additive nature of volume has been discredited for a considerable time it is only very recently that any satisfactory substitute for his constants, or any reliable rules connecting volume and constitution were suggested.

It was pointed out by McLeod²⁶ that the following relation between surface tension and density appeared to hold over a wide range of temperature and for very different chemical substances. In this equation :

$$S = C (D - d)^4$$

S is the surface tension, D and d are the liquid and gas densities all at the same temperature. C is thus a characteristic constant independent of temperature for normal unassociated liquids. By rearranging the above equation and multiplying by M, the molecular weight, Sugden²⁷ showed that for different liquids P in the relation :

$$P = \frac{M}{D - d} S^{\frac{1}{4}}$$

represents the molecular volume for temperatures at which

the liquids have the same surface tension. Thus for different liquids this quantity which Sugden terms the "parachor" can be considered as the molecular volume measured at the same internal pressure. The quantity $\frac{M}{\bar{D} - \bar{d}}$ has the dimensions of volume and at low temperatures, where \bar{d} becomes negligible, is really the molecular volume. From the study of a large number of liquids Sugden has determined the values of several atomic and structural parachors which are found to be remarkably additive. He assigns carbon the value 4.8, hydrogen 17.1, the double bond 23.2 and the triple bond 46.4.

In column 12 of Table 4 are listed the values of the parachors calculated from the density and surface tension data of these compounds. The next column gives the parachor calculated from Sugden's values. Column 14 shows the percentage differences between the observed and calculated values. In most cases the agreement is very good but irregularities are noticed in the two carbon compounds and for dimethyl-acetylene.

That Sugden's values for the parachor can not always be relied on in special cases dealing with compounds that differ widely in constitution has been pointed out by Mumford and Phillips²⁸ in connection with investigations they have made on a considerable number of compounds.

It has been stated above that dimethyl-acetylene appears to exhibit pronounced properties indicating that its molecule is decidedly polar. In addition to this there is also evidence for the assumption that the molecule behaves as if the attractive forces, due to the triple bond, were masked, apparently by the symmetry of the molecule, so that it resembles a more saturated molecule in certain properties. Thus it is not surprising to find that the parachor, which is directly related to surface tension, should have a value lower than the theoretical based on Sugden's values, which do not take into account "strain factors".

Since the parachor is virtually a measure of molecular volume under comparable conditions in regard to internal pressure, and is, therefore, more or less independent of the cohesion between the molecules²⁷, the contractions referred to as strain constants would appear to cause a real diminution in molecular volume brought about either by the closer packing of atoms and groups within the molecule or by a decrease in the effective size of one or other of the atoms concerned. That a strain constant exists in the case of dimethyl-acetylene may be indicated by the fact that its molecular volume is lower than ethyl-acetylene. In consequence of this strain discrepancies in the value obtained for the parachor are not to be unexpected.

Let us consider the acetylenes and dimethyl-acetylene in particular, from another point of view and confine the discussion to an empirical conception of the behaviour of this group of compounds.

It has been shown that the molecular volume at the boiling point, from a theoretical point of view, should give a comparative value of the actual volume of molecules. This volume has been found to be an additive-constitutive property or, in other words, additive from the point of view of definite values assigned to the atoms of elements that are linked up in a definite way. Thus carbon and hydrogen in all organic compounds may be assigned definite values where the carbon has four ordinary linkages. Unsaturation requires the addition of a constant value depending on whether the unsaturation is of an ethylene or acetylene linkage. The latter has the larger value and the greater the extent of unsaturation the greater is the volume of the compound above that given by the straight additive values of the atoms of the elements involved.

Using Kopp's values for the molecular volumes of carbon and hydrogen at the boiling point, where $C = 2H = 11$, the molecular volumes of the acetylenes derived by these constants are given in the following table and compared with their experimental values determined from the density at the boiling point.

	Kopp's	Exp'mtl	Diff.
Acetylene	33.0	41.9	8.9
Methyl Acetylene	55.0	59.7	4.7
Ethyl Acetylene	77.0	80.8	3.8
Dimethyl Acetylene	77.0	78.6	1.6
Propyl Acetylene	99.0	101.3	2.3

It is at once seen that the difference in volume caused by the triple bond is greatest for acetylene and falls off rapidly as the series is ascended. What is not so easily understood is the fact that the difference between these values in the case of the isomers is much less for dimethyl-acetylene than it is for ethyl-acetylene.

However the interpretation made possible by this apparent anomaly goes further to substantiate the theory that the molecule of dimethyl-acetylene is rendered less unsaturated by the symmetry of its structure. Due to this symmetry the increase of volume over the empirical value, assigned by Kopp's data for the triple bond, is lessened by more than half so that, instead of the increase expected by the introduction of a triple bond, there is found a value that would suggest that the compound was considerably less unsaturated.

This evidence, obtained from an entirely empirical point of view, falls in agreement with and moreover substantiates the same conclusions drawn from a consideration of the calculated values obtained from surface tension measurements.

The correlation of the data from these two points of view lends further strength to the theory that ⁱⁿ dimethyl-acetylene the unsaturation of the triple bond is considerably obscured by the symmetry of the molecule.

Dimethyl-acetylene can be prepared by the action of heat on a mixture of ethyl-acetylene and alcoholic potash¹³. This would tend to indicate that the potential energy of the dimethyl-acetylene molecule is, if not actually at a minimum, considerably less than that of ethyl-acetylene. This is further supported by the lower values obtained for surface tension and total surface energy.

Among other chemical properties the relative ease of bromination of the butylenes and acetylenes may be compared. Coffin,¹⁰ on work done in this laboratory in connection with the bromination of the butylenes, found that the dibrom-butanes could be prepared readily from these compounds. In contrast to this the complete saturation of the molecule of dimethyl-acetylene was accomplished, as described above, with considerable difficulty and under the catalytic influence of ultra violet light. This result is not to be unexpected since, apart from the concept of its lower potential energy, the chemical reactivity of dimethyl-acetylene is probably quite inhibited by the symmetry of its molecule.

Finally it may be said that all the properties of dimethyl-acetylene, relation to members of its own homologous series and to members of the paraffin and olefine series, whether physical or chemical, point to the fact that its

behaviour is greatly influenced and indeed controlled by its polarity and molecular strain. The latter is caused possibly by the shielding effect of the hydrogen atoms which is so noticeable on account of the symmetry of the molecule.

In this respect it would be most interesting, although the time allotted to the work described in this thesis does not permit, to compare the relative rates of reaction velocity for the acetylenes along lines similar and analogous to those followed by former investigators in connection with the reaction velocities of the butylenes and hydrogen chloride. This work is described in an earlier part of this thesis. The results of such an investigation would, it is believed, further substantiate the data already obtained for the acetylenes. It would be expected that an investigation of this sort would show that dimethyl-acetylene, in relation to the other members of its series and in particular to its isomer ethyl-acetylene, would have a much slower rate of velocity of chemical reaction and behave in this respect much as the symmetrical β butylene of the olefine series. This is an avenue for future work which lack of time prevents in this investigation but one that would yield highly interesting and informative results.

In conclusion it may be said that, as a class of compounds, the acetylenes stand out separately and distinctly from the paraffins and olefines as far as the physical

properties and their interpretation is concerned. This is manifested in several instances by the comparison of their physical properties with those of the other two series . Decrease in molecular weight in the paraffin and olefine series causes, as would be expected, for compounds of the same number of carbon atoms, a lowering of such constants as boiling point, critical temperature etc. These constants are seen to rise for the acetylenes in spite of their lower molecular weight. The total surface energies of the acetylenes follow a tendency differing from that of the paraffins and olefines showing that they exhibit polar characteristics not shared by the other series.

That the acetylene linkage imparts to the compounds comprising this homologous series a polar tendency is made strikingly evident by the properties of dimethyl-acetylene, The properties of it's isomer, ethyl-acetylene, exhibit, parallel to the other members of it's series, this observed polarity but the fact that in dimethyl-acetylene the polarity is considerably masked by the symmetry of the molecule brings to the fore with even more emphasis the polar properties of the acetylenes as a whole.

Due to the saturation of the paraffin series it would not be expected that they would exhibit polarity in any of their properties. On passing from this series to that of the olefines it might be thought that some degree of polarity would be involved in consequence of their unsaturation.

That no property of this sort is present may be observed by a consideration of their physical constants. No divergences in the properties of β butylene, the symmetrical olefine corresponding to dimethyl-acetylene, are noticed which would probably be the case if pronounced polarity in this series existed. As unsaturation is increased resulting in the acetylene series an entirely different aspect is presented. All the properties that would be influenced by polarity of the molecule are seen to manifest this characteristic by their divergence from the general tendencies observed in the paraffin and olefine series. This makes it apparent that the acetylene series possesses a property that sets it apart as a separate class of compounds from the paraffins and olefines namely that the molecules of the members of this series exhibit a definite polar tendency.

Summary .

The aliphatic acetylenes, methyl-, ethyl-, and propyl-acetylene have been prepared by the method of Lebeau and Picon. A description of this method, which consists in the alkylation of sodium acetylide in liquid ammonia, is given. Its value as a means of preparing the hydrocarbons in a state of purity is emphasized. A method has been evolved for the preparation of dimethyl-acetylene along lines analogous to those used in preparing the simpler aliphatic acetylenes. For this preparation the sodium-methyl-acetylide was methylated in a reaction medium of liquid ammonia.

These hydrocarbons were prepared and very carefully purified for the purpose of determining their physical constants. The data obtained are melting points, boiling points, density and surface tension measurements over a temperature range suitable for each hydrocarbon and other constants calculated from the values so obtained such as molecular latent heat of vaporisation, critical temperature and parachor etc.

These physical constants have been accurately determined in order to compare the hydrocarbons from the point of view of molecular forces of attraction. The interpretation of these data makes possible a comparison of these acetylenes not only among themselves but with special reference to the paraffin and olefine series. The fact that ethyl-acetylene and dimethyl-acetylene are isomers, each possessing four carbon atoms, and, moreover, can be compared with the butylenes

lends an added significance to the theoretical aspect of the work.

It is found, when the physical data for paraffins and olefines are compared, that the acetylene series exhibits pronounced polar tendencies that distinguish it from the other two series. The reality of this distinction is apparent from considerations of various properties with special reference to the total surface energy.

The properties of ethyl-acetylene are compared with those of its symmetrical isomer dimethyl-acetylene. The most striking difference is observed in the values obtained for the parachor and molecular volume. Both these constants are seen to be considerably lower for dimethyl-acetylene. The interpretation put upon these differences leads to the conclusion that dimethyl-acetylene, due to the shielding effect of its symmetrically arranged hydrogen atoms, behaves as if it were considerably more saturated than its fellow members of the acetylene series.

The existence of a greater saturation in the symmetrical dimethyl-acetylene is further demonstrated by the fact that its polarity is considerably lessened so that in this respect it resembles the members of the olefine series.

In spite of the fact that the acetylenes have lower molecular weights those constants usually dependant on such a property as melting point, boiling point, critical temperature etc. are shown to be consistently higher than for the members

of the paraffin and olefine series. This, together with the concept of their polarity, leads to the conclusion that of the three series the acetylenes are to be classified separately as far as their physical properties are concerned.

The author's claims to originality and contribution to knowledge are :

1. Certain modifications in the Lebeau Pivon method for the preparation of aliphatic acetylenes and the fact that ethyl-, and methyl-acetylene can be dried by passing the gases over phosphorous pentoxide without the possibility of their polymerization.

2. (a) The determination of the physical properties of methyl-, ethyl-, propyl- and dimethyl-acetylene by physical chemical methods.

(b) Where methyl-acetylene had been investigated before this work includes a refinement and correction of the values previously obtained.

(c) Melting points of these hydrocarbons have been accurately determined for the first time.

(d) Vapor pressures of the hydrocarbons were determined for the first time over a temperature range resulting, by this physical chemical method, in a more accurate measurement of all the boiling points.

(e) Measurements of the density and surface tension were made for these hydrocarbons over a temperature range. These data, together with the constants calculated from them, have been determined for the first time.

(f) Dimethyl-acetylene has been prepared for the first time by methylating the sodium-methyl-acetylide in liquid ammonia although this method has been indicated before.

(g) Dimethyl-acetylene shows in its properties distinct anomalies. The parachor is considerably lower than that of its isomer ethyl-acetylene. This is interpreted to mean that dimethyl-acetylene behaves as a more saturated compound than the acetylene linkage would imply. The possibility of a strain constant to be applied in the calculations for the parachor is suggested.

(h) The acetylene series is distinguished from the paraffin and olefine series in that it possesses pronounced polar tendencies.

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