1 THE EFFECT OF UNSATURATION ON THE FORMATION OF MOLECULAR COMPOUNDS 2. A METHOD FOR THE DETERMINATION OF THE DENSITIES OF GASES





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MOLECULAR COMPOUNDS"

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OF GASES."

THESIS PRESENTED IN PART FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF MASTER OF SCIENCE.

JOHN RUSSELL

MAY 15th., 1 9 1 8.

I - "THE EFFECT OF UNSATURATION ON THE FORMATION OF MOLECULAR COMPOUNDS.

THE EFFECT OF UNSATURATION ON THE FORMATION OF MOLECULAR COMPOUNDS.

McIntosh and Maass a few years ago conducted a series of investigations on the formation of oxonium compounds at low temperatures. Many compounds of organic substances containing oxygen with the halogens or halogen acids were found to exist. The formation of these compounds was explained on the assumption that at these low temperatures oxygen became tetravalent and consequently addition compounds could be formed. So , to show that where no oxygen was present, no such compound was formed, they investigated the system toluol + hydrobromic acid, and were surprised to find that a compound was formed between these two substances. Toluol, however, was apparently the exception among non-oxygen containing substances; some other substances such as Chloroform (2), not containing oxygen, as expected, formed no such compounds. This present investigation was carried out with the purpose of ascertaining the nature of this compound between toluol and hydrobromic acid, and to see whether it was an isolated instance, or but one example of some general rule.

It might be well, just here, to give an outline of our conception of the mechanism of the formation of these compounds.

(1) J. A. C. 33, 71 (1911) 34, 1273 (1912) 35, 535 (1913)
(2) J. A. C. 34, 1273 (1912) Modern theories are reverting more and more to a modified form of Berzelius views, the most notable example being seen in the recent papers of Langmuir. Atoms under ordinary conditions through the polarity induced by some irregularity in the vibration of the electrons about the nucleus, are attracted towards one another, meet and form a molecule. Now just as when two magnetic fields of unequal intensity neutralize one another, there will be a resultant field of much diminished intensity, so one atom may have been more strongly polar than the other, probably to a very small extent, and thus the resultant molecule would still be slightly polar, the intensity of the polarity being very small indeed compared to the initial intensities of the polarity of the two atoms. Now at ordinary temperatures the speed of the molecule is of such a magnitude that this slight force cannot come into play, but at very low temperatures presumably, this residual polarity of the molecules causes them to associate to form molecular compounds.

It is thought that the forces of attraction between molecules may be of all magnitudes, from the very small up to those of of the intensity of atomic linkages. So one may have molecular compounds which are very pronounced in character, while in another case the compound may be quite easily dissociated, or rather, disassociated. Langmuir even carries these ideas so far as to deduce from them the phenomena of

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surface tension, freezing, etc. Another deduction from these ideas for which some experimental evidence has been obtained, is, that as these compounds are allowed to warm up, the molecules with their several atoms being now so close together, the atoms may rearrange themselves and form compounds in which the forces of attraction are the ordinary stable linkages, that is to say, compounds in the usual sense of the word. Also when two polar molecules associate to form a molecular compound it is not probable that even yet the more complex molecule will be without polarity, although its intensity will be of still smaller magnitude. But. if the molecular compound formed is very well defined and stable, that is to say, if the forces attracting the molecules are approaching in magnitude the intensity of inter-atomic forces, or going further back, if both, or one of the two initial compounds are strongly polar, the probabilities of their being a residual polarity of sufficient magnitude to attract another molecule, are increased. Such a case has been found experimentally, for the well defined compound between ethyl ether and hydrobromic acid will in turn form a trimolecular compound with water.

It must be understood that this hypothesis is provisional but offers, as the word hypothesis implies, a convenient mechanical picture of the details and as such provides a foundation for further speculation and experiment. An extended investigation into the nature of these compounds

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is necessary before this view can be definitely accepted or discarded, as a true representation of the details of these phenomena, and this piece of research will be valuable as affording information in this field.

Let us now consider the case of toluol and hydrobromic acid. Here we have a substance containing only carbon and hydrogen. The valencies of both are well-defined and not subject to variation under changing conditions. Why should it exhibit a force of attraction for another molecule at low temperatures? The unsaturated linkages immediately suggest themselves as a probable factor in the explanation. To investigate this point it seemed desirable to determine whether compounds were formed between hydrobromic acid and various unsaturated hydrocarbons and we wished to try the following, - benzene, ethyl benzene, ortho, meta and para xylene,mesitylene, acetylene, allylene, ethylene, and for comparison some of the saturated, such as the saturated cyclic compounds or some of the paraffin series.

Various methods have been used to study molecular compounds. That which most readily suggests itself is the determination of the freezing point curves of the various systems of which the two components are the two substances to be investigated. This method was used by McIntosh and Maass in much of their work. Here too we have the low temperatures most favorable for the formation of these compounds. The height of the maximum above the average

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position of the eutectics is found to be a qualitative criterion of their strength. Of course, their separation as the solid phase from a mixture gives no indication of the extent of their association or disassociation in the solution. To study their existence in solution conductivity, surface tension, and viscosity measurements have been used. In the following piece of work the freezing-point method was followed.

In the experimental part of the work many difficulties were encountered. Due to the low temperatures requisite, and the nature of the substances themselves, old methods had to be modified and new ones devised. The difficulties were, however, in a great measure overcome, although in some cases the procedure became very tedious, yet accurate results were obtained where otherwise no results would have been possible.

The temperatures throughout were determined by means of a platinum resistance thermometer, the arrangement of which is indicated in Figure 1. It will be seen from the diagram that the ordinary Wheatstone bridge method was used with this innovation, that a Kohlrausch bridge wire K with permanent contact was used as variable resistance, the wire being wound on a marble slab. Its whole length was calibrated for its resistance and also various sections of it to ascertain that the fractions represented on the scale were true fractions of its total resistance. R. was an

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ordinary resistance box which was maintained as a fixed resistance during each series of determinations. R1 and R2 were the ratios which in this case were included in the equipment of the resistance box. The current for the system was supplied by an almost exhausted dry battery B, i.e., one with a small voltage, which was found to give just the convenient swing to the beam of the galvanometer G. To make a determination the thermometer was placed in the series by immersing its terminals in two pools of mercury. P. and then by varying the resistance of the Kohlrausch bridge wire, the reflected beam from the Galvanometer G was brought back to zero. The reading was then taken from the scale on the Kohlrausch bridge. Thus one can see that this whole arrangement was permanent and when once set up required no further attention. The thermometer itself consisted of a fine platinum wire in the form of a coil and fused into solid quartz so that there should be no lag in the registering of the true temperature. The resistance of the platinum was such that no compensating leads were required. The thermometer was standardized by measuring the resistances when immersed in ice-water, in steam, and in solid carbon dioxide moistened with ether. The three resistances when plotted were found to be almost in a straight line. At various times the ice and carbon dioxide points were redetermined to make sure that bad contact somewhere had not perhaps changed the resistance of the series. The readings

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of the resistance in the determinations were transformed into degress Centigrade by means of a graph formed by joining the ice-point to the carbon dioxide point. It was found that twenty-four divisions on the bridge wire scale corresponded to one degree and thus by estimating between the divisions, which were quite large, one could determine the change of resistance for a change of temperature of one-fiftieth of a degree. Accuracy to one-third of a degree was all that was deemed necessary and so it can be seen that this could be obtained with surety.

Before continuing to the description of the individual determinations it might be well to mention the preparation of the hydrobromic acid which was used as one component in all the systems. It was prepared by dropping bromine on a mixture of red phosphorus and water, passing the gas then evolved through wash-bottles containing phosphorus and water to prevent contamination by bromine, then through a tube of phosphorus pentoxide to be dried, and condensed in a large test-tube surrounded by solid carbon dioxide, wellmoistened with ether.

The first hydrocarbon whose freezing-point curve with hydrobromic acid was determined was benzene. The benzene used was Kahlbaum'sthiophene free, distilled over sodium and finally kept with sodium wire in it. Its boiling-point was found to be 80.3 degrees Centigrade and its melting-point 5.4°c.

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The determinations were carried out in a large testtube represented by B in Fig. 2, the rubber stopper of which was bored to admit the thermometer D, stirrer C, and with a larger hole to admit additions of other components. In the case when the component to be added was a liquid, the larger hole was closed by a small stopper which was removed and the addition made by means of a pyknometer. If the second component was a gas, the small stopper was replaced by another in which was a delivery-tube E, indicated in the diagram, through which the gas was passed. In the case of additions of benzene the delivery-tube of the pyknometer was of capillary size, so that loss by evaporation from the end should be a minimum. A blank test was run to determine its exact amount. and it was found that by quick weighing it was too small to affect the percentages with the amounts of the components which we were using.

As the means of cooling and freezing the mixtures, the usual carbon-dioxide moistened with ether was used. With this, temperatures down to -75° C. can be obtained, and if lower temperatures are required, the tube could be fitted with a stopper as in the diagram and connected with a vacuum pump through the tube F. Temperatures as low as -115° C. were reached quite easily in this way.

The procedure in detail was as follows. The empty tube with its stopper, stirrer and thermometer was weighed clean and dry. Then hydrobromic acid was distilled into the

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tube in sufficient quantity to just cover the coil of the platinum thermometer. The delivery-tube through which the distillation was made was then removed and the stopper with stirrer and thermometer fitted to it. It was then weighed again and thus the amount of hydrobromic acid determined. The pyknometer with benzene was weighed, a certain amount added to the hydrobromic acid in the tube, and then quickly weighed again. Thus we knew the percentage of the mixture. This was thoroughly mixed and its freezing-point determined. Another addition of benzene was made, the freezing-point of the new mixture determined and so on. It was found that consequent upon the warming up of the solution after each addition of the hydrocarbon, some of the acid eavporated. After each two or three additions of benzene, therefore, the tube with all its contents was weighed and the loss of hydrobromic acid so determined, distributed in proportion over the previous percentages and thus the correction made. At the end of a series of determinations, usually six or seven was the most that could be made at a time, the whole contents of the tube were dissolved in a large quantity of water and the amount of hydrobromic acid determined by standard alkali. This analysis necessitated a very slight correction to the percentages.

It might be well to mention that for the first few points a pentane thermometer was used, but it was found to be not very accurate, due largely to the fact that pentane settles slowly, while the manipulation at the precise time

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of determining the point must be very quick. So the platinum thermometer was arranged and used throughout.

By this method points on the curve from 100% hydrobromic acid to 56% hydrobromic acid were obtained. At the concentrations of the last few points the components were only difficultly soluble one in another and the loss of hydrobromic acid while stirring to thoroughly mix them rendered the accurate calculation of the percentage impossible. So this portion of the curve had to be discontinued and we began again from the pure benzene side.

The stopper was fitted exactly as in the diagram, addition of hydrobromic acid being made through the tube E. The tube with known amount of benzene was weighed, some hydrobromic acid distilled in and the tube reweighed. So the percentage of the mixture was ascertained. The freezing-point was then determined. More hydrobromic acid was distilled in, the tube reweighed and another freezing-point determined. In this way points from zero percent hydrobromic acid to 14.5% hydrobromic acid were determined, but above this concentration the hydrobromic acid would not dissolve under atmospheric Thus by methods similar to those used by other pressure. experimenters a considerable portion of the curve was completed, but there remained the gap from 14.5% hydrobromic acid to 56% hydrobromic acid. To determine points in this part of the curve, new methods evidently had to be devised. The method adopted was as follows. A tube with a bulb

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and constriction just above was made. This was weighed and into it by means of a glass tube drawn out into a very fine capillary a certain amount of benzene was introduced. The tube was then reweighed, all weighings being made of course with a cork over the mouth of the tube. The bulb was then immersed in the solid carbon-dioxide ether mixture and hydrobromic acid distilled in by means of fine capillary tubes. When sufficient hydrobromic acid was thought to have been added, the delivery tubes were withdrawn, the cork inserted and the tube reweighed. If the percentage was about where a point was desired on the curve the next stage was begun. If not, more hydrobromic acid was distilled into it, using, of course, fresh capillaries, for the others would have collected moisture. When a satisfactory percentage had been obtained a stiff wire was attached just below the constriction and by means of a small blow-pipe flame, the little "bomb" was sealed off, its appearance being as indicated in Fig. 3. The stiff wire was for the purpose of holding the bomb, the lower portion of which was immersed in solid carbon-dioxide ether mixture while being sealed off. The bomb itself was about one inch in length. The mixture was then allowed to warm up, the contents to mix thoroughly and the freezing-point determined by a method to be outlined presently. After the freezing-point was determined the wire was removed from the bomb and it was weighed accurately. The long entrance tube formerly attached to it was also weighed accurately and thus

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the amount of hydrobromic acid exactly determined. The feezing-points of these bombs were redetermined some weeks later and found to be identical. To check the percentages the mixtures were analysed as follows: - The bomb previously weighed accurately was immersed in carbon-dioxide ether mixture and the tip cut off. It was then dropped into a large Erlenmeyer flask, filled with distilled water and a cover placed over the top. The hydrobromic acid was absorbed by the water and the amount determined by standard alkali. The bomb itself with the tip which was broken off was carefully dried and weighed accurately. Thus by analysis the percentage of the mixture was determined. This analysis gave results concordant with the percentages as determined by weight, as the following figures taken from the first few bombs will indicate.

Percentages

By Weight:- 27.01, 38.21, 33.61, 42.38, 51.44 By Analysis- 27.05, 38.13, 33.68, 42.02, 50.99

The results by analysis were probably the more accurate as there was less opportunity for such disturbing factors as the evaporation of the benzene, to enter, and these were taken as the final percentages.

There remains to be described the method of determining the freezing-points of the mixtures in the bombs. A bath of ether was employed in an unsilvered Dewar flask A, illustrated in Fig. 4. This bath was cooled by the addition

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of a few lumps of solid carbon dioxide and conversely warmed by the addition of a little more ether. A current of air blown through D served as stirrer. C. is the thermometer and B the bomb, whose contents, during the determination of a point, were well-stirred by shaking and twisting the bomb. By changing the temperature of the bath the point was obtained, at which the last traces of solid in the bomb did not grow on being left for some time. This was a minimum. Now the bath was warmed up a few degrees, the solid would disappear, therefore, that temperature was too high. The bath was cooled a very little more, the solid still disappeared and so the temperature is still toohigh. So,by stages the wath was cooled till the point was reached, a little below which the solid would remain but at which the solid disappeared. This was taken as the freezing-point of the mixture. The difference between the minimum point obtained and the first point after warming the bath was only one or two degrees, thus the points were determined with great acuracy.

By this method, therefore, the remainder of the curve was completed. The following values for the points were obtained shown in Table 1, represented in Fig. 5.

It will be seen that no compound is formed between these two substances, as there is no suggestion of a maximum at 50.09% acid, corresponding to a one to one compound or 36.6% corresponding to a compound two benzene to one acid.

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TABLE I

Acid_	Freezing Temperature
0	5.4 degrees C.
5 .9	1.3
12.9	-3.5
14.5	-4.0
27.0 5	-12.5
33 .6	-20.5
38.2	-26 ,5
42.4	-31.0
46.6	-39.0
48.02	-40.0
51.0	-42.0
57.1	-47,0
65.2	-56.5
73.5	6 5 .0
77.8	-70.5
85.7	~?9. 5
88 .97	- 37. 5
92.96	-95.0
96.13	-90.0
100.0	-86,0

Since a compound was formed between toluol and hydrobromic acid and yet no combination occurred between benzene and the acid it was thought that ethyl benzene would logically be the next hydrocarbon to investigate. Much difficulty was encountered in its preparation due to lack of chemicals but finally a very pure sample was obtained from the laboratories of the University of Illinois. Its boiling point was 136.5 degrees Centigrade and its melting point -92.4 degrees Centigrade. With this substance as with the benzene the slight cloudiness visible on cooling, due to minute traces of water, could only be removed by prolonged standing over sodium. The treatment of the ethyl benzene was precisely similar to that of benzene with the exception of the use of bombs. This was not necessary as the hydrobromic acid was quite soluble in the hydrocarbon at ordinary pressures. It is interesting to note that the acid was also soluble in toluol and mesitylene both of which formed compounds with the acid, while in benzene which did not form a compound the acid was insoluble except under pressure. By additions of the hydrocarbon to the acid, points on the curve were obtained from 100% acid to 26.3% acid.

The last two points were very difficult to determine as the metastable phase would persist in coming out. Its melting point of course was at a much lower temperature. By repeated trials the stable higher melting phase was also obtained. Thus for a short period we have a metastable prolongation of one section of the curve. The remainder of the curve was completed by additions of the acid to the hydrocarbon. Liquid air was necessary for cooling purposes, for temperatures as low as -130 degrees Centigrade were required.

The values obtained are given in Table II represented by Fig. V1. It will be noticed that here there are two compounds formed, one of the constitution one ethyl bengene - one hydrobromic acid with melting point at -105.5 degrees Centigrade, its composition being 43.3 % acid; the other two ethyl benzene one hydrobromic acid with melting point -103.8 degrees Centigrade and composition 27.6 % acid.

TABLE II

Freezing Temperature
-92.4 degrees C.
-97.7 "
-103.6
-(-118.5)
-104 (-115.2)
-104(-112.6)
-110.2
-109
-106
-106.3
-108.8
-112.2
-116.7
-120.5
-125.2
-125.0
-105.8
~96. 5
-90.8
-86.0

The temperatures in brackets represent the temperatures on the metastable portion of the curve corresponding to the compositions indicated. The fact that ethyl benzene formed two compounds, one of which had the constitution two molecules of ethyl benzene to one of hydrobromic acid led to a closer investigation of the nature of the toluol-hydrobromic acid curve obtained by Maass and McIntosh. The maximum here corresponded with a compound two toluol - one hydrobromic acid. However, it was decided to make check determinations on the part of the curve near the maximum to see that that was the true maximum. The experimental manipulation was similar to that in the previous curves, carbon - dioxide - ether mixture under vacuum being used as the freezing agent.

The values are represented in Table III and in Fig.V11 are indicated in their relation to the values obtained by Maass and McIntosh. The values at the maximum are seen to correspond very closely, indicating a compound of the constitution two toluol - one hydrobromic acid with melting-point -26.5 degrees Centigrade, and composition of 30.5 % acid.

TABLE III

% Acid	Freezing Temperature
6.7	-96.6 degrees C.
23.6	-89.0 "
26.8	-88.3
29.5	-87.6
34.8	-88.0
39 . 9	-89.0

TABLE III (Cont.)

% Acid	Freezing Temp.				
43.7	-90.6 degrees C.				
90.2	-101.5				
92.7	-95.8				
95.1	-91.6				

Continuing the series it was thought that the dimethyl substituted benzene ring might be very interesting. But we were unable to procure any of the ortho-and para- xylenes, and the sample of meta-xylene obtained was found to be too impure.

The symmetrical trimethyl substituted benzene derivative, mesitylene was however obtained. The sampleused was Kahlbaum's purified by repeated distillation over sodium and allowed to stand for some days over sodium wife. Its boiling point was 164.5 degrees Centigrade and its melting point -53.5 degrees Centigrade.

The procedure was identical with that in the case of toluol, carbon-dioxide under vacuum being again resorted to for freezing purposes.

The values obtained are shown in Table 1V. represented by Fig. V111.

It will be seen that there is a well-defined maximum corresponding to a compound one mesitylene - one hydrobromic acid of composition ± 0.3 % acid.

% Acid	Freezing Temp.	% Acid	Freezing Temp.
0	-53.5 deg. C.	48,8	-61.7 deg.C.
2.7	-56.5	50.2	-62.2
4. 5	-57.5	51.7	-62. 5
11.6	⊷65. 5	55.9	-67. 5
18.5	-68, 5	5 7,9	-68.4
25.6	-66. 5	68.2	-52.0
30.3	~64. 5	72.7	-90.0
35.0	-63.0	77,95	.±103.5
40.3	-61.5	84.5	-105.0
41.5	-61.7	91.8	-98.5
		100.0	-26.0

TABLE 1V.

The experimental treatment of the liquid hydrocarbons, with the exception of benzene, it has been seen, presented no outstanding difficulty. The mutual insolubility of the two components in the case of the benzene was overcome by the somewhat tedious yet very accurate bomb method. The case of acetylene however presented much more difficulty. The two components were gaseous at ordinary temperatures, introducing the awkwardness attendant upon the handling of such substances. Furthermore, the boiling-point of acetylene was so low (-82 degrees Centigrade) that to preserve it in the liquid or solid form the carbon-dioxide ether mixture had to be kept continuously under vacuum. The most cogent argument against using the ordinary method was furnished by the fact that at room temperatures the two components react with one another and thus while distilling one gas into the other their vapours would meet above the surface of the liquid and this phase would be contaminated, producing an irregularity in our results, this irregularity not being constant, but increasing with the number of new additions of gas made to the systems. The bomb method which had been already tried out in the case of benzene was the apparent solution of the difficulty, but how could it be modified for the treatment of gases, so that the compositions of our mixtures should be accurately known? Addition of the components by volume would solve the problem and the following apparatus was evolved to accomplish this. after trials of various other methods.

First an outline of the method for the purification of the acetylene might be necessary. The gas was generated by dropping water on calcium carbide covered by alcohol, passed through two wash-bottles containing dichromic acid and potassium hydroxide respectively, through a tube of phosphorus pentoxide and condensed in a large test-tube by means of carbondioxide-ether mixture under vacuum. The dichromic acid removed the phosphine which is as a rule present, the potassium hydroxide removed the carbon dioxide and the phosphorus pentoxide removed the water. The condensation by solid carbondioxide under vacuo eliminated the nitrogen and carbon monoxide which are sometimes present in samples made by this method. The substance thus collected was redistilled through wash-

bottles containing fresh reagents and passed into a large gasometer. A sample taken from this was found to be absorbed without residue in saturated bromine water. It is interesting to note, as other experimenters have, that the gas when carefully purified no longer had the unpleasant odour usually associated with it. The gasometer containing the pure product was connected to the apparatus represented in Fig 1X., at A. At first the purified gas was distilled into a tube sealed on at A similar to the one at B, but so much trouble was caused by the necessity of maintaining the carbon dioxide under vacuum that the gasometer method of storing it was adopted.

The hydrobromic acid was prepared in the usual way and distilled into the tube B, the delivery tube being sealed off at the end.

Fig. 1X represents the apparatus used. Vi and V2 were large flasks of approximately one liter capacity, C and D smaller flasks whose volumes were about 150 CC. These volumes had been accurately calibrated as well as the volume of the tubing from the two-way tap at X to the manometer M. At E a series of bombs were arranged twelve in number, only six being shown in the diagram. Immediately above each bomb there was a small constriction in the tubing and a little higher a tap by which it could be shut off from the system. It will be seen that the bomb itself was similar to that used in the case of benzene. All joints throughout the apparatus were of glass. The procedure was as follows. The taps on the tubing leading from the

reservoir to V1 were closed and the tap leading to the vacuum pump at P1 opened, this section thus being exhausted. The tap connecting the system to the reservoir was opened once or twice, to allow a rush of acetylene through the tubing, to thoroughly eliminate any air in that section of tubing. Similarly the tap connecting B to the vacuum pump Pi, was opened suddenly once or twice thus drawing the air out of that section. Meanwhile the whole apparatus from the taps at Vi& V2 to the manometer M had been completely evacuated by an automatic mercury pump connected to P2. Then the taps on the tubes leading to the bombs at E and the bulbs at C and D were turned off. Acetylene was admitted to the large flask V1, till about atmospheric pressure was reached. It was then shut off from the reservoir and connected to the small bulb C. When equilibrium was established the tap at X was closed, the pressure read as registered on the manometer at M. The tap was then opened to one of the bombs which was surrounded by liquid air. The acetylene from the bulb C was thus condensed. A calculation had been made previously of the drop in pressure necessary to give the amount of acetylene which we wished, and as the mercury reached this height in the manometer the tap connecting the bomb to the system was closed. The volume formerly occupied by the gas was known, the change in pressure in the system, and therefore the quantity condensed accurately calculated. The tap at C was now closed, the tap at P being once more opened to exhaust thoroughly the tubing from X to M.

When this had been accomplished the pump was cut off by closing the tap; and the two-way tap at I opened to V2. which had been previously evacuated. Hydrobromic acid was then admitted to this flask by warming up the liquid in B. The procedure now was the same as in the case of acetylene except that the small bulb D was used instead of C, the acid being condensed on top of the hydrocarbon in the bomb. A calculation had been made beforehand of the change in pressure which would be requisite to give the desired percentage with the amount of acetylene already condensed, and the condensation of the acid was stopped at the right point by turning the tap at the head of the bomb. This was then sealed off at the constriction with a small blow-pipe flame and the freezing-point of the mixture determined. For the handling of the bomb during the sealing off and after the sealing off, a stiff wire was attached in the following manner. A small strip of black adhesive tape was wound round the neck and round this the piece of stiff wire bant, but not very tightly on account of the danger of breaking the bomb off at the small constriction It was then bound in place by fine flexible wire. above.

At first condensation was carried out from the large flasks only, but the change in pressure obtained was so small that any error in its reading would have had too great an effect on the accuracy of the work. So the small bulbs C and D were introduced so that the drop in pressure was 50 or 60 centimeters. Sometimes to obtain the required amount of

hydrocarbon or acid in the bomb the small volume C or D would require to be filled from the large flask V; or V2 once or twice or more times. When the supply in V1 or V2 became very low more could be obtained from the reservoir in the one case or by warming up the liquid in the other.

At all times after the first condensation of the acetylene the bomb was kept immersed in liquid air, and thus when the acid was condensed on top of it, at the temperature of the liquid air the solid hydrocarbon had no appreciable vapour^{*} pressure and thus there was no vapour which could react with the incoming acid vapour. The acid condensed as a solid and the two substances were kept in that condition until the bomb was placed in the bath and warmed up gradually to about -90 degrees Centigrade, when for the first time the two components were allowed to mix thoroughly.

The freezing points of the mixtures in the bombs were determined in precisely the same way as those of benzenehydrobromic acid. The low temperatures required in this case necessitated the use of liquid air to cool the bath and to do this conveniently it was arranged as in Fig. 1X A. B and T represent the bomb and thermometer respectively. C is a small bulb into which goes as indicated the tube from the Dewar flask containing the liquid air. Thus when desired to cool the bath, a little liquid air was introduced into this bulb. S is a tube from which issued a constant stream of dry air to keep the liquid of the bath well stirred and thus at a uniform

temperature. The liquid was in this case petrol ether on account of its low melting point. With this arrangement the temperature of the bath was under complete control and by introducing from time to time just the right amount of liquid air into the bulb C, the bath could be kept at constant temperature for almost any length of time desired. The values obtained for the various percentages are given in Table V, represented in Fig. X. Inasmuch as this method depends upon the addition of gases by volume an accurate value for the density of the gases was necessary. This was obtained in a separate research. It can be seen here that there is but one eutectic, that is to say, no compound-formation occurs between the two components.

Acid	Molecular 9 Acid	Freezing Temp.
0	0	-81.7 degrees C.
19.4	7.2	-82.5
30.0	12.9	-85.7
35.2	15.4	-28.2
49.9	24.2	-93.2
56.0	28.4	-97.3
61.9	34.3	-101.3
64.0	36.1	-103.7
69.9	42.8	-109.7
74.5	48.4	-113.1
76.0	50.0	-115.2
78.0	53.2	-117.6
83.4	61.7	-125.2
85.3	65.6	-126.0
87.5	69.4	-120,2
89.3	74.3	-115.0
100.0	100.0	-86.0

TABLE V.

The marked bend on the acetylene side of the curve is caused

by the method of plotting, due to the small molecular weight of acetylene relative to that of hydrobromic acid. This is seen to disappear if the curve is plotted molecularly as indicated by the dotted line in Fig. X.

Some interesting facts were noted as to the behaviour of the bombs when allowed to warm up to room temperature. Those whose contents were represented on the right side of the eutectic, after a short time exploded violently, probably due to a reaction between the components. The remaining bombs when broken some weeks later still contained large amounts of hydrobromic acid even though there was in the mixture a large excess of acetylene, that is to say, no combination between the substances had occurred. Apparently the fact that the gases were so carefully dried prevented the reaction from taking In the first me thod which was attempted to determine place. the freezing point curve of the two components, a platinum stirrer was used and it was noticed that a dark brown oil formed at the surface of the platinum, which oil persisted on the warming up of the mixture. It was thought that the platinum had catalysed a reaction between the two components and therefore a bomb was made in the usual manner containing a piece of platinum. This bomb remained at room temperature for about a day and then exsmall ploded with great violence, shattering to, pieces a large glass jar in which it was standing. This apparently indicates that the platinum had catalysed some reaction between the components.

It should be pointed out that this method not only applies to the above system but can be used for any system of gases desired. Its precision is well seen in the manipulation of the two gases, acetylene and hydrobromic acid, and the same apparatus is now being used for the systems chlorine-acetylene and hydrobromic acid-ethane.

To summarize the experimental work, the existence of a compound of the composition two toluol - one hydrobromic acid with melting point -36.5 degrees Centigrade has been verified, compounds of the composition one ethyl benzene - one hydrobromic acid with melting point -105.5 degrees Centigrade. two ethyl benzene - one hydrobromic acid with melting point -103.8 degrees Centigrade. one mesitylene - one hydrobromic acid with melting point -61.0 degrees Centigrade, have been shown to exist. It is interesting to notice that phenol has been shown to form a compound two phenol - one water(3), two phenol - one sulphuric acid(4), and two phenol - one acetone(5). and to think that perhaps considering the results obtained in this work, the phenyl group may be the cause of the compound formation and not the oxygen. In the cases of benzene and acetylene however no compound is formed.

Some difficulty was encountered in obtaining the chemicals desired. Some needed very careful purification while others too after much time were still found to be, impure for use. For

⁽³⁾ Proc. K. Akad. Wetensch, Amsterdam 14, 192(1911).

⁽⁴⁾ J.A.C. 38,1314 (1916)

⁽⁵⁾ Ber. 43,2812 (1910)

example, a sample of metaxylene was procured from which after prolonged treatment the paraxylene could not be removed. At the time of writing some pure samples of the three isomeric xylenes are in preparation. It is intended to continue this work, as at first desired, to a study of a few other hydrocarbons, such as the xylenes, allylene and ethylene, as a confirmation of the conclusions arrived at here.

In the field of molecular compound formation a certain amount of work has been done. but its nature has not been such es to add very much to our knowledge or rather understanding of these phenomena. Many isolated facts have been determined and from these attempts have been made to theorize on the causes of this compound formation. The substances used were in most cases very complex in structure containing various arrangements relative to one another of aryl and alkyl groupings and also different elements, upon the behaviour of which at these low temperatures we have no information. For example Norris finds compound formation with such a substance as tetra-brom-tetraphenyl ethylene (6), and from this draws the conclusion that the unsaturated linkage is the critical factor here, a conclusion unwarranted by isolated phenomena in the case of one such complicated substance. Obviously the bromine or the phenyl groups might just as well be the explanation. McIntosh and Maass in their investigations on ox onium compounds and

(6) J.A.C. 38, 702 (1916).

tetravalent oxygen (7), isolate compounds of substances containing aromatic nuclei of very complex nature which require the somewhat improbable hypothesis of a hexavalent oxygen to explain their formation, while even this supposition will not explain further compounds such as benzophenone with six hydrobromic acid. The experimenters have naturally gonducted their investigations each from his own point of view, but their introduction of complicating factors, on whose effect not even speculation can be attempted, has rendered impossible any correlation of their work for the formation of a comprehensive conception of the fundamental causes of these phenomena. Of course the reason such complex substances have been used is found in their ease of manipulation, but not so much has been accomplished as might have been with simpler substances in spite of their awkwardness. This piece of work has been confined to an investigation of one point, the effect of unsaturation, and to do this adequately, complicating factors have been eliminated as far as possible. Substances closely alike in nature, namely hydrocarbons, were used thus avoiding any effect which another element, such as oxygen, might introduce and since the valency of hydrogen is invariable and that of carbon in the fourth group, well-defined, the results obtained could be used as a sound basis from which to draw conclusions. Thus by investigating each point alone a clear conception can be

(7) J.A.C. 32, 542 (1910). " 33, 71 (1911).

obtained of the real factors involved in this compound formation. With toluol. ethyl benzene. and mesitylene. compounds exist at low temperatures but in the cases of benzene and acetylene they do not. In the latter case the symmetrical arrangement of the linkages apparently establishes a stable equilibrium of the interatomic forces in which there is no externally directed force to exert an attraction upon other molecules. In the cases of the alkv1 substituted benzene rings this equilibrium of forces was disturbed and so intermolecular combination could take place. This accords well with the ordinary aromatic reactions. for toluol and the other homologues are much easier nitrated, for example, than is benzene. In this connection it might be interesting to point out that saturated solutions of hydrobromic acid in the substituted benzene compounds when allowed to stand in contact with the air, gave evidence of chemical interaction contrary to the usual conception of the behaviour of aromatic hydrocarbons towards halogen acids. Benzene here too exhibited its usual chemical inertia. Norris in his work came to the conclusion that linkages which were unsaturated, by that very fact, induced molecular compound formation. It is apparent that this conclusion was erroneous, which is not surprising, for with the substances used by him, the compounds might well have been due and probably were due to the disturbed equilibria in the benzene nuclei and not to the ethylene linkage as he

thought. So the rule seems to be that the presence of an unsaturated bonding does not necessarily induce compound formation but the presence of other groups in the structure of the substance may cause these linkages to exert an attraction upon other molecules.

The results of this piece of work may be stated briefly:

A method has been developed for determining the freezing point curve of components which are mutually insoluble at ordinary pressures.

A method has been developed for determining the freezing point curve of two gases which combine at ordinary temperatures.

The following compounds have been shown to exist: Two toluol - one hydrobromic acid. Melting Point -86.5 deg.C. One ethyl benzene - one hydrobromic Ħ Ħ -105.5 17 acid Two ethyl benzene - one hydrobromic Ħ Ħ 17 -103.8acid One mesitylene - one hydrobromic acid Ħ -61.0 Ħ 11

and it has been shown that no molecular combination occurs between either benzene or acetylene and the acid.

It has been shown that unsaturation in itself does not necessitate molecular compound formation but that other groups in certain positions may induce such formation.

II - "A METHOD FOR THE DETERMINATION OF THE DENSITIES

OF GASES.

A METHOD FOR THE DETERMINATION OF THE DENSITIES OF GASES.

In the research on "The Effect of Unsaturation on the Formation of Molecular Compounds" it was found necessary to know accurately the densities of certain gases, namely, acetylene, hydrobromic acid and methyl ether. The values given in the literature were so divergent from the theoretical values and some of them determined so long ago that for the accuracy of the work a redetermination was considered necessary. The idea of using the following method suggested itself and the sources of error were so few that it seemed a practicable method for determining the densities of gases in general, both conveniently and with great precision.

In outline the method is as follows. A known volume of the gas at known temperature and pressure is condensed in a small tube by means of liquid air and weighed. The apparatus represented in the diagram was used. This is drawn to scale with the exception of M, the manometer. V designates a large flask of known volume, which was carefully determined as follows. The flask was dried by keeping it under a vacuum of .001 mm. for some time, then weighed full of air. It was next filled with distilled water and carefully weighed. The temperature of the water was taken. Correcting for the weight of the air and the density of the water at that temperature the volume of the flask was found to be

2242.4 CC. Correcting for the expansion of glass the volume at zero degrees Centigrade would be 2240.9 CC. The manometer M was made by a method described by McIntosh and Maass (1) using specially purified mercury. This method makes sure the mercury is pure and that there is no pressure of gas in the Toricellian vacuum. The scale, which was etched on a mirror, was calibrated by means of comparometer and could be read to .1 mm. By means of plumb lines it was ascertained that the manometer was perfectly upright. At the end of the determinations the volume of the tubing between the taps A, B, C & D was determined accurately by weighing with and without water. This was 22.4 CC. The manometer also was taken apart and the capacity of its tubing determined so that the volume above the mercury at any pressure could be calculated. At E were four tubes, about 6 centimetres in length, of such a size that the condensed liquid would just about fill them. These tubes were made of especially thick glass. All joints were of glass and all taps mercury sealed. The substance whose vapour density was to be determined was distilled into X in the liquid or solid form and the delivery tube sealed off. The air in the tubing from it to the tap was eliminated by opening the two-way tap A to the atmosphere and boiling the liquid in X for some time. The large flask V with all tubing and tubes or "bombs" at E, was evacuated to .0001 mm. pressure by means of an automatic mercury pump with MacLeod gauge,

(1) Trans. Roy. Soc. Can. VIII 65(1914).

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connected to two-way tap B. This pump was of an especially efficient type and would accomplish this in a very short The tap B was then shut off and the tap at A opened time. connecting the flask to the tube X. In this the liquid was boiled till the flask V was filled with gas to about atmospheric pressure and then the tap A closed. The system was now allowed to stand for some time till the gas in the flask V previously surrounded by fresh cracked ice had become of uniform temperature. The manometer was read every five minutes until there was no change in pressure over a period of fifteen minutes. The tap at C was then closed and the tubing and bombs thoroughly exhausted. There was then in V a known volume of gas under known pressure and temperature. When the tubing was completely evacuated the tap at C was opened and the gas condensed in one of the bombs at E by means of liquid air, or solid carbon dioxide. This bomb was then sealed off and the pressure of the gas remaining in the system read after equilibrium was again established. The bomb with its contents was allowed to warm up to room temperature and weighed very carefully, then immersed in liquid air, the tip cut off, the contents allowed to evaporate and the dried bomb with its tip weighed again. This weight was about sixteen grammes. Correction was made for the weight of the air. Thus the weight of the gas condensed was determined accurately. The temperature of the room at the time of experiment was taken in order to correct for mercury expansion in the manometer to

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and the temperature of the gas remaining in the tubing. The following formula was used in the calculation of the weight of one liter of the gas.

$$D = \frac{76 \cdot W \cdot 1000}{(P - p) \overline{V} - \frac{p \cdot V \cdot 273}{273 + t}}$$

- W = the weight of the condensed gas
- V = the volume of large flask, P = the initial pressure of the gas in the large flask, the height of the mercury column being corrected to 0°C.
- p = the pressure remaining in the system after condensation
 of the gas
- v = the volume of the system from the taps at B and C to the tap at A and the level of the mercury in the manometer.
- t = the temperature of the room, that is to say the temperature of v.

Obviously v will change in each determination with changes in the final pressure p and with the number of bombs which havebeen sealed off. The volume of the bombs was found at the end by weighing them full of air and full of water, and thus this was taken into account. It can be seen that the precision of the determination depends on the accuracy of our measurement of \overline{V} , P, T and W., for an error as large as five percent in v, would, in the total, make an error of less than one in ten thousand. The error in \overline{V} can be taken as one in ten thousand, while the error in P-p might be .2 mm. that is three in ten thousand. The error in W is not greater than one in ten thousand. The maximum error, therefore, in D should be of the order of five in ten thousand. It is seen that the largest error enters in the determination of P. This could have been largely reduced if instead of reading the pressure directly, a cathetometer could have been obtained.

Before proceeding to an enumeration of the results it might be well to describe the preparation of the gases. Acetylene was the first gas tried. It was prepared by dropping water on calcium carbide covered with alcohol, passed through two wash-bottles containing dichromic acid and potassium hydroxide respectively, through a tube of phosphorous pentoxide and condensed in a large test-tube by means of carbon dioxide-ether mixture under vacuum. The dichromic acid removed the phosphine, which is invariably present, the potassium hydroxide removed the carbon dioxide, and the phosphorus pentoxide, the water. The condensation by solid carbon-dioxide under vacuum eliminated the nitrogen and carbon monoxide, which are sometimes present in samples made by this method. The substance thus collected was redistilled through wash-bottles containing fresh reagents, through a phosphorus pentoxide tube and into the tube X. Α sample taken from this was found to be absorbed without residue in saturated Bromine water. An attempt was made to purify the acetylene by a method given in Fremy, namely, the

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precipitation by means of the gas of copper acetylide and the regeneration of the gas by addition of warm hydrochloric acid. The product was so contaminated by large quantities of vinyl chloride that the method was found to be impractical for the preparation of such quantities as were needed.

The next gas whose density was determined was methyl ether. This was prepared by dropping methyl alcohol on concentrated sulphuric acid, passing the gas thus evolved through water into concentrated sulphuric acid which will absorb large quantities of the ether. When needed the gas could be regenerated from this by dropping water on the acid solution. The product thus prepared was condensed by means of carbon-dioxide ether mixture, redistilled twice through phosphorus pentoxide taking only the middle portions.

The hydrobromic acid was prepared in the usual manner by dropping bromine on phosphorus in water and passing the gas thus evolved through wash-bottles containing phosphorus and water to free from bromine, through phosphorus pentoxide tubes and condensed by means of carbon dioxide ether mixture. It was redistilled twice using only the middle portions.

In the treatment of the bromide, to avoid contamination of the mercury in the manometer and the consequent introduction of inaccuracy into the readings of the pressure,

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the following procedure was adopted. The system was evacuated Then the tap D was turned off, the tap at A opened as usual. to the bromide and after a time the tap at B opened to the atmosphere. When the acid had issued for a short time from B, A was closed and the pressure of gas allowed to reach The gas was now at atmospheric pressure in the equilibrium. system and this was read from a barometer whose length had been previously calibrated with respect to the manometer described above. B and C were then closed and the tubing between the four taps evacuated by opening the two-way tap at B this time to the pump. The gas was then condensed as above in one of the small bombs at E and the bomb sealed off. Then only was the tap D opened to the manometer and the pressure quickly read, and as soon as possible the tubing evacuated. Thus there was but a small pressure of the bromide

in contact with the mercury for a very short time.

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The following table represents the results of the determinations-

Exp't.			V(cc)	P (corr- ected)	▼(co	е) р	t	W(g r ms)	D
Acetyle	ene #	1	2240.6	75.34	46.6	1.16	19.8°C.	2.5490	1.16985
11	#	2	2240.6	76.89	38.5	2.13	19.8	2.5671	1.16925
Methyl	ether	1	2240.6	77.74	31.0	4.59	23.4	4.5289	2.1104
17	19	2	2240.9	71.99	51.2	11.24	24.2	3,7464	2.1101
Hudrohromie									
	Acid	l	2240.9	75.79	48.4	1.96	23.0	7.8844	3.6381
11	17	2	2240.9	75.79	41.0	.28	23.0	8.0802	3.6372
Ħ	TŤ	3	2240.9	75.90	26.9	3.42	24.0	7.7515	3.6420

It can be seen that the error is of the order calculated and thus the practicability of the method established. The apparatus when once set up can be used for such determinations as long as desired, the actual determination requiring very little trouble. The accuracy of the method in comparison with others depends very largely on the fact that, whereas in other methods the gas was weighed as such, in this way the substance was in the The weight of the large flask alone was liquid state. about 210 grammes, while the weight of the bomb alone was 15 grammes; the weight of the substance being 5 grammes. Thus ten times the accuracy would be necessary in the weighing of the large flask to equal that obtained in the

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determination of the weight of the gas by weighing the small bomb. This is impossible of attainment for in the manipulation of a large flask other factors enter, such as condensation of moisture on the flask and the necessary use of a large, and, therefore, not so accurate, balance. The small bomb can be weighed in an ordinary analytical balance and thus accuracy is attained, and also convenience, for large balances are not available in all laboratories.

The comparison between the values obtained by this method and those given in the literature is shown on the following table:-

	Density, deter- mined.	Density,from literature.
Acetylene	1.16955	1.18
Methyl ether	2.1103	2.090
Hydrobromic acid	3.6391	3 ,50

It is to be noted that the densities of those gases which are heavier than air, as determined by others, are too small, but the converse is true in the case of gases lighter than air.

In conclusion, it should be mentioned that a simple apparatus based upon this principle is under consideration, for the ordinary vapour density determinations of the laboratory, such as were previously determined by the Dumas' method.

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Fig. III.

Fig. II.

