MOLECULAR ATTRACTION

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GENERAL INTRODUCTION.

The Progress of science for more than a century has been associated with the development of two concepts, that of force and that of matter. One of the most important discoveries which man made in his study of the universe was that the attractive force between bodies was proportional to the product of their masses and inversely proportional to the square of the This same law of attraction was found distance between them. later to govern the forces between electrically charged particles and the forces between magnetic poles. The hypothesis that matter is discontinuous has been very successful in explaining the phenomena occurring in the transformations of matter. It has however brought with it another problem, namely that of the nature and magnitude of the attractive forces between the constituent particles. When it is recognized that the ultimate particles known as molecules of which any one substance is composed, are themselves constructed of a number of discrete entities named atoms, the problems resolves itself into two. Chemistry and physics are faced with these two problems, an elucidation of the law of force between atoms and an elucidation of the law of force between molecules. This thesis is devoted to a study of this latter force, which is variously known in the chemical literature as molecular attractive force, molecular attraction, residual affinity and etc.

In the following investigation two methods of approach have been utilized. In Part I a study is made of molecular compound formation in liquid systems, particular attention being paid to the relation between the structure of the molecule and the occurrence of the phenomenon. Parts II and III are devoted to careful measurements of the deviations from the Ideal Gas Laws for one and two component systems respectively, substances being chosen so that information was obtained upon both molecular association and molecular combination in the vapour state.

The following pages of the introduction will attempt to show in the light of the modern knowledge of the atom and the molecule, what the writer considers to be the general nature of intermolecular attraction and its effect upon the properties of chemical systems. The place taken by the experimental work here reported in the broader problem will then be more apparent.

The transformations which matter undergoes are explained by the assumption that the atoms composing the molecules rearrange themselves to form new structures. These transformations will obviously be governed by the strength and character of the forces between the atoms, in other words by the chemical forces or the chemical affinities. The properties of the substance as such, its density, boiling point, freezing point and etc.,

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will depend on the forces between the molecules, which we have called the molecular attraction. While the solution of the problem of interatomic attraction has made great strides that of intermolecular attraction has received relatively little attention.

Consider a substance initially in the solid state and note how the behaviour of the substance on heating is modified by the forces between the molecules. As a solid the forces are of a sufficient magnitude for the thermal agitation of the molecules not to displace them from their position relative to one another. The tensile strength of the solid will obviously bear some functional relationship to this cohesive force which holds the molecules in position. As the thermal agitation increases a point will be reached at which this cohesive force is just overcome and the molecules will be able to move freely with respect to one another. The melting point depends therefore on these forces. Likewise the energy change accompanying the dissolution of the rigid structure of the solid will depend on them. Thus for the solid state these three important properties are intimately related to the forces in question.

In the liquid state while the cohesive forces are not now of sufficient magnitude to hold the molecules in a rigid structure, still they are great enough to hold the

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particles together in an aggregate. Within the liquid a molecule is subject to forces from other molecules which are At the surface the forces are not balanced and we balanced. have in consequence the phenomenon of surface tension. Langmuir has shown that on the average the molecules in the surface layer of many liquids are oriented, one portion of the molecule being pulled downwards more than another. This work has afforded a beautiful confirmation of modern theories of molecular attraction, and of polar molecules which are discussed, in an ensuing paragraph. Many molecules will attain sufficient speed to carry them through the surface beyond the range of attraction of the other molecules. The Number that do this will depend on the relation between the velocities of the particles, that is, the temperature of the liquid, and the cohesive force between the particles. Thus the vapour pressure as a property is dependent on the molecular attraction. Finally as the temperature of the liquid is further increased, a point is reached when the average path of the molecule in its thermal movement carries it always beyond the range of molecular attraction. It then will continue its motion till collision with another particle or the walls of the vessell changes its The molecules will now fill the whole space in which course. they are confined and the substance is in the gaseous state. The point at which vapourization takes place, that is the boiling point, and the energy necessary to accomplish this, that is, the heat of vapourization, are thus intimately connected

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with molecular attraction.

It should be pointed out that two other properties of liquids and solids, the compressibility and the coefficient of expansion, must also depend on these forces, because compression involves work against them, to push the particles closer to one another and the expansion by heat measures the rate at which the thermal agitation gradually increases the average distance apart of the particles in spite of the forces which tend to hold them together. The very high pressure and temperatures necessary to cause quite small changes in volume for liquids and solids are as indication of the magnitude of these forces when the distances between the particles are small.

In the gaseous state the particles are moving throughout the space in which they are confined, and the average path of a particle, which we can call the mean free path, is greater than the range in which the attractive forces are effective. Assuming now that at least the effect of these forces has been eliminated, the pressure of the gas may be considered as due to the impacts of the particles on the walls of the vessels and a simple relation may be derived connecting the pressure, temperature and volume of the gas, a relation which agrees with the early experimental work of Boyle, Charles and Gay-Lussac and which is known as the Ideal Gas Law. The conclusion that the attractive force can now be neglected is erroneous however, for while the particle is certainly free

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from this force during the major portion of its path, still it does meet with other particles and therefore for a short distance before and after collision will be subject to this force, and will have its motion accordingly modified. The fraction of its path during which this force is effective, will be greater the shorter the path, that is the higher the pressure, and it is indeed found on making exact measurements that the deviations from the Ideal Gas Law are greater the higher the pressure. Also if the pressure is increased sufficiently, the substance returns to the liquid state, that is, the substance returns to the point where the mean free path is no longer greater than the range of the attractive However an increase of temperature offsets this. force. There is a temperature beyond which the motion of the particle will always be able to overcome the cohesive force and liquefaction will not be possible. This is known as the critical temperature. In the case of gases therefore, molecular attraction may be studied through critical temperatures and through deviations from the Ideal Gas Laws.

Thus far only pure substances have been considered. Solutions of one substance in another present many interesting phenomena in connection with this problem. Solid solutions do not readily lend themselves to study from this point of view. Liquid solutions have however received a very extensive study, particularly in respect to Raoult's Law. This law in its

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generalized form is most easily stated thermodynamically but for the purpose of this discussion it will be considered in the form In a solution which obeys Raoults of a vapour pressure law. Law, the Ideal Solution, the partial pressures of the components are proportional to their respective mol-fractions. In other words, the relative number of molecules of type A and B which escape from the surface of the liquid is proportional to the actual number of molecules A and B present in the liquid. Actually there are not many solutions which obey this law and the reason will appear from a consideration of the following facts in the manner due to Hildebrand, a method which is in close accord with the method of the preceding discussion. If the field of force around the molecule A is quite similar to that around molecule B, then in the solution it will be quite immaterial to A as far as its motion is concerned, whether it is surrounded by 4 molecules of type A and 3 of type B, or whether it is entirely surrounded by molecules of So its escaping tendency will be unaltered its own type. and its partial pressure will depend only on the number of The solution will obey Raoult's type A present in the solution. If however the field of force around B is much larger Law. or smaller than that around A then it does matter how many of B are grouped around A and the escaping tendency of A will be affected to a measurable extent. Now Hildebrand made an exhaustive tabulation of the properties which we have shown to depend on the attractive force and was thus able to place all

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ordinary substances in a table in the order of the greatness of the attractive force which they possessed. In spite of the fact that the exact relationships between the properties and the forces are unknown, the different properties place the substances in the same sequence in such a table. This in itself is important confirmation of the point of view adopted but he found further that precisely those solutions which consisted of substances possessing molecular fields of equal strength, according to the above methods, were the solutions which did obey Raoults Law. Solutions whose components differed widely in attractive forces showed large deviations from Raoults Law.

In the case of gases the rule analogous to Raoult's Law is Dalton's Law. In the Ideal Gas Solution the total pressure of the gas is the sum of the partial pressures, which the component gases would exert at the same temperature and in the same volume. Studies of the deviation from this rule have only been made in a very few cases, but the results are in agreement with the mechanism assumed in all the preceding discussion. There is, however, some indication of a further phenomenon which might mean that the field of force around the molecule is not symmetrical, in other words that one part of the molecule should exert a stronger attractive force than another. The work of Langmuir mentioned is of course indication of this same thing. The

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phenomenon is sometime referred to as regional polarity in a nomenclature which refers to molecules with an attractive field of force as polar molecules and to the force itself as polarity.

An enquiry into the reasons for such a phenomenon as a regional polarity necessitates a brief discussion of the modern theory of valence and at the same time a more intimate picture will be obtained of the cause of the polarity itself, whose effects we have shown to be so far-reaching upon the properties of matter. Without going into the historical development of the picture the following summary can be given. Atoms have been shown to consist of positively charged and negatively charged constituents known respectively as protons The exact proton-electron content of all the and electrons. atoms is now known. A study of Roentgen Rays and of spectra has shown that the electrons are grouped around the positive nucleus in classes, the electrons of one class differing from those in another in their energy-content. The periodic table and the valences of the elements show that there is a tendency for certain elements to lose or gain electrons in an attempt to obtain certain electron configurations which for some reason are more stable than others. The inert gases have already these configurations and therefore show no tendency to lose or gain electrons, that is, they have zero valance. Interaction between atoms consist therefore in a redistribution of their electrons so that all approach as near as possible the

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stable configurations represented by the inert gases. If an atom lost an electron it would be positively charged and one that gained an electron would be negatively charged. Sodium chloride is a good example of a compound formed by the occurrence of both those processes, the sodium attaining the configuration of neon and the chlorine atom the configuration In other cases the electrons available are not of argon. sufficient for both atoms to attain the stable arrangement independently and in those cases they accomplish the result by sharing pairs of electrons. Under these conditions the pair of electrons may occupy all positions intermediate between the two atoms, the position being dependent on the relative attractive forces of the nuclei. Stereochemical facts have shown that this pairing tends to take place in definite positions around the nucleus. In other words, the valence forces are directed, and the molecule of the resulting compound has a very definite spatial architecture. Electronically we may consider that the electrons occupy definite positions around the nucleus or, which is more probable, that the orbital motion of the electron has a definite position with respect to the nucleus.

In connection with molecular attraction the important point in the above picture is that there is an electron shift when atoms combine to form a molecule. This means that in general in a molecule the centre of positive electrification will no longer coincide with the centre of

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negative electrification. In the case of sodium chloride the separation of the centres is very great and such a substance is said to be very polar. A structure consisting of positive and negative electricity a finite distance apart is an electric doublet and as such possesses an electric It therefore would have an attraction for like moment. structures, consequent upon the tendency of the whole system to reach an arrangement with minimum potential energy. If this this argument is valid therefore every molecule in general will have an attractive field of force. Furthermore. since the valence forces are directed in space, a molecule of a rather complex architecture might possess an electric moment in one section much greater than the moment of other sections and under certain conditions the molecule would therefore tend to be oriented, and to orient other molecules with respect to itself. This regional polarity might be expected to have important effects upon possible reactions between two molecules.

That such electrical doublets pictured above have an existence has long been a part of the optical theory associated with the study of refractive indices and dielectric constants. Recently a number of men from these properties have calculated the actual magnitudes of the electric moments (2) for the molecules of very many substances. The agreement

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between the relative polarities of groups of substances as determined from chemical behaviour and as calculated from optical theory is truly striking.

Polarity in molecules induces still other phenomena besides those already discussed. In some cases attractive forces are so great that complexes are formed in which the molecules still retain their molecular structures but the structures as a whole associate to form larger structures the units of which are molecules. These, when the constituent molecules have been unlike have been known as molecular compounds; when the constituent molecules are alike the phenomenon is known as association. Water and the alcohols are the commonest examples of the latter class of substances, and deviations from the generalizations connected with surface tension and the heat of vapourization have shown that undoubtedly in the liquid state these substances are associated, although nothing more than a rough estimate of the extent of the associations can be determined. The study of molecular compounds from this point of view has been obscured by the attempt to explain them on the basis of subsidiary valences of the same general character as the ordinary valences but smaller in intensity. In the case of oxygen containing compounds, the oxonium compounds, this theory was in general quite successful, but the majority of molecular compounds do not admit of such an explanation and recourse must be had to the more general theory outlined

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In the case of the oxonium compounds even, the above. polarity theory might well apply, since the two valences of oxygen have a spatial direction and thus every compound containing oxygen would be very polar, if the two valences were directed to the same side of the atom, say, towards the corners of a This latter picture is not improbable since tetrahedron. the external group of 8 electrons in the case of carbon takes that configuration and the oxygen atom in combination has the same group of 8 electrons. If the polarity theory of molecular compound formation is correct this phenomenon will afford a good method for the study of the relative polarity of the members of a series of compounds and from this it should be ascertained how the field of molecular attraction is dependent on the molecular structure.

It is hoped that the above review will suffice to indicate the importance of an investigation devoted to a study of molecular attraction, its causes, magnitude and if possible the laws which govern it. Since the field is relatively speaking new the intial generalizations and hypotheses must perforce be rather sketchy in character and must be considered as tentative explanations only. Still, the recent advances in the knowledge of the structure of the atom and the molecule offer a foundation for the attack of the intermolecular problem which has hitherto been entirely wanting and so advance in this field should now be rapid.

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PART I

MOLECULAR COMPOUND FORMATION IN THE LIQUID STATE.

Molecular Combination has been shown to occur in a wide variety of systems by the application of the Phase Rule to the freezing point-composition diagrams. This method is particularly good because there is no ambiguity in the interpretation of the results inasmuch as a compound formed between the two components shows that a very strong attraction exists. Other workers have shown that organic substances containing oxygen, such as the alcohold and ethers form additive compounds with the halogens and the halogen hydrides. The hypothesis advanced to account for the existence of these compounds was based on the supposed tetravalency of oxygen. (3)

In the course of an investigation of these oxonium compounds several systems of non-oxygen containing substances with the halogen hydrides were examined with the (object of showing that, in the absence of oxygen, compounds were The system chloroform-hydrochloric acid illustrated not formed. But contrary to expectation, toluene was found to form this. an additive compound with hydrobromic acid similar to an oxonium compound, and further experiments showed that toluene and chlorine combined to form such compounds. It has been pointed out in the introduction that molecular combination may be explained by means of the forces of molecular attraction which polar molecules possess, and that therefore on this view

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the oxonium compounds need no special hypothesis as distinct from that required for other molecular compounds.

The present investigation has been arranged to determine the nature of these toluene compounds by ascertaining whether aromatic and unsaturated hydrocarbons in general behave in a similar manner. Toluene is composed of carbon and hydrogen, two elements whose valencies are especially well defined and invariable. Moreover in the case of carbon in general the four pairs of electrons in the outer group have each an element or radi cal attached to them so that the minimum of polarity will be induced by the asymmetrical distribution of the elements or radicals. The unsaturated groups in the case of toluene are assumed to be the basic cause of the polarity in the molecule. Norris has before suggested that unsaturation might induce molecular compound formation. How far this view is justified will appear in the course of this report.

The above outline may suffice to show the value of a research confined to investigating the effect of the structure of a hydrocarbon on additive compound formation. With this object in view it was thought desirable to examine the following systems: benzene, toluene, ethyl-benzene, mesitylene, acetylene and allylene; hydrobromic acid to be the second component in every case.

The principle of the experimental method was

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the ordinary one of measuring the freezing points of various concentrations of hydrocarbon-hydrobromic acid. Many experimental difficulties had to be overcome, and, as these varied from system to system, no general description can be given, but the special methods used in examining each system may best be outlined separately, together with the results obtained.

The temperatures throughout were measured by means of a platinum resistance thermometer consisting of a coil of fine platinum wire fused into a quartz rod. The variable resistance in the Wheatstone $\operatorname{bridge}_{\Lambda}^{\operatorname{was}}$ accurately calibrated, making it possible to read the temperature to 0.1° . The freezing points quoted, however, may be taken as accurate to only 1.0° , this being the error involved in observing the disappearance of the solid phase. This was deemed sufficiently accurate, as the relative variation of freezing point with concentr tion is quite large.

It might be well to mention that for the first few points in the benzene-hydrobromic acid curve a pentane thermometer was used, but it was found to be not very accurate, due largely to the fact that pentane settles very slowly, while the manipulation at the precise time of determining the point must be very quick; so the platinum thermometer was arranged and used throughout.

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The hydrobromic acid was prepared by dropping bromine on a mixture of red phosphorus and water, passing the gas evolved through wash bottles containing phosphorus and water to prevent contamination by bromine, then through a tube phosphorus pentoxide, and condensed in a large test tube surrounded by solid carbon-dioxide, well moistened with ether.

To determine the desired percentage composition of the hydrocarbon-hydrobromic acid mixture the weight method, (3) described in detail by McIntosh and Maass was used wherever possible.

The determinations were carried out in a large test tube, the rubber stopper of which was bored to admit the thermometer, the stirrer, and also had 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 pycnometer. If the second component was a gas, the small stopper was replaced by another in which was a delivery-tube through which the gas was passed. In the case of additions of benzene the delivery-tube of the pycnometer was of capillary size, so that loss by evaporation from the end should be a A blank test was run to determine its exact amount, minimum. and it was found that by quick weighing it was too small to affect the percentages, taking into account the large amounts of the components which were being used.

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As the means of cooling and freezing the mixtures, the usual carbon-dioxide moistened with ether was used. With this, temperatures down to -78° C. can be obtained, and if lower temperatures are required, the tube could be fitted with a stopper and the carbon dioxide-ether mixture subjected to evacuation. 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 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 pycnometer with hydrocarbon was weighed, a certain amount added to the hydrobromic acid in the tube, and then quickly weighed This gave the percentage of the mixture which was then again. thoroughly mixed and its freezing-point determined. Another addition of hydrocarbon 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 hydro-carbon, some of the acid evaporated. After each two or three additions, therefore, the tube with all its contents was weighed and the loss of hydrobromic acid so determined

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distributed in proportion over the previous percentages and thus the correction made. At the end of a series of determinations, (usually six or seven were 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.

In the case of benzene, points on the curve from 100% hydrobromic acid to 56% hydrobromic acid were obtained by this method. 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 a fresh start was made from the pure benzene side. The tube with known amount of benzene was weighed, some hydrobromic acid distilled in and the tube reweighed. Thus the percentage of the mixture was ascertained. The freezing-point was then determined. More hydrobromic acid was distilled in, the tube reweighted and another freezing-point determined. In this way points from zero per cent hydrobromic acid to 14.5% hydrobromic acid were measured, but above this concentration the hydrobromic acid would not dissolve under atmospheric pressure. Thus by the weight method, similar to that used by other experimenters, a considerable portion of the curve was completed, but there remained the gap from 14.5% hydro-

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bromic acid to 56% hydrobromic acid. To determine points in this part of the curve, new methods evidently had to be devised.

Resource was had to the following manipulation. A small bulb was blown at the end of a small glass This was weighed, the bulb partly filled with benzene tube. The bulb was then immsersed in the solid and reweighed. 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, a cork inserted and the tube reweighted. 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. When a satisfactory percentage had been obtained a stiff wire was attached just above the bulk and by means of a small blow-pipe flame the bulk was sealed off. The stiff wire was for the purpose of holding the bulb, the lower portion of which was immersed in solid carbon dioxide-ether mixture while being sealed off. The mixture in the bulb 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 bulb and the latter was weighed accurately. The

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long entrance tube formerly attached to it was also weighed accurately and thus the amount of hydrobromic acid exactly The freezing points of the contents of these estimated. bulbs were redetermined some weeks later and found not to To check the percentages the mixtures were have changed. The bulb, previously weghed, was analyzed as follows: 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 covered. The hydrobromic acid was absorbed by the water and determined by standard alkali. The bulb itself with the tip which was broken off was carefully dried and weighed accurately. This analysis gave results concordant with the percentages as determined by weight, as the following figures taken from the first few samples will indicate.

Percentages

By	weight .,.	•	۹	٠	27.01	38.21	33.61	42,38
By	analysis .	•	•	٠	27.05	38.13	33.68	42.02

The results by analysis were probably the more accurate as there was less opportunity for the entrance of such disturbing factors as the evaporation of the benzene; they were therefore taken as the true percentages.

In order the measure the freezing-points of the mixtures in the bulbs, use was made of a cooled ether

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bath contained in an unsilvered Dewar flask. The temperature of the ether bath could be lowered by the addition of a few lumps of solid carbon dioxide and raised by the addition of a little more ether. A continuous stream of air bubbling through the bath kept it stirred and maintained a uniform temperature, as registered by the thermometer immersed This arrangement makes it possible to keep the bath in it. at any desired temperature between the limits 0° and -75° The bulb held by the wire was placed in the bath and its contents thoroughly stirred by shaking and turning it. By changing the temperature of the bath the point was obtained, at which the last traces of solid in the bulb did not grow on being left for some time; this was a minimum. Now the solid was completely melted by warming up the bath a few degrees, and the bath was then cooled by stages till a point was reached at which the solid just 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, so that the points were determined with sufficient accuracy.

The values obtained for the freezing-points of the benzene-hydrobromic acid system are given in Table I and represented in Figure I. It will be seen that no compound is formed between these two substance, as there is no suggestion of a maximum at 50.1% acid, corresponding to a one-to-one compound or 36.6% corresponding to a compound two benzene to one acid.

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Figure I. The System Benzene-Hydrobromic Acid.

TABLE I.

Freezing Points of the Benzene-Hydrobromic Acid System.

% Acid by weight.	Freezing Temperature Degrees C.
0,0	5.4
5 •9	1.3
12.9	-3.5
14.5	-4.0
27.05	-12.5
33.6	-20.5
38.2	-2 6.5
42.0	-31.0
46.6	-39.0
48.02	-40.0
51.0	_42.0
57.1	-47.0
65.2	∽ 56 . 5
73.5	-65.0
77.8	-70.5
8 5 .7	-79.5
88 .9 7	-87.5
92.96	-95.0
96.13	-90.0
100.0	-86.0

Since a compound forms between toluol and hydrobromic acid and yet no combination occurs between benzene and the acid, it was thought that ethyl benzene would logically be the next hydrocarbon to investigate. A verv pure sample was obtained from the laboratories of the University of Illinois; its boiling point was 136.5° and its melting point -92.4°. 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 bulbs. This was not necessary as the hydrobromic acid is soluble in the hydrocarbon at ordinary pressures. It is interesting to note that the acid is also fairly soluble in toluene and mesitylene, both of which form compounds, while in benzene, which does not form a compound, it is relatively insoluble. By the 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 there is a metastable prolongation of one section of the curve. The remainder of the curve was completed by additions of the acid to the Liquid air was necessary for cooling purposes hydrocarbon.

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since temperatures as low as -130° were required.

The values obtained are given in Table II and are represented by Figure II. It will be noticed that here there are two compounds formed, one containing 43.3%acid corresponding to one ethyl benzene-one hydrobromic acid, melting at -105.5° , the other corresponding to two ethyl benzene-one hydrobromic acid melting at -103.8° and containing 27.6% acid.

The temperatures in brackets represent the temperatures on the metastable portion of the curve corresponding to the compositions indicated.




TABLE II

Freezing Points of the Ethyl Benzene-Hydrobromic

Acid System.

% acid by weight	Freezing temperature Degrees C.	
0.0	-92.4	
ø.94	-97.7	
19.4	-103.6	
23.3	• • • • •	(-118.5)
2 6.3	-104.0	(-115.2)
28.6	-104.0	(-112.6)
33 . 8	-110.2	
36.2	-109.0	
40.0	-106.0	
45.7	-106.3	
52.4	-105.5	
58.9	-112,2	
65.4	-116.7	
70.1	-120.5	
75.2	-125.2	
79.7	-125.0	
85.2	10 5.8	
90.7	-9 6.5	
95.1	-90,8	
100.0	-86.0	

The fact that ethyl benzene forms two compounds, one of which is a two to one compound, led to a close investigation of the nature of the toluene-hydrobromic acid curve obtained by Maass and McIntosh. The maximum here corresponds to a compound -- two toluene-one hydrobromic acid. However. it was decided to make check determinations on the part of the curve near the maximum to see if 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 Figure III 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 constituion two toluene-one hydrobromic acid, melting at -86.5° and containing 30.5% acid.

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TABLE III

Freezing Points of the Toluene-Hydrobromic Acid System.

Freezing Temperature

% acid by weight	Degrees C.
6.7	-9 6.6
23.6	-89.0
26.8	-88.3
29.5	-87.6
34.8	- 8 8.0
39 •9	-89.0
43.7	-90.6
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 at the time the pure xylenes had not as yet been prepared. The symmetrical trimethyl substituted benzene derivative, mesitylene, was, however, obtained. The sample used was Kahlbaum's, purified by repeated distillation over sodium and allowed to stand for some days over sodium wire; its boiling point was 164.5° and its melting point -53.5° . The procedure was identical with that in the case of toluene, carbon dioxide under vacuum being again resorted to for freezing purposes.

The values obtained are shown in Table IV and represented in Figure IV. It will be seen that there is a well-defined maximum corresponding to a compound one mesitylene-one hydrobromic acid of composition 40.3% acid.

It might be interesting to point out that

saturated solutions of hydrobromic acid in the substituted benzene compounds when allowed to stand for some time at room temperature give evidence of chemical interaction, contrary to the usual conception of the behavior of aromatic hydrocarbons towards halogen acids. Benzene here, too, exhibits its usual chemical inertia, a solution of hydrobromic acid in benzene remaining unchanged after months.

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Figure IV. The System Mesitylene-Hydrobromic Acid.

TABLE IV

Freezing Points of the Mesitylene Hydro-

bromic Acid System.

% acid by weight.	Freezing Temperature. Degrees C
0.0	-53.5
2.7	-56.5
4.5	-57.5
11.6	-65.5
18.5	-68.5
25.6	-66.5
30.3	-64.5
35.0	-63.0
40.3	-61.5
41.5	-61.7
48 . 8	-61.7
50.2	-62.2
51.7	-62.5
55 •9	-67.5
57.9	-68.4
68.2	-82.0
72.7	-90.0
77.95	-103.5
84.5	-105.0
91.8	-98.5
100.0	-86.0

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 The cases of acetylene and allylene, however, bulb method. presented much more difficulty. The two components are gaseous at ordinary temperature, introducing the awkwardness attendant upon the handling of such substances. Furthermore. the melting point of acetylene is so low 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 temperature the two components may react with one another and thus while distilling one gas into the other their vapors would meet above the surface of the liquid and this phase would be contaminated, producing an irregularity in the results, this irregularity not being constant, but increasing with the number of new additions of gas made to the system.

The bulb method which had already been tried out in the case of benzene was the apparent solution of the difficulty but had to be modified for the treatment of gases, so that the composition of the mixtures would be

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accurately known. This was done by the addition of the components by volume and the apparatus described in a subsequent paragraph was evolved to accomplish this, after trials of various other methods.

The acetylene was generated by dropping water on calcium carbide covered with alcohol, passed through two wash@bottles containing chromic 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 chromic acid removed the phosphine, which is as a rule present, the potassium hydroxide removed the carbon dioxide and the phosphorous pentoxide removed the water. The condensation by solid carbon monoxide 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 and passed into a large gasometer. A sample taken from this was found to be absorbed without residue in saturated bromine water.

The gasometer containing the pure product was connected at <u>A</u> to the apparatus represented in Figure V. The hydrobromic acid was prepared in the usual way and distilled into the tube <u>B</u>, the delivery tube being sealed off at the end. <u>L</u> and <u>K</u> were large flasks of approximately one-liter capacity, <u>C</u> and <u>D</u> smaller flasks whose volumes were about 150 c.c. These volumes had been accurately

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Figure V.

calibrated as well as the volume of the tubing from the twoway tap at \underline{X} to the manometer \underline{M} . At \underline{E} a series of bulbs were arranged 12 in number, only 6 being shown in the diagram. Immediately above each bulb there was a small constriction in the tubing and a little higher a tap by which it could be shut off from the system. All joints throughout the apparatus were of glass. The procedure was as follows: The taps on the tubing leading from the reservoir to L were closed and the tap leading to the vacuum pump at P 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 wash out thoroughly any air in that section of tubing. Similarly, the tap connecting <u>B</u> to the vacuum pump <u>P</u> was opened suddenly once or twice, thus drawing the air out of that section. Meanwhile the whole apparatus from the taps at \underline{L} and <u>K</u> to the manometer <u>M</u> had been completely evacuated by an automatic mercury pump connected at Q. Then the taps on the tubes leading to the bulbs at \underline{E} and the bulbs at \underline{C} and \underline{D} were turned off. Acetylene was admitted to the large flask L until about atmospheric pressure was reached. It was then shut off from the reservoir and connected to the small bulb \underline{C} . When equilibrium had been established the tap at X was closed and the pressure read as registered on the manometer at \underline{M} . The tap was then opened to one of the bulbs surrounded by liquid air and the acetylene from the

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bulb C thus condensed. A calculation hadbeen made previously of the drop in pressure necessary to give the required amount of acetylene and as the mercury reached this height in the manometer the tap connecting the bulb to the system The volume formerly occupied by the gas was known was closed. and the change in pressure in the system: therefore the quantity condensed could be accurately calculated. The tap at \underline{C} was now closed, the tap at \underline{Q} 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 \underline{X} opened to \underline{K} , which had been previously evacuated. Hydrobromic acid was then admitted to this flask by warming up the liquid in \underline{B} . The procedure now was the same as in the case of acetylene, except that the small bulb \underline{D} was used instead of \underline{C} , the acid being condensed on top of the hydrocarbon in the bulb. A calculation had been made before hand 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 bulb. This was then sealed off at the constriction with a small blow-pipe flame and the freezing

(#) The density of the gases used had been determined by a method described in the Appendix.

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point of the mixture determined. For the handling of the bulb during the sealing off and after sealing off, a stiff wire was attached in the following manner: amsll strip of adhesive tape was wound round the neck and round this the piece of stiff wire was bent, but not very tightly, on account of the danger of breaking the bulb off at the small constriction above; it was then bound in place by fine, flexible wire.

At first condensation was carried out from the large flasks only, but the change in pressure obtained was so small that any end in its reading would have had too great an effect on the accuracy of the work. Therefore the small bulbs \underline{C} and \underline{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 bulb, the small volume $\underline{\breve{C}}$ or \underline{D} would require to be filled from the large flask \underline{L} or \underline{K} one, two or more times. When the supply in \underline{L} or \underline{K} 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 bulb 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 vapor pressure and thus there was no vapor which could react with the incoming acid vapor. The acid condensed as a

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solid and the two substances were kept in that condition until the bulb had been placed in the bath and had warmed up gradually to about -90° , when for the first time the two components were allowed to mix thoroughly.

The freezing points of the mixtures in the bulbs were determined in precisely the same way as those of benzene-hydrobromic 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 the diagram, Figure VI; \underline{N} and \underline{T} represent the bulb and thermometer, respectively. R is a small bulb into which was led a tube from the Dewar flask containing the liquid Thus when desired to cool the bath, a little liquid air. air was introduced into this bulb. \underline{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 used was in this case petroleum 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 \underline{C} , the bath could be kept at constant temperature for almost any length of time desired. The values obtained from the various percentages are given in Tavle \underline{V} , and are graphically represented in Figure VII.

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Figure VI.



The System

TABLE V.

Freezing Points of the Acetylene-

Hydrobromic Acid System.

% acid by weight	Molecular % acid	Freezing Temp. Degrees C.
0.0	0.0	-81.8
19.4	7.2	-82.5
30.0	12.9	-85•7
39.8	15.4	- 68 . 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	-109.6
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
89.9	74.3	-115.0
100.0	100.00	- 86.0

It can be seen here that there is but one eutectic; that is to say, no compound formation occurs between the two components.

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 Figure VII.

Some interesting facts were noted as to the behavior of the bulbs 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. The remaining bulbs 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 interatomic combination between the substance had occurred at relatively high temperatures. In a previous attempt to determine 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 catalyzed a reaction between the two components and therefore a bulb was made in the usual manner containing a piece of platinum.

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This bulb after a short time exploded with great viclence, shattering to small pieces a large glass jar in which it was standing. This apparently indicates that the platinum had catalyzed the interatomic reaction between the components.

In view of the results obtained in the case of benzene and toluene, the study of the system allylene-hydrobromic acid had especial interest and importance. The preparation of the hydrocarbon, which was attended with many difficulties and took much time, presented in itself many points of interest and is discussed in the Appendix.

The procedure to determine the freezing-point curve was quite similar to the case of acetylene. Since its boiling point was considerably above that of the solid carbon dioxide-ether bath the storage tube described in the Appendix could be sealed directly to the apparatus and the substance drawn off for use in warming the tube as in the case of the hydrobromic acid.

The values obtained are given in Table VI. and are graphically represented in Figure VIII. It can be seen that there is a definite maximum at a point corresponding to a compound one allylene-one hydrobromic acid.

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Figure VIII. The System Allylene-Hydrobromic Acid.

TABLE VI.

Freezing Points of the Allylene-Hydrobromic Acid

System.

% acid by weight	Freezing Temperature. Degrees C.
0.0	-106.0
30.6	-113.3
45 •3	-122.6
54.2	-131.0
54.3	-130.9
57.6	-130.5
60.5	-128.6
64.6	-127.5
66.3	-128.4
68.0	-127.1
70.5	-129.0
73 .9	-130.2
81.5	-136.0
55.0	-139.4
90.3	-121.5
95.4	-102.1
100.0	- 86.0

The behavior of acetylene and allylene towards hydrobromic acid supports the hypothesis that the formation of compounds in the ordinary sense, that is, those in which the linkages are atomic, is preceded by molecular compound formation. It was noticed that when the bulbs containing the allylene and hydrobromic acid were allowed to warm up to room temperature, the atomic compound was gradually formed, while in the case of acetylene bulbs, no reaction seemed to take place. This may throw light on the vexing problem of the velocity of organic reactions.

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SUMMARY.

To summarize the experimental work. Acetylene and benzene fo not form molecular compounds with hydrobromic acid at low temperatures. The existence of a compound of the composition two toluene-one hydrobromic acid melting at -86.5° has been verified; compounds of the composition one ethyl benzene-one hydrobromic acid melting at -105.5° , two ethyl benzene-one hydrobromic acid melting at -103.8° , one mesityleneone hydrobromic acid melting at -61.0° , one allylene-one hydrobromic acid melting at -127.0° , have been shown to exist.

One can conclude therefore that unsaturation does

tend to induce molecular compound formation but may not necess arily do so, as is exemplified in the cases of benzene and acetylene. In these two substances the symmetrical arrangement of the linkages apparently corresponds to a symmetrical distribution of the positive and negative charges in the molecular structure. When there is an alkyl substitution in this structure this symmetrical distribution is disturbed, the molecule as a whole, acquires an electric moment, a polarity, and thereby acquires the ability to form molecular complexes. This is in accord with the behaviour postulated in the introductory discussion and agrees with the calculated electric moments of these molecules as derived

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from optical data by Smyth (loc.cit). The following are his figures. For benzeng .20; toluene, .40; ethyl benzene, .46; mesitylene, .36; hydrobromic acid, .79; all moments being multiplied by 10¹⁸. As far as is possible from measurements of this kind the general postulates may be considered as being substantiated.

PART II

DEVIATIONS FROM THE IDEAL GAS LAWS IN ONE-COMPONENT SYSTEMS.

When a substance is in the vapour state it fills the whole space in which it is confined. The pressure it exerts upon the boundaries of the volume in which it is enclosed, may be considered as due to the impacts of its constituent particles, and an increase in temperature may be considered as affecting the properties of the substance only by adding to the kinetic energy of the moving particles. This simplified picture yields upon mathematical treatment the Ideal Gas Law, PV-RT, which as has been mentioned agrees with the early experiments of Boyle, Charles and Gay-Lussac. Later and more accurate experiments have shown that all actual gases deviate from this simple law to a measurable degree. It is obvious that these deviations are due to a too great simplification of the kinetic picture and that a more exact relation will be obtained by taking into account the space occupied by the particles themselves and the attractive forces between the particles.

While the reasons for the deviations from the Ideal Gas Law have been apparent, great difficulty has been encountered in the mathematical treatment of the more complex picture. Many relations between the pressure, temperature and volume of a gas have been derived but none has given a satisfactory agreement with experiement. Partington and Shilling (6) have listed 56 such Equations of State as they are called.

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One of the earliest attempts to solve the problem was made by Van der Waals and his equation is the best known and perhaps, in general, the most satisfactory. It takes the form, $\left(P + \frac{a}{V^2}\right)\left(V - b\right) = RT$. -----(1)

where P, V, R and T have their usual significance and where
'a' and 'b' depending respectively on the molecular attraction
and the size of the molecule. The inadequacy of Van der
Waals equation is probably due to the fact that both 'a' and
'b' are not independent of temperature. At very high
temperatures the molecule possibly will be deformed, affecting
'a' and Richards has demonstrated that molecules must be
considered as compressible. Even when the gas is not subjected
to these extreme conditions Maass (7) has recently shown in
a simple manner that 'b' should not be independent of pressure
and temperature. By a different mathematical treatment than
that of Van der Waals he shows that 'b' is only proportional to
the 'v' volume of the molecules if a constant mean free path
is assumed. Now the mean fright has long been known to
depend on temperature and Sutherland has pointed out (
$$\frac{3}{6}$$
) that
that dependence is due to molecular attraction which may cause
two molecules at a low temperature to collide, whereas at
a higher temperature and consequently greater velocity they
will pass one another. Sutherland in the same paper derives
a relation between the viscosity of a gas and its temperature,
and since the viscosity depends in a simple manner on the mean

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freepath, a more generalized form of Van der Waals equation may be obtained, in which the variation of 'b' with temperature is not neglected. This was done by Maass (loc.cit.) and the new equation takes the form

$$PV^2 - RTV + a - RT/3(1 + \frac{c}{r}) = 0^{-r} (2)$$

(3)

where C is a constant appearing in Sutherlands viscosity formula and is known as Sutherlands constant, and

where 'r' is the radius of the molecule and N is the number of molecules in one gram-mole. This is the equation which has been applied to the experimental results in this thesis. It is seen that besides giving information upon the forces of molecular attraction it also gives a measure of molecular sizes. In the cases of many of the ordinary gases whose molecular radii have been determined in other ways, it has been shown that the radii determined by measure of equation 2. are in exact agreement. Such agreement gives one confidence in the data upon molecular forces obtained from the equation.

To apply the equation to experimental results the graphical method is the most convenient and the equation has therefore been used in the following manner. If for V is substituted $\frac{M}{M} \cdot \frac{RT}{P}$ where M is the molecular weight of the substance, at constant temperature the quantity $\frac{M'}{M}$ equates to a series expansion in powers of P, in which all higher powers of P than the first may be neglected. In other words, the isotherms of the equation take the form

$$M' = M(I + AP) - - - - - - (4).$$

which is that of a linear equation.

An additional method of using the equation may be obtained in the following way. The equation 2 re-written takes this form

$$PV^{2}-RTV = R\beta T - (a - R\beta C) - ... (5)$$

In other words if the observed quantity represented by the left-hand side of equation is plotted against temperature a straight line should result, whose slope is equal to $R\beta$ and whose intercept at the ordinate of zero temperature if equal to $(R\beta C - a)$. Knowing C for the substance the radius can then be calculated, and also the value of the quantity 'a'.

Four substances were studied, hydrogen chloride, ethyl ether, methyl alcohol, and ethyl alcohol. The latter two substances were examined because deviations from the equation .4 were expected due to association. Such deviations in the case of water have already been studied by Maass and Mennie (9).

The Preparation of the Materials.

The hydrogen chloride was prepared by dropping concentrated sulphuric acid, C.P., upon concentrated aqueous hydrochloric acid, C.P., the evolved gas being passed through a wash bottle containing concentrated sulphuric acid, then through a tube of phosphorus pentoxide and finally condensed in a tube immersed in a bath of ether which was cooled to the condensation point of hydrogen chloride by means of liquid air. The liquid obtained was then distilled twice through tubes containing phosphorus pentoxide, the final condensation taking place in a container attached to the density apparatus. It was kept in the liquid state and admitted to the apparatus as desired.

The ether was prepared in the ordinary manner. Starting with a so-called pure product it was thoroughly washed with water to remove alcohol and given a preliminary drying by means of calcium chloride. A repeated distillation over sodium gave a product in which no impurity could be detected.

The methyl was prepared from a C.P. commercial product. It was first treated with a few crystals of iodine to remove the acetone, distilled over potassium hydroxide, and then distilled three times from calcium metal. The final product showed no sign of impurity.

The ethyl alcohol was treated first with potassium hydroxide to resinify the aldehydes, distilled from the potassium hydroxide and then repeatedly distilled from metallic calcium. The presence of the aldehyde had not been suspected at first, and so the first preparations were impure. A careful determination of the density of this final product was

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made and the result d, 25/4 = .78508 was found to be in exact agreement with the Bureau of Standards value .78506. In point of fact the actual experimental work reveals any appreciable amount of impurity in any of the substances, since the extrapolation of the isotherms to zero temperature should give the value M'=M. This was always found to be so except in the case of the first alcohol samples as mentioned, which were of course discarded.

The Apparatus and Method.

Since hydrogen chloride at ordinary temperatures and pressures is a gas the procedure in its case was different from that employed for the other three substances. Its density was first measured over the range of pressures desired at 25 degrees C. in a special apparatus and the results so obtained enabled the measurements at the other temperatures to be carried out in the same apparatus as was used for the alcohols and the ether.

The method employed in measuring the density was a modification of that described in Appendix II. Essentially it consists of observing the pressure of the gas contained in a known volume, maintained at a known temperature; condensing the gas by means of liquid air into a small glass bulb, strong enough to withmatand considerable pressure; sealing off the bulb and weighing it after it has reached room temperature.

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The bulb is again cooled in liquid air, the tip is broken off, care being taken to lose none of the glass, and the bulb is finally weighed empty.

This method possesses over other methods of obtaining gas density by direct weighing, such as the well known Dumas method, the advantage that the weight of the container is of the same order as the weight of its contents and a comparatively large volume of gas can be weighed on an ordinary analytical balance.

The known volume consisted of a glass globe of about one litre capacity, fitted with a tap, contained in a bath. The volume of the globe had been determined by weighing it filled with distilled water, and all corrections made to give the volume accurately at 25 degrees C., the temperature used in the experiments.

The bath consisted of a large battery jar, stirred by a small motor drive propellor, and the temperature was hand regulated by means of the addition of hot and cold water. Since the room temperature was very close to 25 degrees C. the bath could be easily be maintained within $\frac{+}{-}$.02 degrees of the required as long as temperature was necessary for making the pressure readings.

The temperatures were observed on a thermometer calibrated by the Physikalische-Technische Reichanstalt which could be read easily to .05 degrees. The constancy of the

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the bath temperature was maintained by observation of a Beckman thermometer.

Pressures were read on a manometer with a scale graduated in millimeters and etched on a mirror. It could be read to 0.1 mm. A mercury reservoir, to which suction or pressure could be applied, permitted adjustment of the mercury level in the manometer. The mercury on the side connected to the apparatus was always brought up just to touch a glass joint sealed into the manometer tube, so that a single reading gave the pressure.

The procedure was then as follows: The volume with all connecting tubing was first evacuated by means of the automatic Toepler pump, swept out with hydrogen chloride and re-evacuated several times. Hydrogen chloride was then admitted, by opening the tap to the storage bulb, to approximately the The pressure could be observed on a second desired pressure. rough manometer connected to the system. The bath, which had meanwhile been brought to the desired temperature, was carefully regulated and the pressure was read on the manometer. The tap on the volume was then closed and the connecting tubing evacuated. Sealed on to a series of side tubes were several glass bulbs with thick walls and long, constricted. One of these was immersed in liquid air, capillary necks. the tap leading to the pump and storage bulb was closed and the tap on the volume opened. The hydrogen chloride condensed in the small bulb, which was then sealed off at the

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constriction. A small residual pressure was always observed. This was subtracted from the original pressure, but an additional correction had also to be applied for the uncondensed gas in the "dead space" between the volume, the tap leading to the storage bulb, and the level of the mercury in the manometer. It was for this reason that the mercury level in the manometer was always brought to the same point before a reading was made. The volume of this dead space had been determined when the apparatus was built. As the residual pressure was very small, usually less than 2 mm., the mass of gas in the dead space could be calculated with sufficient accuracy from the Ideal Gas Law. The amount found was added to that determined by weighing the bulb.

The bulb was allowed to warm up to room temperature before weighing. This was done with a calibrated set of weights, against which those used in determining the volume had also been calibrated. After weighing the bulb was cooled again in liquid air, a nick was made in the neck with a sharp file and the tip broken off over a sheet of glazed paper, to avoid any loss of fragments of glass. The hydrogen chloride was allowed to evaporate the bulb was dried in the oven, air being sucked through by introducing a fine capillary connected to water pump. The empty bulb was then weighed, along with the broken tip. Finally it was filled with distilled water and weighed again to obtain the volume in order to correct for the air contained in it during the second weighing.

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Weighings were made to 0.0001 gm. The probable error in the weight is about 2 in 5000 at the lowest pressures used and at the highest pressures, not over 2 in 20,000. The probable error in the pressure readings is not over 1 in 7000 at the higher pressures. Temperatures were read to 0.1 degree, the probable error being thus about 1 The accuracy of the measurements thus depends on in 3000. the accuracy of the temperature readings and may be taken as better than 1 in 2000. These results at 25 degrees were utilized in a method for accurately weighing out desired amounts of liquid hydrogen chloride, because the results are essentially a relation between the weight of gas in the globe and the pressure recorded on the manometer. So weighed amounts of hydrogen chloride could be prepared, and used in the apparatus about to be described just as easily as weighed amounts of ether or alcohol.

The method employed for the hydrogen chloride at the higher temperatures, the ether and the alcohols was in principle the same as that already described but the procedure was reversed. That is to say, the substance was first weighed, then introduced into the calibrated volume and a number of pressure readings made at various temperatures. The manometer could not be connected directly to the volume, since it was desired to hear the bath to 200 degrees and at that temperature mercury has a vapour pressure of 17 mm. This would introduce a third component into the system; besides, it would be

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difficult to ensure that the equilibrium pressure of mercury vapour had been reached. Consequently the pressure was exerted against a column of mercury in a U-tube which was contained in a second smaller bath, maintained at a temperature just above the boiling point of water. This pressure was balanced by admitting air to the other side of the U-tube, and the air pressure was read on the manometer.

The apparatus is shown diagrammatically in Figure IX which is not drawn to scale. The main portion was constructed of Pyrex glass. R is a graduated Pyrex-to-soft glass seal, which made possible an all glass connection to the manometer M, and the tubes G_1 and G_2 , which were made of soft glass. The other connections between Pyrex and soft glass were through sealing wax joints, I_1 , I_2 and I_3 the construction of which is evident from the diagram, V is a Pyrex flask, the volume of which, and including the tube K, and along with that of the connecting tube C, as far as the point marked X, was accurately determined by weighing it filled with distilled This was carried out with calibrated weights on a water. balance sensitive to 0.001 gm. The volume, at 20 degrees of the connecting tube was found to be 4.3cc. and of the flask. 1039.0 cc. A volume temperature curve, from the volume at any temperature could be read off, was prepared using the -1 formula (10); 0

$$V_{t} = V_{0} \left(1 + 9.68 \times 10^{-6} t + 3.11 \times 10^{-9} t^{2} \right) - .60$$

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A bath B_{i} , which was of metal, jacketed with a double layer of thick felt, could be placed in the position shown. The bath liquid was a high boiling hydrocarbon oil commercially known as Glycoline. It fumed only slightly below 150 degrees and even at 200 degrees decomposition was not great, although with repeated heating it gradually became darker and somewhat more viscous. It was heated by two electrical heating elements, E, which were hand regulated by means of rheostats, and a third small auxiliary heater, E, consisting of nichrome wire wound on a Pyrex tube and controlled with a thermoregulator. Stirring was accomplished by four motor driven brass stirrers, S, Each one carried a pair of two bladed propellors, which were set so that two adjacent stirrers pushed up and the other two, down, maintaining a constant circulation of the oil. The arrangement of heaters, stirrers, and etc. in the bath is shown in plan. Thev were all supported from above, so that the bath could be lowered and removed when necessary.

Temperatures were read by means of three mercury thermometers T_{f} , calibrated by the Physikalische-Technische Reichanstalt and covering the ranges 0-100⁶, 100-150⁶, 150-200⁶. These were graduated in tenths and could be read easily to 0.05° . The ice points of all three were tested and they were compared with each other at the points where their scales overlapped. They were found to be exact when the corrections indicated on the calibratio certificates had been made.

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the dimmanic it was stirteFigure IX.gle, sotor-driven glass

stirrer inter and show in the diagram) and the temperature regulated by hand to cennin approximately the same as that of the cube 5. White semistrators was also read to the nearest degrees on an estimate selectory therebesier. The bath liquid yas the same as the large bath. The Hypeline is originally wellow when it the large bath. The Hypeline The bath was kept at the desired temperature by the use of a spiral bimetallic thermoregulator. If the rheostats in the main heating circuits were adjusted to give a temperature just below the desired temperature the auxiliary heater operated by the thermoregulator would keep the temperature exactly at the point desired with but very little attention. With long use the contacts on the regulator clogged a little from the fumes of the oil, and had to be cleaned with ether, but this was the only difficulty experienced.

The connecting tube C, was covered with asbestos and wound with nichrome wire, through which a current was passed sufficient to heat the tube to 110^{-120} C. This temperature remained quite constant over the length of time necessary to take a pressure reading, and was read to the nearest degree on the thermometer T_{2} .

The bath B_g was also heated electrically by means of a heating element similar to those used in B_r (not shown in the diagram). It was stirred by a single, motor-driven glass stirrer (also not shown in the diagram) and the temperature regulated by hand to remain approximately the same as that of the tube C. This temperature was also read to the nearest degree on an ordinary mercury thermometer. The bath liquid was the same as that used in the large bath. The Glycoline is originally quite clear and colourless and only becomes faintly yellow after prolonged heating at $100^{\circ}-120^{\circ}$ C. The

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bath vessel was a four litre Pyrex beaker. A lantern was arranged behind it, which threw an image of the U-tube on a ground glass screen about four feet away. The movement of the mercury in the U-tube could thus be readily observed and the taps controlling it were placed conveniently in front of the screen. The latter was ruled with lines 0.1 inch apart, this distance being found to correspond approximately to 0.1 cm. in the U-tube. The screen was carefully before each run with the aid of a cathetometer, so that the rulings were perfectly horizontal.

Pressure readings were made on the manometer M, which was the same one already described (details are not shown in the figure, which is purely diagrammatic). In this case, however, the glass point was neglected and the mercury level on both sides of the manometer was read.

The remainder of the apparatus can be most clearly described in connection with an account of the experimental procedure.

The method in obtaining bulbs with the required amount of hydrogen chloride has already described in connection with the determination of its density at 25 C. The procedure in the case of the ether and the alcohols was as follows. A bulb of the shape shown in Figure IXA and of about 1-2 cc. capacity was filled with distilled water to the point 'a' and weighed to determine its volume. It was then carefully cleaned,

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dried in the oven and weighed empty. A suitable amount of the liquid to be studied was introduced by means of a capillary The stem of the bulb was then forced through a pipette. one-holed stopper as shown. This latter fitted closely into the end of a tube leading to a Hyvac, a motor-driven oil vacuum pump, and part of the liquid boiled off by evacuation. This effectually removed any air dissolved in the liquids. While still under vacuum it was sealed off at point 'a'. The stem was removed from the rubber stopper and carefully wiped clean; when the bulb had reached room temperature it was also wiped clean and weighed along with the stem. The bulb now contained a known weight of the desired liquid. After a few bulbs had been made it was easy to estimate the correct point at which to stop the evapouration so that a suitable amount of liquid was obtained for the experiment.

The end of the tube G, being open, the bulb was introduced into the position shown in the diagram, at A_{6} the hammer H_{7} , which consisted of an iron nailsealed into glass tube, being raised meanwhile by means of the solenoid which is shown surrounding the tube. The open end of the side-tube was then sealed off.

The tube G_2 was used the case of the hydrogen chloride, which, due to its large pressure at ordinary temperatures had to be frozen with liquid air before the tip of its containing bulb was broken.

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Taps 1, 2 and 3 being turned as shown in the diagram and taps 4, 5 and 6 being open, the entire apparatus could be evacuated. The preliminary evacuation was done rapidly by means of the "Hyvac" through tap 7 and evacuation was then completed by means of the automatic Toepler through tap 5, All taps were then closed; tap 3 was opened to the air and tap 6 clowly opened, allowing the mercury in the reservoir tube L_2 to rise into the U-tube Y. This cuts off the main portion of the apparatus from all taps, ensuring that the vapour comes in contact only with glass and mercury and that no air call leak in.

The bath B_{i} , having previously been removed, the projecting tube K was immersed in liquid air. The hammer H_{i} was raised by means of the solenoid and dropped, breaking the stem of the small glass bulb A_{i} . The liquid distilled over through the connecting tubing and condensed in K, The pressure, as registered in Y and M, rose to one cm. or so and then slowly fell. The tube G_{i} was finally cautiously warmed with a flame, to make sure that the bat traces of liquid were gone.

The volume of all the connecting had been determined in order to collect, if necessary, for any uncondensed vapour. It was approximately 125 cc. A residual pressure of 0.1 mm. could be detected with certainty, while a pressure of 1 mm. would mean a correction of only 0.0001 gm. Actually no residual pressure at all was registered on the manometer and

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no such correction was necessary,

The liquid having thus all been transferred to the tube K, air was admitted to the reservoir Ly, by opening tap I to the air and cautiously opening tap 4. The mercury was thus forced through the capillary connecting tube into U. The liquid in V was now isolated from the rest of the system. The mercury was then drawn out of Y by opening taps 3, 6, and 7 to the "Hyvac" Pump. The freezing agent could now be removed from K. The bath B_t was replaced and the heating elements in B_r and B_r and on C turned on. As the pressure in V rose, air was admitted through taps 2 and 5 to balance it on the other side of U. Air was also admitted to L_r , as required, to maintain the level of the mercury in U. When atmospheric pressure was reached in L_r , the ground glass stopper could be removed and mercury added if required.

When B_{λ} and C had reached a temperature about the boiling point of the liquid, B_{j} was brought to the temperature desired. Readings were then made at 25 degrees intervals up to 200°C, and as a rule after checking the initial reading, the pressure of the system was low enough, a final reading was made below the boiling point of the substance. In this way readings were made for ether at 25°, methyl alcohol at 50° and for ethyl alcohol at 75°.

The bath B_j, being maintained at the desired temperature, as already described, tap 7 was opened to the "Hyvac", the lantern was switched on and taps 1, 2,4, and

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5 manipulated to bring the mercury in U up to the point **X**, and exactly level in the two arms. Q_1 and Q_2 are two large volumes of about one litre capacity, enclosed in a box and packed in wool to maintain their temperature constant. They could be cut off from the system when desired by the taps 9 and 10 but these latter were normally open. Their volume being large compared with that of the systems to which they were connected, they served as stabilizers, facilitating control of the mercury and preventing changes in pressure due to variations in room temperature.

It was found that a difference of 0.1 mm. in the mercury levels could readily be detected on the screen and allowed for in making the pressure reading on the manometer. The latter could be read to within 0.1 mm. on each side, so that the pressure readings should be accurate within 0.2 mm. The accuracy of both temperature and pressure readings is attested by the fact that on several occasions readings were repeated at the first temperature point as the bath cooled down, after being heated to 200°, and the original pressure reading duplicated.

The possibility of mercury vapour affecting the measurements had to be taken into account, since even at the temperature of the bath B, mercury possesses an appreciable vapour pressure (about 0.7 mm.). However, the equilibrium pressure would be attained exceedingly slowly on account of the very slow diffusion of the heavy mercury atoms through the narrow

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tube C, filled with gas at at least half an atmosphere pressure. The fact that two or three hours intervened between the duplicate readings just mentioned, seems convincing evidence that not enough mercury vapour could have entered the volume V in the time of an experiment to affect the pressure readings materially.

The accuracy of the method is then conditioned by the accuracy with the weight of the liquid is known. Weighings were made to 0.0001 gm. admitting a possible error of 0.0003 gm., the probable accuracy in the case of methyl alcohol, the substance with smallest molecular weight, is about 1 in 2000.

When the desired readings had been obtained, the mercury was drawn back from U into L_1 by opening taps 4, 1 and 7 to the "Hyvac". Tap 7 was then closed for the moment while the taps 2, 3, 5 and 6 were opened to the suction line. Tap 7 was then re-opened and the whole system evacuated; whereupon the heaters and stirrers were switched off and the run was over. EXPERIMENTAL RESULTS.

The results are given in Tables VII, VIII, IX, X, and XI, Table VII containing the results for hydrogen chloride at 25° C. with the simple apparatus, and the other tables the results with the more elaborate apparatus. The temperature is given in degrees Centigrade, the mass in grams, the pressure in millimetres of mercury at 0° Centigrade, and the volume in cubic centimetres. M' was calculated from the pressure, temperature and volume observed, assuming the Ideal Gas Law. In Figures X,

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XI XII and XIII the quantity M' is plotted against pressure.

DISCUSSION OF RESULTS.

The linearity of the isotherms in Figures IX and X indicates that the theoretical equation fits the facts. In the case of the hydrogen chloride very few points were taken, since the deviations from the Ideal Gas Law were, under the conditions of the experiments, not much greater than the experimental error. An actual measure of the magnitude of these deviations was needed for the work on two components systems and so the above measurements were made.

The curvature in Figures XI and XII is an indication of association as was shown by Maass and Mennie (loc.cit.). In their investigation to test equation (4) carbon dioxide and water were chosen as examples of the two classes, non-associated and associated substance respectively. A curvature was in evidence even at the higher temperatures in the case of water.

TABLE VII

The System Hydrogen Chloride at 25° C.

Pressure	Weight	Volume	<u>M *</u>
726.6	1.6005	1116.7	36.672
395.5	.8701	n	36.636
498.5	1.0957	ग	36.592
761.8	1.6771	च	36.653
685,2	1.5084	ft	36.652
603.2	1.3266	Ħ	36.616

TABLE VIII.

The System - Hydrogen Chloride.

Temperature	Mass	Pressure	Volume	<u>M</u> !
24.8° C.	1.0040	490. 5	1039.0	36.601
501	1.2068	638.9	1039.3	36.636
Π	1.0037	532.1	11	36.586
100.8	1.2060	739.4	1039.8	36.582
Ħ	1.0031	615.1	11	36.575
151.0	1.0025	697.8	1040.3	36.532
201.2	1.0019	781.5	1040.9	36.438



520.8

TABLE IX.

The System - Ether.

Temperature	Mass	Pressure	Volume	<u>M</u> *
25.0°C.	2.0548	482.5	1039.0	76.203
	1.5340	361.9	π	75.847
Π	1.3355	316.2	n	7 5•575
50.1 [°] C.	2.0542	52 5.2	1039.3	75.862
Π	1.5334	394.2	n	75.447
n	2.6796	679.1	۳	76.532
n	1.3351	344.2	11	75.232
75.5°C.	2.6787	736.0	1039.5	76.123
11	1.3348	371.9	Ħ	75.070
Π	2.0536	567.9	11	75.637
Π	1.5329	426.3	Ħ	75.208
100.5°C.	2.0530	611.1	1039.8	75. 348
Π	1.5325	458.0	Ħ	75.04 5
ŧ	2.6780	792.6	Ħ	75.780
π	1.3343	39 9.4	Ħ	74.928
125.3°C	2.0523	652.3	1040.1	75.168
11	1.5321	4 8 8.9	Ħ	74.870
17	1.3340	426.1	Ŧ	74.798
151.0°C.	2.0519	695.7.	1040.3	74.998
Π	1.5317	520.8	Ħ	74.786
Ħ	1.3336	454.1	Ħ	74.678

TABLE IX (CONTINUED)

Temperature	Mass	Pressure	Volume	<u>M</u> *
175.5°C.	2.0513	736.6	1040.6	74 .8 82
Π	1.5313	551.4	ग	74.674
n	1.3333	480.8	Ħ	74.568
201.2°C.	2.0508	779.9	1040.9	74.738
n	1.53309	583.2	π	74.608
Π	1.3330	508.4	**	74.520



The System - Ether.

TABLE X.

The System - Methyl Alcohol.

Temperature	Mass	Pressure	Volume	<u> </u>
75.5°C.	1.0373	658.4	1039.5	32 .9 53
Π	.7897	505.8	Ħ	32.656
79	.7189	461.1	Ħ	32.610
11	1.2210	769.6	Ħ	33.184
**	• 5482	353.5	n	32.436
100.8 ⁰ C.	1.0371	713.4	1039.8	32.605
**	.7894	545.6	n	32.451
Ħ	.7188	498.0	n	32 . 372
Ħ	.5481	380.4	Ħ	32.315
125.3°C	1.0368	762.8	1040.1	32.474
Ħ	•7892	582,5	n	32.36 9
**	.7185	531.5	Ħ	32.298
11	• 5479	406.3	11	32.217
151.0°C.	.7890	621.0	1040.3	32.307
99	.7184	565 .9	Ħ	32.281
**	•5478	432.2	Ħ	32,229
175.5°°.	.7888	657.7	1040.6	32.249
**	.7182	5 9 9.6	11	32.209
Π	• 5476	457.9	11	32.156
201.2 [°] C.	.7886	696.3	1040.9	32.189
11	.7180	634.3	ŧŧ	32.172
Ħ	• 5475	484.4	11	32.124



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The System - Methyl Alcohol.

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TABLE XI.

The System - Ethyl Alcohol.

Temperature	Mass	Pressure	Volume	<u></u>
75.5°°.	•9677	430.4	1039.5	47.027
Π	•79 72	3 5 5 .9	Ħ	46.851
71	1.4192	620.5	Ħ	47.838
Π	1.4265	624.5	11	47.776
85.6°C.	•9675	448、 4	1039.6	46.851
Π	.7971	367.5	۳	46.676
Π	1.1623	530.5	Ħ	47.122
Π	1.4171	643.7	Π	47.376
TI	1.5269	692.0	11 1	47.483
n	1.4262	648.1	π	47.350
100.5	.9674	464.5	1039.8	46.710
11	.7970	384.0	11 *	46.550
11 2	1.1621	556.2	Ħ	46.861
8	1.4169	675.1	n	47.072
Π	1.5267	726.6	11	47.123
Ħ	1.4260	679.9	n	47 . 03 9
125.3°C.	.9671	496.4	1040.1	46.545
Π	.7968	409 .8	11	46.453
Π	1.1618	5 94.7	tī	46.673
π	1.4165	722.4	Ħ	46.845
Π	1.4256	727.9	Ħ	46.792

TABLE XI. (Continued)

Temperature	Mass	Pressure	Volume	M*
151.0°C.	.9668	529.2	1040.3	46.454
Ħ	•7965	436.4	n	46.411
Ħ	1.1615	633.8	11	46 .59 9
175.5°C.	.9 666	560.4	1040.6	46.380
Ħ	.7963	462.1	TT :	46.336
Ħ	1.1611	671.7	Ŧ	46.4 80
201.2 [°] C.	.9663	593.0	1040 .9	46.314
11	.7961	489.1	π	46.261
11	1.1608	711.4	π	46.375



The System Ethyl Alcohol.

It was pointed out that the quantity, PV^2_{-RTV} . should be a constant at any temperature and should vary linearly with the temperature for any one substance. In other words, each isotherm in Figures X and XI corresponds to one only value of PV^2 -RTV. This was found very definitely to be the case for the substance ether, although it must be remembered that the quantity PV^2 -RTV is a small difference between two large quantities, and so here the experimental errors appear much magnified. For the two associated substances these generalizations will not hold. At any temperature PV²_RTV will vary with the pressure. This will be discussed Figures XIV and XV give the plot of PV^2 -RTV shortly. against temperature for hydrogen chloride and for ether. The curve for the hydrogen chloride can only be regarded as approximate since the deviations on which it is based are so small. In Table XII are given the quantities derived from this curve together with the corresponding quantities in the case of the alcohols which were derived in the following manner.

The curves obtained at various temperatures when PV^2 -RTV is plotted against pressure for methyl alcohol are given in Figure XVI and for ethyl alcohol in Figure XVII.

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Figure XIV.





Figure XV. The System - Ether.

TABLE XII.

	R B	a-RBC	C	₿	а,
HCL	.0096	6.1	357 [#]	.032	9. 5
Ether	.070	46	3251 ^{##}	.220	68.7
Methyl Alcohol	.080)1 ,1			
Ethyl Alcohol	.100	55			

- C = Sutherlands Constant.
- **B**= Actual volume of one mole of substance in litres.
- # Harle, Proc. Roy. Soc. London 1922, 100A, p.429.

- Landolt & Bornstein, Tabellen, p.101.





The System - Methyl Alcohol.





It is seen that they are linear. If therefore the lines are produced to zero pressure, the value of PV^2_RTV so obtained should be that of the non-associated alcohol. That such is more probably the case is seen when the values so obtained are plotted against temperature in the way used in the case of non-associated substances. Good straight lines result, given in Figures XVM and XIX. In this way the same data can be obtained for associated substances as for associated.

Values of Sutherland's constant C are known for hydrogen chloride and for ether only, so it is unfortunate that a complete comparison cannot be made between the attractive forces exerted by the four substances.

The ability to derive the function PV^2 -RTV for associated substances as it would be if association did not occur is however of major importance. Knowing this function an exact separation can be made of the effects due to association and the effects due to deviations from the gas laws. And thus the exact degree of association may be obtained. The method is as follows. The lowering of pressure due to association is obtained by substracting the observed pressure from that calculated on the basis of the PV^2 -RTV obtained as above. If the association is to form a bimolecular polymer the following relation should hold between the various pressures.

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$$\frac{P \text{ calc.} - P \text{ observed}}{(2 P \text{ observed} - P \text{ calc.})^2} = K_1$$

If the association is termolecular the following equation should be true -

$$\frac{P \text{ calc.} - P \text{ observed}}{2} = K_2$$
(P calc. - 3 P calc. - P.observed)³

If the association is quadramolecular the following relation should hold between the pressures.

$$\frac{P \text{ calc.} - P \text{ observed}}{3} = K_3$$
(P calc. - 4 x 3)

These equations result from the application of the Maass Law to the gaseous equilibria involved. In Table XIII are given in parallel columns the constants, K, obtained for methyl alcohol at 75° C. on these three assumptions.

TABLE XIII.

Pressure	log K _l	log K ₂	log K3
350 mm.	-5.09	-7.94	-10.08
650 mm.	-4.81	-7.93	-10 .9 2
760 mm.	-4.74	-7.93	-10.99

This is only one example of a number of cases in which the comparison was made for the three substances water, methyl alcohol and ethyl alcohol at a number of temperatures. It should be emphasized that while theoretically K might vary with temperature, still there is no reason why there should be a regular variation of K with pressure. In this case as in the case of all examples tried the evidence is all in favour of the assumption that a termolecular association product is formed. Debye has pointed out in a long discussion of molecular association (11), that the position of minimum potential energy of two like electric couples gives a structure with an increased electric moment, while the position of minimum potential energy for three electric couples gives the total structure zero electric moment. This may have a bearing on the above findings.

If now the K's are calculated for the various temperatures on the termolecular hypothesis and the logarithm of K is plotted against the inverse of the temperature, the energy of the association may be calculated. The curves are given in Figures XX. and XXI. They are within the accuracy of the determination of K straight lines, indicating as would be expected that the molecular heats of the factors and the products are not very different. The heats of association so obtained are 14,800 calories, for methyl alcohol, and 15,600 calories for ethyl alcohol, in marked contrast to

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that obtained for water, namely 1400 calories. The degree of association at the boiling point and one atmosphere pressure is 3.3% for methyl alcohol and 2.6% for ethyl alcohol.

PART III.

DEVIATIONS FROM THE IDEAL GAS LAWS IN TWO-COMPONENT SYSTEMS.
Dalton's Law of Partial Pressures states that the pressure exerted by a mixture of gases is equal to the sum of the pressures which would be exerted by each component separately if it alone occupied the entire volume. Like the Laws of Boyle and Gay-Lussac, this applies rigorously only to ideal gases. Deviations from Dalton's Law may be of two kinds, the first in general a large effect, due to a partial combination of the components, the second, a smaller effect, due to the change in the mean free path of the molecules of one kind by the collisions with those of the other This latter effect has been studied in detail by kind. Maass and Morrison (12). In this investigation attention has been paid only to the first effect, that is, to the extent to which molecular combination occurs in the vapour state.

The careful density measurements recorded in Part II allow one to calculate by Dalton's Law what pressure a mixture of two substances would have in the vapour state. Deviations from this were measured in the cases of the two systems hydrogen chloride-ether, and hydrogen chloride methyl alcohol. These deviations were relatively large and so the much smaller effect due to the mixing mentioned above, could be neglected without large error in the calculation of the degree of combination of the substances. These two systems were chosen for study because in both cases the combination in the liquid state is very pronounced and as large deviations as possible were desired for measurements.

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APPARATUS AND METHODS

The same apparatus was used as in the major part of the work in Part II and the procedure was the same as that already described. Bulbs of ether or alcohol were introduced at Gl and bulbs of hydrogen chloride at G2. The ether or alcohol was distilled first into K, and then the hydrogen chloride. When finally the tube K was warming up, some difficulty arose due to the fact that the HCl first became vapour, then dissolved in the organic liquid as soon as it melted. This latter solution had a pronounced tendency to bump and a number of runs were spoiled in this way. In the end smooth vapourization was obtained by condensing the liquid in ∇ by surrounding the latter with solid carbon dioxide. From then on no difficulty was experienced.

It may be pointed out how very much time was consumed altogether in these latter experiments. In addition to the relative simple filling of the liquid bulbs, there was the more elaborate process associated with the preparation of the hydrogen chloride bulbs. Then the slow distillation of the mixture from K into V and the subsequent warming up of the system required at least 24 hours and finally the actual measurements lasted for another 24 hours. The whole process would require a complete week. In addition to the time required for the successful runs, much time was also lost in these spoiled runs which have been mentioned.

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THE EXPERIMENTAL RESULTS.

The results for the mixtures of hydrogen chloride and ther are given in Table XIV and for methyl alcohol and hydrogen chloride in Table XV.

TABLE XIV.

Mass of Ether - 1.0019 gms. Mass of HC1 = 0.5047 gms.

Temperature	PEther	P _{HCl}	Pcalc.	Pobs.	Diff.
50.1°C.	258.3	267.1	525.4	512 .9	-12.5
75.5	279.0	288.0	567.0	558 .8	- 8.2
100.8	299.5	308.8	608.3	602.3	- 6.0
125.3	319.4	328.8	648.2	643 .9	- 4.3
151.0	340.2	350.0	690.2	686.3	- 3.9
175.5	360.0	370.0	730.0	727.3	- 2.7
201.2	380.7	391.0	771.7	76 9.8	- 1.9

TABLE XV.

Mass of Methy	yl Alcoho	1 -,•4928	gms. Ma	ss of HCl -	.5539 gms.
Temperature	PCH ₃ OH	PHC1	P calc.	Pobs.	Diff.
75.5°C.	317.2	315 .9	633.1	628.5	-4.6
100.8	341.1	338.8	679.9	677.5	-2.4
125.3	363.6	360 .9	724.5	723.3	-1.2
151.0	387.4	384.0	771.4	770.4	-1.0

DISCUSSION OF THE RESULTS:

In the case of the system methyl ether-hydrogen chloride Maass and Morrison (12), measured deviations from Dalton's Law and were able to make an estimate of the mass law constant K and the heat of the reaction, an estimate which was very rough however due to the fact that no accurate density data were available for the simple gases. The deviations here obtained contain besides the experimental error only the small error due to a neglect of the mixture effect. An accurate mass law constant should then be obtained. Table XVI contains the results of such a calculation for both systems, and the plots of log K against $\frac{1}{m}$ are given in Figure XXII Within the accuracy of the work the curves are linear indicating that the heat of the reaction is constant. This calculated from the slopes is 5400 calories for the ether hydrochloride and 9200 calories for the methyl alcohol hydrochloride.

TABLE XVI.

T	<u>]</u> T	log ^K l	log K2
50.1°C	.00309	-3.68	
75.5	.00287	-3.96	-4.34
100.8	.00267	-4.17	-4.68
125.3	.00251	-4.38	-5.04
151.0	.00236	-4.47	-5.17
175.5	.00223	-4.69	
201.2	.00211	-4.89	

 K_1 - is the mass law constant for the ether- hydrochloride.

K₂ - " " " " " " methyl-alcohol hydrochloride.



Figure XXII.

APPENDIX I

THE PREPARATION OF ALLYLENE

In the course of the work discussed in part I, it became necessary to obtain some pure allylene (methyl acetylene). A search of the literature revealed only one method of preparation whereby the substance could be obtained in any quantity or pure, this being reported by (13) Lebeau and Picon. This method, with modifications in experimental procedure, was the one used.

The method, as outlined by Leabeau and Picon consists of the following steps: first, the solution of sodium metal in liquid ammonia to form a deep blue fluid solution; secondly, the decolorization of the solution by passing in acetylene gas, the process consisting of the formation of the acetylide, presumably NaC₂H; thirdly, the addition of methyl iodime drop by drop after distilling off a fraction of the ammonia to remove the excess acetylene; fourthly, the gradual warming of the vessel to permit the evolution of the allylene.

A large tube \underline{T} (figure XXIII), about 7 cm. in diameter and 25 cms. long, was used as the vessel in which to carry out the reaction. After evacuation and filling with pure dry hydrogen several times, a weighed piece of fresh sodium was dropped on the perforated porcelain plate in the bottom of the tube \underline{S} , which was connected with the vessel \underline{T} as indicated by the dotted lines. If this was carried out quickly and a vigorous current of hydrogen

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kept flowing from the vessel \underline{T} into \underline{S} , only a very thin layer of oxide was formed on the sodium. The vessel \underline{T} was then immersed to the point \underline{X} in oil and heated to $100^{\circ}C$. The sodium was melted by means of a free flame carefully applied to \underline{S} and pushed into \underline{T} by a slight pressure of hydrogen. The porcelain plate effectually removed any oxide and the tube \underline{S} was sealed off from \underline{T} as indicated in the figure. The sodium thus introduced kept its bright appearance for many hours, resembling, when molten, a large globule of mercury.

By means of carbon dioxide snow moistened with ether, pure dry ammonia was then condensed upon the sodium until the solution was quite fluid. This ammonia was prepared by distillation from commercial ammonia water through towers filled with sticks of sodium hydroxide and was stored in pure ammonium nitrate which absorbs large amounts of gas to form a clear solution. From this latter, when required, it was distilled into large test-tubes containing sodium metal, and from these finally into the vessel \underline{T} , by means of the delivery tube \underline{A} . The manometer \underline{M} was found necessary to indicate the efficiency of the condensation. It was found that if the end of the delivery tube was immersed in the ammonia solution, the sodium metal would creep up the outside of this tube, finally reaching a point where it could

not be reached by the liquid ammonia. This creeping resulted from the slight evaporation of ammonia around the tube by the in-

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coming warm stream of gas and the further capillary rise of solution in the crevices between the sodium so deposited and the glass. As suggested, it was completely eliminated by keeping the end of the delivery tube above the solution.

When sufficient ammonia had been introduced, a current of acetylene was substituted for that of the ammonia, the acetylene being prepared by the action of water on calcium carbide and purified by passage through washbottles containing solutions of sodium hydroxide and chromic acid, respectively. A very vigorous passage of the acetylene into the ammonia solution was required for two reasons: first, because, unless thoroughly stirred, the sodium acetylide tended to precipitate out around the end of the delivery tube and finally to completely close it; and secondly, because towards the end of the reaction the solution separates into two layers, an upper blue one of sod-ammonium and a lower one of the acetylide in ammonia. This latter solution will absorb large quantities of acetylene and therefore it is advisable to have a vigorous stirring by the entrance of the gas itself as well as by shaking the tube, in order that the sodium shall all be acted on with the least excess of acetylene in the lower layers of the liquid. At this stage a large quantity of white crystals separate out in the bottom of To eliminate the excess acetylene all the ammonia the vessel. was then distilled off and a fresh quantity introduced.

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The tube <u>A</u> was then replaced by a small dropping funnel and a calculated amount of methyl iodide added drop by drop. Much heat was evolved by its reaction with the acetylide, and fresh quantities of carbon dioxide snow had to be continually packed in the Dewar cylinder. As the iodide was added a white precipitate of sodium iodide was deposited. If the solution was kept quite cold no gas was evolved during the whole addition.

After standing for an hour to insure the completion of the reaction, the vessel was allowed to warm up slowly and the gas evolved was passed through water to free it from ammonia, and collected in large gasometers, the displaced liquid being a saturated sodium chloride solution, The salt reduced the loss of the product through solution in the water.

In two successive runs finally made, 13 gms. and 30 gms. sodium were used, about 300 c.c. of solution being employed in the latter case. The volume of allylene obtained corresponded approximately with the amount of sodium used, an exact correlation of quantities being impossible, due to loss of sodium by oxidation before introduction into \underline{T} , and a certain loss of allylene through solution in the water of the washbottles and the gasometers.

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It was finally condensed in tubes arranged as in Figure XXIV each of which contained about 10 cc. Before doing so it was passed at least three times through tubes of phosphorus pentoxide, the whole, after the first condensation, being accomplished in vacuo. This was done by freezing the hydro-carbon with liquid air, precautions being taken not to include any air in the substance as it froze. When the tube at \underline{A} was sealed off, the pure allylene remained only in contact with glass and its own vapor. When required for use, this container was sealed at \underline{B} to the apparatus to be used which could then be evacuated and the allylene admitted by breaking the tip of the capillary tube in the manner which will be evident from the diagram. The allylene was, of course, immersed in solid carbon dioxideether mixture at this stage. The substance was thus stored and used whenever desired, without risk of contamination,

The following tests were made as to the nature of the product. It was totally absorbable in fuming sulfuric acid and in ammoniacal cuprous chloride. The complete absence of acetylene was proved by a method given by Berthelot. An ammoniacal solution containing excess ammonium chloride precipitates acetylene as copper acetylide while the allylene stays in solution. No sign of a precipitate was obtained by passing the gas through such a solution, although in the

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usual cuprous chloride solution the copious yellowishwhite precipitate of copper allylide was obtained.

A density determination by the Dumas method gave the molecular weight 39.6, an agreement within the error of experiment.

Its freezing point was determined by means of a platinum resistance thermometer, the value -105.0° C. being obtained. Very strong indication of the purity of the substance was offered by the constancy of the temperature from the time the first crystals appeared in the test-tube untill the stirrer could not be moved.

The following values were found for the vapor pressures at various temperatures:

Pressure	Temperature
380.5 mm.	-32.2°C.
642.0 mm.	-28.0°C.
732.0 mm.	-26.8°C.
760.0 mm.	-26.7°C.

Its boiling point derived from this vapor pressure curve is therefore -26.6° C. The values given in the literature (15) are -23.5° C. for the boiling point and -110° C. for the freezing point, the divergence from the values here obtained being of the kind which would be expected if an impurity were present in their substance. In an attempt to prepare allylene by the method used by them it was found impossible to obtain a product which did not contain chlorine, probably in the form of vinyl chloride. A careful molecular weight determination gave the value 40.0.

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APPENDIX II.

AN ACCURATE METHOD OF MEASURING THE DENSITIES OF GASES. In the course of the investigation described in Part I densities of certain gases, which had not been established with adequate accuracy, were required. They were therefore redetermined by a method which is of sufficiently general application and capable of such a degree of accuracy that a description should be useful and interesting. Without this method the work described in Parts II and III would have been impossible.

The method is applicable to gases which can be condensed by liquid air or some other freezing agent. A known volume of the gas at known pressure and temperature is liquified in a small bulb attached to the containing vessel; the bulb is sealed off and the liquified gas weighed at room temperature. This procedure is advantageous in enabling one to weigh a large quantity of gas on a small sensitive balance, and to weigh it in a vessel whose weight is of the same order as that of the gas itself. Once the apparatus employed has been calibrated, density measurements can be made rapidly.

Reference should be made at this point to a (16) somewhat similar method by Jacquerod and Pintza which had been brought to the author's attention. There the gases, sulfur dioxide and oxygen were obtained from vessels containing these, respectively, as the liquid and as a constituent of potassium permanganate. The quantity of substance was determined by first weighing the containers and the gas was

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then evolved into the known volume. It may be pointed out that this procedure would not be feasible with many gases; for instance, liquid acetylene at ordinary temperatures can only be weighed in a sealed vessel, as no tap would withstand the high pressure without leaking.

The details of manipulation are best brought out in conjunction with the accompanying diagram, which is drawn to scale with the exception of the manometer. V designates a large flask, the volume of which was carefully determined as follows: the flask was dried by keeping it for some time under a vacuum of 0.001 mm., first weighed full of air, and then when filled with distilled water. Correcting for the weight of the air and the density of the water at the temperature of measurement, the volume of the flask at 0° was calculated to be 2240.9 c.c. The manometer M was made by a method described by McIntosh and Maass using specially purified mercury. The manometer scale, which was etched on a mirror, was calibrated by means of a comparometer and could be read to 0.1 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 \underline{A} , \underline{B} , \underline{C} and \underline{D} was determined accurately by weighing with and without water: it was 22.4 cc. The manometer also was taken apart and the capcity of its tubing determined so that the volume above

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the second way and the share is the table is in a second and the second way are started and the share is the same size of a second are second and a preserve, when the tap A was size and the second is the second is share for A way that this way gas a second is in a second of a second for a second to a period a second is a second of a second for a second second a second a second is a second for a second for a second second a second a second is a second for a second for a second second a second a second is a second for a second for a second second is a second a second second second for a second for a second second is a second a second second second for a second for a second second is a second a second second second for a second for a second second second for a second a second second second for a second for a second second second for a second a second second second for a second for a second second second for a second a second second second for a second for a second second second for a second second a second second second for a second second second second second second second a second second second for a second secon

the mercury at any pressure could be calculated. At \underline{E} were 4 tubes, about 6 cm. in length, of such a size that the condensed liquid would just about fill them, and capable of withstanding a pressure of 100 atmospheres. All joints were of glass and all taps mercury sealed. The substance whose vapour density was to be determined was distilled into \underline{X} 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 Xfor some time. The large flask \underline{V} , with all tubing and bulbs at \underline{E} , was evacuated to 0.0001 mm. pressure by means of an automatic mercury pump connected to two-way tap \underline{B} ; the pump was of an especially efficient type and would accomplish this in a very short time. The tap \underline{B} was then shut off and the tap at \underline{A} opened, connecting the flask to the tube \underline{X} , in which the liquid was boiled till the flask \underline{V} was filled with gas to about atmospheric pressure, when the tap A was closed. The system was now allowed to stand for sometime till the gas in the flask \underline{V} , previously surrounded by cracked ice, had become of uniform temperature; the manometer was read every 5 minutes until there was no change in pressure over a period of 15 minutes. The tap at \underline{C} was then closed and the tubing and bulbs 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

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the gas condensed in one of the bulbs at E by means of liquid air or solid carbon dioxide. This bulb was then sealed off and the pressure of the gas remaining in the system read after equilibrium was again established. The bulb 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 bulb together with its tip re-weighted, correction being 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 the experiment was taken in order to correct for mercury expansion in the manometer and for the temperature of the gas remaining in the tubing. The following formula gives \underline{D} , the weight of one liter of the gas:

$$D = \frac{76. \text{ W. 1000}}{(P - p) \text{ V} - 273 \text{ pv}/273 + t.}$$

W = the weight of the condensed gas.

- P = the initial pressure of the gas in the large flask, the height of the mercury colume being corrected to 0° .
- p the pressure remaining in the system after condensation
 of the gas.

V = the volume of the large flask (2240.9 cc.)

v - the volume of the system from the taps at <u>B</u> and <u>C</u> to the tap at <u>A</u> and the level of the mercury in the manometer (24.1 cc.)

t = the temperature of tubing etc. outside the ice bath.

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A short discussion of the above formula will bring out the accuracy attainable by this method. When experimental values are substituted (P- p) V is 10,000 times as large as pv273/273 + t. Therefore as large an error as 10% in the latter will cause an error of only one part in 100,000 in \underline{D} , and on this fact depends the ease of manipulation; for the volume \underline{v} , of tubing and bulbs, need be known only approximately, and the changes in this volume, due to the sealing on of fresh bulbs for further determinations may be neglected. Furthermore, the temperature of the apparatus outside of \underline{V} and \underline{M} need not be kept constant; in other words no appreciable error is caused by the so-called dead space. In the particular measurements described here, \underline{W} and \underline{V} were measured to better than one part in 10,000 but a probable error of 0.3 mm. was made in the measurement of P - p and hence the results quoted below are only correct to one part in 2000. If a cathetometer were used for measuring the height of the mercury column in the manometer, the probable error of the method would be cut down to less than one part in 10,000.

As the original object of this research was the rapid determination of the densities of certain gases which were being used, none of the extraordinary precautions were taken in their preparation which are usual in atomic weight work. Acetylene was prepared by dropping water on calcium

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carbide covered with alcohol. It was passed through two wash-bottles containing chromic acid and potassium hydroxide respectively, through a tube of phosphorus pentoxide and condensed in a large test tube by means of carbon dioxideether mixture under vacuum. The chromic 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 twice through wash-bottles containing fresh reagents, through a phosphorus pentoxide tube and into the tube X, only the middle portions being taken.

Methyl ether was prepared by dropping methyl alcohol on concentrated sulfuric acid, passing thegas thus evolved through water into concentrated sulfuric acid where it was absorbed. The gas was regenrated from this by dropping water on the acid solution, and the product thus prepared condensed by means of carbon dioxide-ether mixture, redistilled twice through phosphorus pentoxide, taking only the middle portions.

Hydrobromic acid was prepared by dropping bromine on phosphorus in water and passing the gas thus evolved through wash-bottles containing phosphorus and water, and through phesphorus pentoxide tubes. It was condensed

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by means of carbon dioxide-ether mixture, and was redistilled twice, using only the middle portions.

In the density measurement of the hydrobromic acid. in order to avoid contamination of the mercury in the manometer and the consequent introduction of inaccuracy into the pressure readings, the following procedure was adopted: The system was evacuated as usual, when the tap \underline{D} was turned off, the tap at A opened to the bromide until the pressure in \underline{V} became somewhat greater than atmospheric, by the warming of the liquid bromide in X_{\bullet} . The tap at <u>B</u> was then opened slowly to the atmosphere; when the acid had issued for a short time from \underline{B} , \underline{A} was closed and the pressure of gas allowed to reach equilibrium. The gas in the system was now at atmospheric pressure which was read from a barometer whose length had been previously calibrated \underline{B} and \underline{C} with respect to the manometer described above. were then closed and the tubing between the four taps evacuated by opening the two-way tap at \underline{B} , this time to the pump. The gas was then condensed as above in one of the small bulbs at $\underline{\mathbf{E}}$ and the bulb sealed off. Then only was the tap $\underline{\mathbf{D}}$ opened to the manometer and the pressure quickly read, 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.

That the error due to actual measurements is of the order calculated is brought out by the following

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values of the weight of a liter of gas each determined on a separate occasion: for acetylene, 1.1698 and 1.1692; for methyl ether, 2.1104 and 2.1101; for hydrobromic acid, 3.6381, 3.6392 and 3.6410.

The following table gives the average values of the densities of acetylene, methyld ether and hydrobromic acid, when prepared and purified in the manner described above. The second column gives the values as determined by others.

Acetylene	.1.1695	• • • • •
Methyl ether	.2.1103	2.1096 (18)
Hydrobromic acid	3.6397	3.6438 (19)

Considerable importance is attached of late to the accurate determination of the density of gases, and the advantages of the method described above as compared to the ordinary globe method have been pointed out,

The probable error in the density determination is less than 0.05%; with the aid of a cathetometer it can be reduced to 0.01%. is a strong method for the attack of the problem.

Finally since gaseous equilibria are easily subject to a quantitative study, if sufficiently accurate gas densities are available, an exact measure of the amount of compound formation may be obtained through density measurements upon two component gaseous systems.

In Part I the tendency of a series of hydrocarbons towards molecular compound formation with hydrobromic acid was measured. It was shown definitely that the attraction which a symmetrical molecule exerts upon the third standard molecule is much less than that exerted by an asymmetrical molecule, benzene and acetylene being of the former class, and aliphatic derivatives of benzene and acetylene of the latter class.

In Part II density measurements were made on one-component gaseous systems. It was shown how from these measurements using a special equation of state an exact measure both of the size of the molecule and of the molecular cohesive force may be obtained. This was done for ether. Furthermore, it was shown how a definite separation might be effected, of the deviation due to molecular association and the deviation due to the attractive forces. Such calculations were carried out in the cases of methyl and ethyl alcohols, which were proved to be partially termolecular polymers in the vapour state, the association at the boiling-point being respectively 3.3 and 2.6%.

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SUMMARY AND CONCLUSION.

In the General Introduction was given an outline of the problem of molecular attraction and it was pointed out how far reaching were the effects of this attraction upon the behaviour of matter in all its forms. The basic reason for the existence of such a force undoubtedly lies in the structure of the molecule and in the distribution of the electric parts of the molecule. A quantitative calculation of the magnitude of this force is not therefore possible, since the exact structures are unknown, although it was suggested that the electric moment of the simpler molecules, as derived from optical data may be a measure of the force.

Although it is not possible from this fundamental point of attack to obtain quantitatively the magnitude of the molecular attraction, still a study of certain phenomena, intimately dependent on molecular attraction may afford a measure of the relative magnitudes of the attractive forces of a series of substances. The tendency towards molecular compound formation can so be studied.

Furthermore it was pointed out that the various equations proposed to account for the deviations from the Ideal Gas Law contain a factor which is a measure of the molecular forces. The precision with which such a factor may be regarded as a measure of molecular attraction depends on the exactitude with which such an equation fits the experimental facts. The study of deviations from the Ideal Gas Law as measured by the correction factors in an equation of state

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In Part III the molecular combination in the vapour state of the substance ether and hydrochloric acid, and methyl alcohol and hydrochloric acid. Satisfactory mass law constants were obtained for the equilibria on both cases and the heats of combination calculated.

It should perhaps be emphasized that the work described in Parts II and III was only possible because there was available the accurate method for determining the densities of gases, the first use of which is described in Appendix II.

While the data obtained above is not numerous enough to permit extensive generalizations, it has however been completely demonstrated that all three methods of attacks upon the general problem of molecular attraction are entirely feasible, and that the way has been opened to that day when a complete elucidation of molecular forces will have been achieved.

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