

⁹ Gibson, K. S., *Phys. Rev.*, [2], viii, 38, 1916.

¹⁰ Tanaka, J. *Opt. Soc. Am.*, viii, 287, 1924.

¹¹ The beginning of the first step is chosen arbitrarily and determines the beginnings of all the following steps.

THE EFFECTS OF AN HOMOLOGOUS SERIES OF AMINES
ON THE MOBILITIES OF IONS IN HYDROGEN GAS

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Introduction.—One of the writers¹ has undertaken a study of the mobilities of ions in gaseous mixtures with the hope of arriving at some clue as to the nature of the gaseous ion. That this study has not been in vain is shown in a recent summary of the results published by one of the writers.¹ It indicates that while in some gaseous mixtures the mobilities follow Blanc's² law which indicates no change in the fundamental nature of the ion (its physical radius, not the electrical shortening of its mean free path) in mixing the gases, other mixtures show marked changes. One type of change indicates what may be a sort of change in ionic dimensions, (a statistical clustering); the other the formation of a definite ion due to the rearrangement of the molecule or molecules surrounding the ion caused by an especially great affinity of the ion for one of the type of molecules of the mixture. In such mixtures the first trace of the more active constituent added to a binary mixture abnormally decreases the mobility of the ions, or, using a more convenient form of representation, abnormally increases the resistance to the motion of the ion so that a marked departure of the linear law of resistances in mixtures characterizing Blanc's behavior manifests itself.

One of the most striking results obtained was with NH_3 ⁶ in air and hydrogen where the mobility of the positive ion is increased to nearly the value of the negative ion for quantities of NH_3 of the order of 0.1% or less. This indicates the formation of a less bulky ion (possibly NH_4^+), due to the replacement by NH_3 of some large molecule of impurity to which the positive ion normally attaches itself in air or H_2 . In discussing this phenomenon with Professor C. A. Kraus the latter suggested that a study of some of the amines might prove of interest in this connection since in those cases the size of the molecule could be varied without markedly changing the electro-chemical properties of the gas. Measurements were therefore undertaken in mixtures of hydrogen and methyl-amine (CH_3NH_2) and hydrogen and *N* propyl-amine $\text{CH}_3\text{-CH}_2\text{-CH}_2\text{NH}_2$. The chief difficulty in such studies of organic derivatives lies in the difficulty of obtaining

specimens of the amines which do not contain other members of the same series, for in organic chemistry the reactions are such as to give several different products which are so nearly alike chemically as to be exceedingly hard to separate in the pure state where quantities as small as 0.1% of foreign constituents are liable to seriously change the results.

Method.—The methyl-amine was prepared by dropping concentrated aqueous solutions of NaOH onto a commercially pure sample of the hydrochloride $\text{CH}_3\text{NH}_2\text{Cl}$ (Eastman Kodak Co., white label) at reduced pressure, passing the amine over a cooling bath to remove the greater part of the water vapor, than over a meter-long tube of powdered NaOH into a freezing tube immersed in liquid air. After 25 cm.³ of the liquid had been collected the generator was shut off and the solid in the tube was allowed to warm up. The first third of the liquid was distilled off and the second third was allowed to pass over another meter-long tube of NaOH into a reservoir at liquid-air temperature in vacuum. The final third was run out through a filter pump. The gas from the reservoir was used in the measurements by warming it up to about 15 cm. or more vapor pressure and distilling it into the ionization chamber as needed. The only substance which came in contact with the amine frozen in the reservoir was mercury vapor from the manometer which gradually over a period of time distilled over into the reservoir. The propyl-amine was taken from a sealed flask of the liquid as sold by Eastman Kodak Co. (white label). It was distilled into a trap using liquid air. From there it was fractionated into a second trap immersed in liquid air, passing over a meter-long tube of NaOH crushed into a fine powder. Thereafter it was fractionated as was the methyl-amine into a reservoir with liquid air.

The measurements were made following the standard practice of one of the writers.^{3,4,7} For the measurements in methyl-amine an auxiliary field of 6 volts per cm. was used, while for the propyl-amine an auxiliary field of 5 volts per cm. was used, the gauze, electrodes, chamber⁴ and procedure being the same as used in the study of other gaseous mixtures.^{3,7}

Results in Pure Methyl-Amine.—In using both amines a great deal of trouble was encountered due to condensation or adsorption of the amine on the metal walls of the chamber. With methyl-amine this produced what may have been contact potential effects on the gold-plated electrodes so that the results at higher pressures were accompanied by disturbances that made measurements above 40 cm. pressure unreliable. Among other effects the curves below the potential where ions cross were characterized by irregular negative readings and the intercepts with the zero axis were such as to make accurate evaluation questionable. The curves at these higher pressures even appeared to indicate a break point suggesting two mobilities. Where the break point occurred in the table of results the values in parentheses give the mobility estimated. As work with mix-

tures later showed it seems unlikely that the ions of different mobilities were really present, the effect being due to irregular deflections near the point where the ions ceased to cross in the period of alteration, possibly due to condensation of amine on the insulating surfaces of the chamber. The mobilities of the ions observed were all corrected to values at 760 mm. pressure by the inverse pressure law.

MOBILITIES IN METHYL-AMINE AS ACTUALLY OBSERVED REDUCED TO 760 MM. PRESSURE

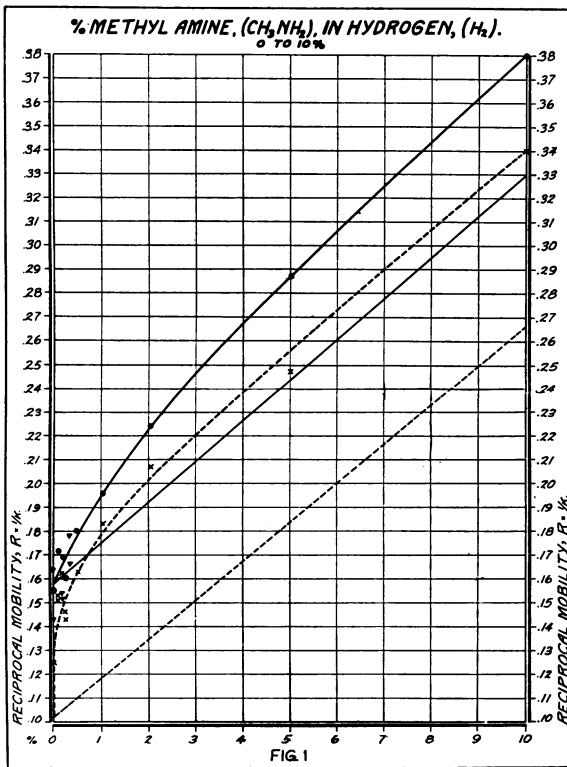
POSITIVE IONS	NEGATIVE IONS	PRESSURE IN MM.
0.482	0.587	686
0.598 (1.99)	0.598 (1.99)	613
0.509	0.576	412
0.516	0.540	256
0.544	0.590	149
Average 0.530	0.574	

On the old accepted standard of mobilities in air as 1.4 cm./sec. for positive and 1.80 cm./sec. for negative ions per volt/cm. the values obtained are 0.494 cm./sec. for positive ions and 0.535 for negative ions per volt/cm., while on the new absolute standard of one of the writers⁵ they are 0.590 and 0.640 cm./sec. per volt/cm., respectively. The values in NH_3 as given elsewhere⁶ are 0.62 cm./sec. for the positive ions and 0.67 cm./sec. for the negative ion per volt/cm. on the old standard and 0.707 and 0.77 cm./sec. per volt/cm., respectively, on the new absolute standard. The mobilities in the amine therefore are somewhat less than in NH_3 , an effect probably due to the larger size of the methyl-amine molecule.

Results in Methyl-Amine Hydrogen Mixtures.—The results in the methyl-amine hydrogen mixture are given in the curves below. In computing these results the average mobilities in the amine *as observed* were used while the mobilities in H_2 used were 6.32 cm./sec. and 9.85 cm./sec. per volt/cm. for positive and negative ions, respectively, uncorrected for the effect of the auxiliary field. The mobilities were largely observed between 20 and 40 volts per cm. alternating field and with an auxiliary field of 6 volts/cm. in order to make them comparable without correction. The curve of figure 1 gives the results for mixtures from 0 to 10% amine, while figure 2 gives the results from 0 to 100% amine. The abscissae give the percentage of amine in hydrogen while the ordinates are in reciprocals of mobility (i.e., equivalent resistance). The two straight lines represent the computed values on the basis of Blanc's law from the values for pure hydrogen and amine, the dashed curve and line being for negative ions, the full curve and line for positive ions. The points and curved lines represent the *observed* values of the *reciprocals* of the mobilities.

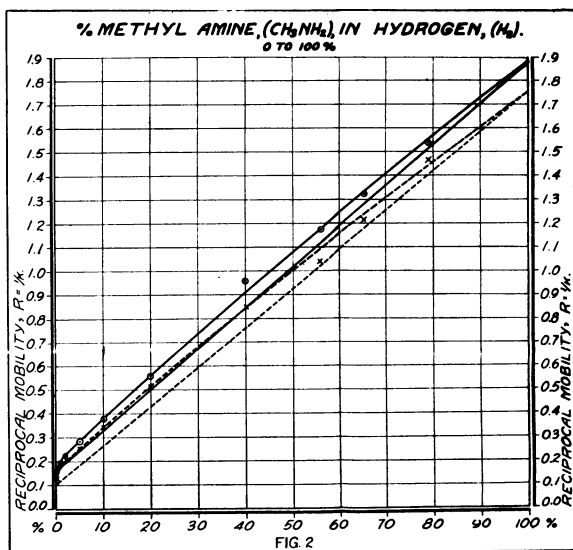
The results are very interesting for they indicate that the *negative* ion shows a marked departure from Blanc's law for small percentages of

amine, while the positive ions retain their normal mobility. Experiments with less than 0.25% amine were uncertain due to the adsorption of gas by the walls of the chamber. To remove effectively the amine from the chamber required at least ten hours of pumping and washing with hydrogen several times, by a pumping system which could give an x-ray vacuum in a clean chamber in two hours' pumping. It is also seen that after the initial change in mobility the deviation of the curves for both ions from Blanc's law was small and similar to that for NH_3 -hydrogen mixtures.^{1,6} The poorer values at higher percentages of amine are due



to the effect mentioned under a description of the method, that is, the irregular mobility curves for high pressures of amine. That in reality the seeming dual curves indicating two carriers were spurious is shown in these mixture curves by the fact that if mobilities are calculated from the *apparent* break points in the mixture work instead of the extrapolated break points (which would be the case for two classes of ions), the values of the mobilities are very irregular and depart from a regular curve in highly fantastic fashion, which is not characteristic of mobilities in mixtures.

Mobility of Ions in Pure Propyl-Amine.—In the case of the measurements of mobilities in propyl-amine the chance for the presence of higher members of the series and other impurities is much greater than was the case with methyl-amine. Furthermore with this amine the condensation of the amine on metal surfaces could be actually followed. At the temperature of the room (25°C.) the propyl-amine had a vapor pressure of some 280 mm. Measurements of mobility at this pressure were, however, impossible, as was the case even at 130 mm., since the amine had condensed over the polonium source (a copper disc coated with Po and Bi) in such a thick layer that the α -rays could not get through except for the last half-cm. or so of their range of 3.8 cm. in air. At 75 mm., however, the full range of the α -particles emerged through the layer of amine and mobility



measurement was possible. The mobilities observed in the amine reduced to 760 mm. were 0.273 cm./sec. for positive ions and 0.288 cm./sec. for negative ions per volt/cm. On the old standard scale for air of 1.4 cm./sec. and 1.8 cm./sec. per volt/cm. for positive and negative ions, respectively, the values in *n*-propyl-amine are 0.243 and 0.257 cm./sec. per volt/cm., respectively, and on the new absolute⁵ standard scale the values are 0.294 and 0.312 cm./sec. per volt/cm. for positive and negative ions, respectively. It is seen that the large bulk of the propyl-amine molecules is very effective in reducing the mobilities, for the electrical effects are not far different from those in NH₃ or CN₃NH₂ and probably less.

Mobilities in Propyl-Amine Hydrogen Mixtures.—The results of the mixture experiments are reproduced in figure 3. In the figure as for

methyl-amine the abscissae are the per cent of amine in hydrogen and the ordinates are reciprocals of the mobility. The full curves are for the positive ions while the dashed curves are for the negative ions. Blanc's² law is as before indicated by the two straight lines. These curves are calculated from the *uncorrected* values of the mobilities in the pure amine and the *uncorrected* values of the mobilities with hydrogen in the clean chamber which were 6.38 cm./sec. per volt/cm. for positive ions and 8.67 cm./sec. per volt/cm. for negative ions. Once the amine had been admitted to the chamber it was impossible to remove the last traces except by opening the chamber and giving the whole system a vigorous cleaning with cleaning mixture. The amine seemed to stick to the metal and glass walls and distilled all over the apparatus when near its saturation pressure at room temperature.

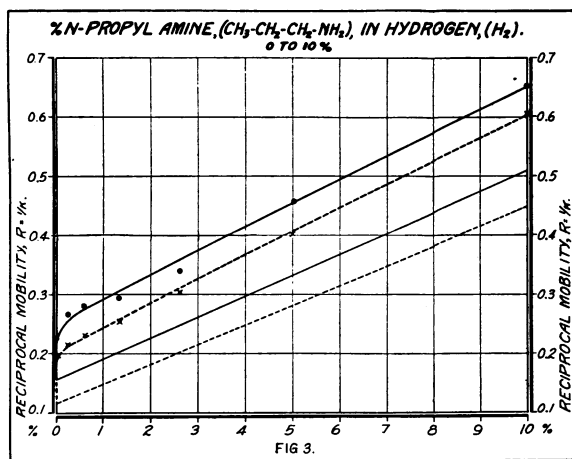


FIG. 3.

It is seen that in the case of both positive and negative ions the smallest trace of amine reduced the mobility (increased the reciprocal of the mobility or the resistance) by at least a factor of two. Thereafter the two curves run nearly parallel to the Blanc's law curve, indicating that the values will eventually approach the values in the pure amine as is the case for methyl-amine and hydrogen and for ammonia and hydrogen.

Effect of NH₃ on CH₃NH₂-H₂ Mobilities.—The effect of the addition of ammonia to methyl-amine hydrogen mixtures was also tried. In mixtures of propyl-amine and hydrogen such quantitative experiments were not carried out as the qualitative trials showed that NH₃ did not materially affect the lowering of mobility produced by C₃H₇NH₂. The results obtained in CH₃NH₂-H₂ mixtures with varying amounts of NH₃ are shown as triangles on the mobility curves of figure 1. They were results obtained for mixtures of 0.33% CH₃NH₂ and 1.05% NH₃ in H₂, 0.156% CH₃NH₂

and 0.388% NH_3 in H_2 and 0.000173% CH_3NH_2 and 0.00043% NH_3 in H_2 , respectively. They are plotted in terms of per cent CH_3NH_2 in hydrogen and it is seen that the points fall slightly above the corresponding curves for the CH_3NH_2 in H_2 alone.

This indicates that the mobilities are decreased slightly more by NH_3 in an amount to be expected from the increased Blanc's law effect of the NH_3 added. The lowering of the mobility is thus sensibly that produced by CH_3NH_2 , and NH_3 does not replace the latter in mixtures with hydrogen.

Discussion and Conclusions.—It is seen at once that *N* propyl-amine adds to both positive and negative ions even when present in small traces producing a very great initial decrease of the mobility. This is doubtless due to its bulk. The long carbon chain even in the event of the addition of a single amine molecule to the ion acts to increase the *real* radius of the ion and thus markedly reduces the mobility. The result is just what one would expect for the positive ion. The addition of the amine to the negative ion was a marked surprise to the writers as NH_3 -like compounds are not expected to attach to negative charges. In pure NH_3 electrons are probably not attached to molecules of NH_3 at all and in NH_3 the negative mobility in hydrogen is little changed by additions of small amounts of NH_3 .^{1,6} There is a chance that other organic substances were present as impurities to which negative ions might attach. The analogous behavior of CH_3NH_2 on negative ions where contamination probably occurred in far smaller measure, and the nature of preparation of these compounds, however, makes it appear that the propyl amine really does attach to negative ions.

The behavior of the methyl-amine is still more interesting. Here the addition of a trace of amine does not raise or lower the positive mobility within the limits of experimental measurement, while the negative-ion mobility is lowered by a considerable factor (i.e., the reciprocal of the mobility is increased). This indicates that if the CH_3NH_2 attaches to the positive ion it makes a molecular addition product or a cluster of the same size as the molecule of impurity to which the positive ion in hydrogen normally attaches itself. The negative ion, however, attaches to the CH_3NH_2 molecule or molecules, and forms a complex of about the same size (the mobilities are nearly equal) as the positive addition product with the amine. Thereafter with increasing amounts of amine mobilities decrease along curves differing comparatively little from the Blanc's law curves. The amount of deviation with higher concentrations of amine is similar to that observed for higher concentrations of NH_3 ⁶ and can be accounted for by the statistical clustering mentioned elsewhere.¹

We thus see that the three substances NH_3 , CH_3NH_2 and $\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-NH}_2$ act as follows on the ions. NH_3 attaches selectively to positive ions replacing some bulkier constituent which usually attaches to positive

ions in hydrogen, making its mobility equal to that of the negative ion in hydrogen or nearly so. The negative ion in ammonia is, however, little affected. In CH_3NH_2 the positive-ion mobility is little changed. It is to be presumed from the behavior of positive ions in NH_3 and $\text{C}_3\text{H}_7\text{NH}_2$ hydrogen mixtures that CH_3NH_2 attaches to the positive ion for NH_3 and $\text{C}_3\text{H}_7\text{NH}_2$ both attach and CH_3NH_2 lies between them in properties. Thus, the fact of no change of positive mobility on addition of CH_3NH_2 to hydrogen can only mean that the addition product of the positive ions to CH_3NH_2 has about the same radius as the normal impurity addition product on positive ions found in hydrogen alone. This conclusion is very important for it delimits the qualities of the unknown addition product on positive ions in H_2 alone. In CH_3NH_2 , contrary to its action in NH_3 , the negative ion attaches CH_3NH_2 and forms an ion of mobility *nearly as low* as that of the *positive* ion usually observed in hydrogen. Whether the small differences in the two mobilities in the mixtures are due to dielectric effects or to actual differences in cluster size cannot be stated at present. Finally in $\text{C}_3\text{H}_7\text{NH}_2$ both ions form such bulky addition products that their mobilities are both reduced by the largest factor yet observed in mixture studies. The dielectric attractions of these ions on amine molecules again are not quite equal or else the ions may have clusters of different size about them, for the two mobilities in the mixture are not quite the same.

While the results detailed above are quite consistent with the idea that the mobility changes can be described through the formation of addition products involving only one or two molecules with ions (i.e., a small ion theory¹ or the recent theory of Erikson⁸), the writers are not convinced that this explanation is necessarily the correct one. In the first place, the fact that the mobilities of positive and negative ions are never exactly the same, even when the presumption is likely that the addition products may be the same, leaves a doubt, inasmuch as these effects can be explained as conveniently by the assumption of clusters of slightly different size as well as by different residual dielectric attractions.¹ Again some peculiar unpublished anomalous results in SO_2 ⁷ and Cl_2 indicate a possibility of positive-ion mobilities as much as twice as high as any positive or negative mobilities observed in hydrogen before. These results which require careful repetition demanding new features in technique are at present under way. Should such values actually be observed beyond doubt the large cluster nature of the ion would be strongly indicated. Accordingly, while the small ion explanation gives a convenient representation of the results the writers are loath to draw conclusions at this juncture.

Note on the Simultaneous Observation of More Than One Mobility in a Gaseous Mixture under Ordinary Conditions of Measurement.—Had not the peculiar apparent break points in one or two of the methyl-amine mobility measurements been indicated as spurious by the measurements in mix-

tures, the writers would have interpreted these as indicating the presence of two types of ions having different mobilities existing in the gas at the same time. It would have been one of the few cases on record where such mobilities were definitely observed by the method used in a form where the nature of the curves left no doubt of interpretation. The experiments of Haines,⁹ Nolan,¹⁰ and Wahlin¹¹ leave much to be desired in the certainty and significance of their results as some of their breaks are largely discontinuities in what would appear to many like a continuous curve with highly irregular readings. If two different carriers are present curves such as observed by Wellisch¹² and one of the writers¹³ indicating free electrons should be observed with this method. With such carriers curves are obtained leaving no doubt as to the presence of two mobilities and the method is sensitive to the presence of as few as ten per cent of one class of carrier in work of this sort.¹⁴ Two of the curves in methyl-amine out of five observed had this dual character to such a marked extent as to leave no doubt. The other curves failed to show the effect and as stated it proved to be spurious. Accordingly, in the long experience of one of the writers with the alternating current method of measuring mobilities in the most diverse gaseous mixtures and gases it has never been possible to observe ions of one sign of more than one mobility in a gas at a given time; although the method would be easily sensitive to ions differing in mobility by 30 per cent if as much as 10 per cent of one of the carriers were present. The conclusion to be drawn is that under the conditions of observation only one positive and one negative ion mobility is observable in a gas at a given time.

Using an air blast method Erikson¹⁵ had observed without question the *transitory* existence of two positive ions in air and some other gases. The change of mobility indicated in Erikson's experiments is affected by water vapor which retards the transition and makes it observable in time intervals of the order of from 10^{-3} to 10^{-2} seconds.^{16,17} Thus, *temporarily at least*, ions of two different mobilities of same sign may exist at once. If, however, the ions are simple addition products of charged molecules with certain especially attracted molecules and these, as shown in this paper, by their bulk profoundly influence mobilities one may well ask why two or more ions of different mobilities are not observed in some of the mixtures studied, such as those above in more permanent form.

The answer becomes simple when the time scale of the phenomena involved as well as the concentrations of molecules present are considered. Mobilities of ions are measured under most conditions (except Erikson's) in periods of time of the order of 10^{-2} seconds. In many cases the ions coming from auxiliary fields are even older (i.e., 10^{-1} seconds). Now a gas *molecule* makes some 10^9 impacts with other molecules a second, while an *ion* from its low diffusion coefficient may make even more collisions.

In 10^{-2} seconds ions have collided with 10^7 molecules. If some very active molecule were present in a gas to the extent of 0.01 of a per cent, 10^3 of these molecules on the average would have collided with an ion in the period during which its mobility was being measured. If the union of ions and molecules is at all stable, and the effects of such gases as NH_3 and ether on positive ions show that they must be stable, all the ions would have had an opportunity to acquire their most stable form. If there were a number of molecules present, each forming an ion of stability different from the others, then only the most stable ion would form with the many encounters possible with the molecules in the time intervals used. It is, in fact, exceedingly rare in any technique so far used in the study of gaseous ion mobilities that less than 0.001 percent of some impurity is not present. It then depends on the stability of the different ions and on the numbers of different molecules present in a cm.^3 of gas which value of the mobility will be observed, but it is obvious that one ion of each sign only will be observed even with higher resolving powers for ions of different mobility in a gas.

The only conditions under which two mobilities could be observed for ions of the same sign in a gas at once, as usually studied, would be the following: Assume that there are a considerable number of molecules present in a gas which has a fairly high affinity for one or both ions. In addition, assume that there are present besides this gas a *small number* of molecules of some impurity with a *much higher affinity* for the ions than the first gas mentioned, such that in only one or two impacts of the ion with the latter molecules the more prevalent gas molecules would be shed for the rarer, more active impurity. If just enough of this active impurity were present so that 20 per cent or so of the ions only collided with these molecules before having their mobilities measured, then it might be expected that two mobilities would appear simultaneously. It is readily seen that such an occurrence will be, to say the least, rare with the numbers of molecules of foreign substance in the chemically purest gases and the wide range of affinities between ions and molecules. Thus, in general, the search for the existence of several ions must be made with methods involving very much shorter time intervals than usually worked with. The search after *several classes* of ions in a gas with the present mobility methods is thus futile and it is hardly surprising that all experiments directed to this end have yielded negative or doubtful results.

In conclusion, the writers wish to thank Mr. F. H. Sanders for his kind assistance in the tedious task of making the many mobility measurements required in this work.

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¹² Wellisch, E. M., *Phil. Mag.*, **31**, 186, 1916; **34**, 55, 1917.
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LATE GEOLOGIC DEFORMATION OF THE APPALACHIAN
 PIEDMONT AS DETERMINED BY RIVER GRAVELS*

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Introduction.—One important phase of the work of a geologist is to determine the structure of the earth's crust, including not only the vast movements that have resulted in the upheaval of mountain ranges, but also the minor flexures of the rocks, generally known as anticlines and synclines, that may or may not have appreciably modified the surface features. The recognition and determination of these minor features in a region composed of horizontal rocks is a comparatively easy matter, but in a region such as the Appalachian Piedmont, where the rocks are extremely old and have suffered untold periods of deformation and metamorphism, the geologic structure is generally so complicated that it completely obscures any minor folds or inclined surfaces that may have been produced by recent warping.

Because of this condition, geologists have not been able, so far, to determine whether or not the Piedmont belt, extending from central Georgia to the Hudson River, has been deformed by recent crustal movements, although the unusual altitudes of 900 to 1100 feet in this belt in Maryland and southeastern Pennsylvania has suggested such an origin.

Some years ago the writer conceived the possibility of discovering slight flexures in this region by careful tracing of high-level gravels which are known to occur near the mouths of the rivers crossing this belt. He found on the Potomac some indications, but no direct proof. No opportunity