

## Formation of Negative Ions in Gases by Electron Attachment Part I. $\text{NH}_3$ , $\text{CO}$ , $\text{NO}$ , $\text{HCl}$ and $\text{Cl}_2$

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## Formation of Negative Ions in Gases by Electron Attachment

### Part I. $\text{NH}_3$ , $\text{CO}$ , $\text{NO}$ , $\text{HCl}$ and $\text{Cl}_2$

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With the same method and apparatus employed in the study of negative ion formation in  $\text{O}_2$  by electron attachment, the results have been extended to all the common diatomic gases and  $\text{NH}_3$ . No negative ions are formed in  $\text{NH}_3$  below an  $X/p$  of 7.5; beyond that point they are formed with increasing probability as the energy of the electrons increases. The phenomenon is interpreted as dissociation of the molecule with the formation of  $\text{NH}^-$  at an electronic energy of approximately 3 volts, the  $\text{NH}_3$  molecule having itself no electron affinity. No negative ions could be formed in  $\text{CO}$  at the electronic energies available, and the molecule is presumed to have no electron affinity. Negative ions are formed by electron attachment in  $\text{NO}$ , the probability increasing with decrease in electronic

energy. A linear variation in probability of attachment with pressure is also observed in  $\text{NO}$  which is due to a collision with a pair of  $\text{NO}$  molecules held together by weak attractive forces. Negative ions are formed in  $\text{HCl}$  with a probability which increases with increasing electronic energy suggesting that dissociation of the molecule occurs here as well. Similar results are obtained in  $\text{Cl}_2$  where it has been known that the energy of the attachment process must be more than sufficient to dissociate the molecule. The experiments indicate several types of attachment processes which can occur in gases and the possibilities of energy dissipation in ion formation. In general the most favored process is the carrying off of the energy by a third body involved in the process.

IT is well known that stable negative ions may be formed in many gases. Their formation is apparently the random capture of electrons by otherwise neutral molecules, though this phenomenon is by no means well understood. Its study in oxygen<sup>1</sup> has shown, however, that the attachment process and its variation with electronic energy furnish a most powerful tool for the study of the behavior of electrons in gases. Not only may the intrinsically interesting factors in negative ion formation be investigated, but the variations in the rate at which attachment occurs may be related to otherwise unobservable interactions between electrons and gas molecules. In addition the variation of the probability of the capture process with electron energy throws light on the most pressing problem of negative ion formation; namely, the disposition of the energy of binding, or the electron affinity, of the molecule. In consequence of these facts it has been of interest and importance to extend the experiments on oxygen to studies of the other common diatomic and polyatomic molecules. Part I of these papers deals with the ordinary diatomic molecules and also  $\text{NH}_3$ , and Part II with the triatomic molecules. They cover all the common gases of these types which are available for laboratory experimentation.

### EXPERIMENTAL METHOD

The experimental apparatus was the same as that employed for the study of negative ion formation in oxygen and a detailed account has already been presented.<sup>1</sup> A brief description, only, will be given here. The principle of the method lies in the analysis of a mixed current stream of ions and electrons which is passed through a grid of fine wires. A high frequency alternating potential of the order of 50 volts and  $10^6$  cycles is applied between alternate adjacent wires of this grid. Under these conditions the electronic component of the current is swept out of the current stream to the grid wires, and the heavier and more slowly moving negative ions pass through essentially undisturbed. The difference between the current to the collector with no potential between the grid wires and that with a potential will be a measure of the ionic fraction of the current. A single grid of this type was used by Cravath<sup>2</sup> to measure the fraction of electrons remaining unattached at a given distance from a source of electrons. However, in practice some negative ions will be captured by the grid, and some electrons will escape. To avoid the resulting errors, *two* grids were employed in the present experiments, either one of which might be removed from the current stream while

\* National Research Fellow.

<sup>1</sup> N. E. Bradbury, *Phys. Rev.* **44**, 883 (1933).

<sup>2</sup> A. M. Cravath, *Phys. Rev.* **33**, 605 (1929).

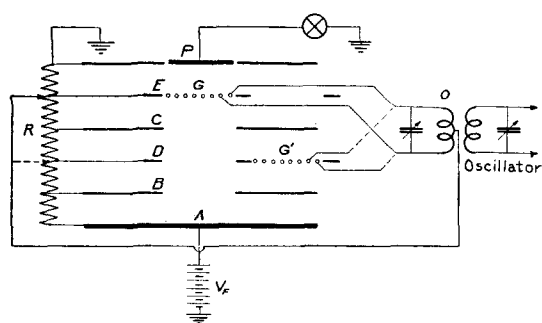


FIG. 1. Schematic diagram of apparatus. Alternate wires in grids  $G$  and  $G'$  are connected together and either grid may be moved into or out of the uniform field space.

the other was being used. Thus it was possible to study the decrease in the number of free electrons by attachment as they were drawn through the gas space between the grids. Any spurious effects due to the grids themselves effectively cancelled out.

A zinc plate parallel to the grids served as a photoelectric source of electrons, and a uniform field was maintained between it and the plane collecting electrode. A schematic diagram of the apparatus is shown in Fig. 1. By removing both grids from the current stream it was possible to obtain an estimate of the electronic mobility using the approximate equation given by J. J. Thomson.<sup>3</sup> This was necessary to evaluate the number of electronic impacts in going a given distance, and hence the probability of capture at a collision, denoted here by  $h$ .

The whole apparatus was contained within a large Pyrex tube which could be baked out and pumped down to  $10^{-6}$  mm Hg before the admission of a sample of gas. A plane quartz window to admit ultraviolet light from a quartz mercury arc was affixed to the tube by means of a graded seal. Suitable filters were employed to cut out radiation harder than 2537Å. A liquid air or solid  $\text{CO}_2$  trap to condense Hg vapor was placed between the tube and all manometers, gauges, and pumps. To avoid contamination by stop-cock greases, mercury cutoffs were substituted for all stopcocks. These could be adjusted to operate suitably under pressures of a few centimeters of Hg and proved very satisfactory. A

specially designed McLeod gauge was employed to read pressures of the order of a few millimeters; otherwise a mercury manometer was used.

It has previously been shown in all work of this type that great care must be taken to maintain extreme gas purity; consequently each gas was purified according to its particular requirements. Several separately purified samples of gas were used in each case, and agreement of the results from the various samples was taken as an indication of purity. Only in rare instances was difficulty experienced in adequately purifying the gas to be studied. These particular cases will be noted later.

### AMMONIA

The formation of negative ions in ammonia has been the subject of investigation and discussion. Bailey and Duncanson<sup>4</sup> observed the presence of negative ions in ammonia gas at values of  $X/p$  greater than 10 ( $X$  in volts/cm and  $p$  in mm Hg). On the other hand, using very pure samples of ammonia Loeb<sup>5</sup> was unable to obtain any trace of negative ions under the conditions of his experiment. The causes and conditions of so marked a discrepancy therefore are of considerable interest.

The ammonia used in the following experiments was obtained from a commercial tank of anhydrous  $\text{NH}_3$  of which approximately one-half had already been used. Most of the residual hydrogen had, therefore, been blown off. The gas was liquefied over metallic sodium and dried for several days. It was then solidified with liquid air and any uncondensable gas pumped off. This process was repeated and the final sample fractionally distilled, only the middle portion being retained for the experiments.

The results of the measurements at different pressures and values of  $X/p$  are given in Fig. 2 in which  $h$ , the probability of attachment, is plotted as a function of  $X/p$ . The curve shows that for low electron energies (of which  $X/p$  is a measure) the ammonia molecule *does not form*

<sup>3</sup> J. J. Thomson, *Conduction of Electricity through Gases*, p. 466, University Press, Cambridge, 1928.

<sup>4</sup> V. A. Bailey and W. E. Duncanson, *Phil. Mag.* **10**, 145 (1930).

<sup>5</sup> L. B. Loeb, *Phil. Mag.* **8**, 98 (1929); H. B. Wahlin, *Phys. Rev.* **19**, 173 (1922).

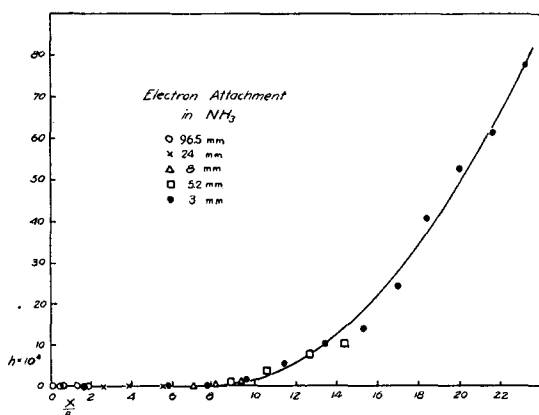
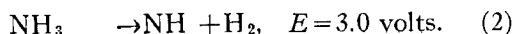


FIG. 2. Probability of electron attachment in  $\text{NH}_3$ . The points indicate data taken at different pressures as shown.

*negative ions*. This is in accord with the observations of Loeb. At a value of  $X/p$  about 9, however, negative ions begin to appear in the gas and are formed in increasing numbers as the field strength is increased. Thus the observations of both Loeb and Bailey are entirely compatible, their observations merely differing in range of electronic energy studied. Loeb did not investigate values of  $X/p$  greater than 0.1.

It is not apparent, however, why an ammonia molecule should possess an electron affinity for high energy electrons and not for those of low energy. The interpretation must be that some change is induced in the ammonia molecule by electrons of energy greater than a certain amount, and that attachment takes place as the result of this change. The most probable process which can occur is some type of dissociation. This possibility of dissociation occurring in certain attachment processes was suggested by James Franck as early as 1928 on the basis of Loeb's observations of various apparent classes of attaching molecules.

The photochemical decomposition of ammonia has been extensively studied and the most probable reactions set forth. Two possible initial steps may be proposed. They are, with the corresponding energies,



Wiig and Kistiakowsky<sup>6</sup> have shown that (1) occurs in the photochemical decomposition of  $\text{NH}_3$  followed by subsequent secondary reactions which lead eventually to the formation of  $\text{N}_2$  and  $\text{H}_2$ . Koenig and Wagner,<sup>7</sup> however, have found that by decreasing the electric current in silent ammonia discharges a reaction to hydrazine may be made to occur almost quantitatively. Such a reaction as the result of electron impact is better explained by (2) above rather than as a secondary reaction of (1). Gedye and Allibone<sup>8</sup> have also observed the formation of  $\text{N}_2\text{H}_4$  in the decomposition of  $\text{NH}_3$  by high speed electrons.

It seemed very probable that some reaction of this type occurred in the process of electron attachment at high  $X/p$ . No resultant  $\text{H}_2$  could be detected, however, after freezing out all the ammonia with liquid air at the conclusion of an experiment. This was to be expected, however, from the volume of the tube and the magnitude of the electronic currents employed. Accordingly a very much smaller tube was constructed with small plane polished zinc electrodes. Electron currents of the same or greater intensity could be obtained from this tube, and the smaller volume multiplied any residual hydrogen pressure by a factor of 10. Using ammonia pressures of the order of 5 mm, the curve shown in Fig. 3 was obtained, the pressures being read on a McLeod gauge after freezing out the  $\text{NH}_3$  with liquid air. To eliminate photodecomposition of the ammonia a 20 cm filter of  $\text{NH}_3$  gas at two atmospheres pressure was employed. The experiments were difficult because of the extremely minute quantities of gas involved, but showed definitely that at even moderately low fields a residual gas, uncondensable by liquid air, is produced by the passage of electrons through ammonia. Furthermore, the appearance of this gas occurs at approximately the same value of  $X/p$  as that at which negative ions begin to be formed.

It is therefore suggested that the  $\text{NH}_3$  molecule *does not* form a stable negative ion, but that

<sup>6</sup> E. O. Wiig and G. B. Kistiakowsky, J. A. C. S. **54**, 1806 (1932).

<sup>7</sup> Koenig and Wagner, Zeits. f. physik. Chemie **A144**, 213 (1930).

<sup>8</sup> Gedye and Allibone, Proc. Roy. Soc. **A130**, 346 (1931).

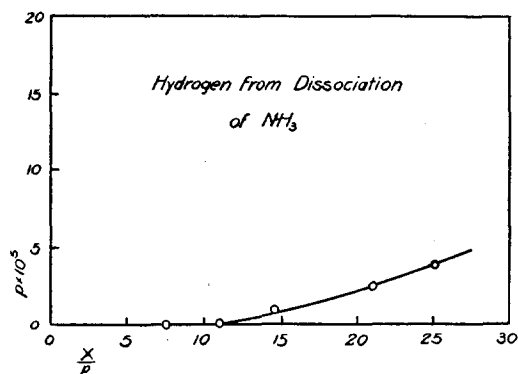
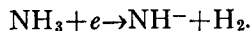


FIG. 3. Residual gas, uncondensable by liquid air, formed by the passage of electrons through  $\text{NH}_3$ .

negative ions in ammonia are formed, probably in a single elementary process, by the reaction



The ion which finally results may be of the order of  $\text{N}_2\text{H}_4^-$  by a secondary process. There are two reasons for suggesting that the decomposition and attachment occur in a single process. In the first place such a reaction affords a most convenient means for dissipating the energy of attachment, as it is not necessary to call upon either radiation or a three body collision to account for its disappearance. This question will be discussed in more detail at another point. Secondly, if dissociation occurs followed by subsequent attachment of *another* electron, then the probability of such an attachment would have to be nearly unity as the actual concentration of the products is so minute.

It, therefore, seems probable that the process of negative ion formation in  $\text{NH}_3$  is not one of attachment to the ammonia molecule, but a simultaneous process of dissociation and attachment to one of the products formed. It is probable that the electron energy required for this process to occur must be close to that required for dissociation, as the electron affinity is small and cannot be available until dissociation can nearly be brought about by the electron itself. The rise in the curve then occurs as the energy of the electrons increases and dissociation becomes more probable.

Further evidence of the fact that inelastic impacts occur in ammonia at values of  $X/p$  of

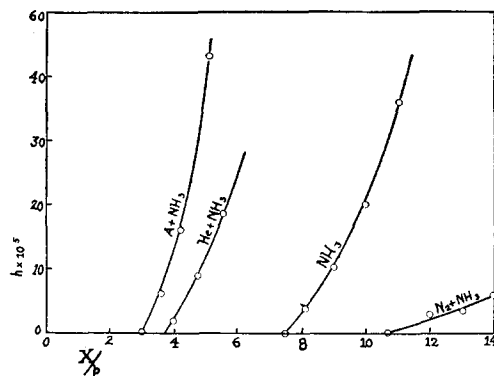


FIG. 4. Probability of attachment in mixtures of  $\text{NH}_3$  with the inert gases showing variation in rate of gain or electron energy.

the order of magnitude of 10 is shown by the mobility curve of electrons in ammonia which was found to increase at that point. On the Compton<sup>9</sup> theory of electronic mobilities this behavior is an immediate consequence of such impacts.

As a further test of this theory of negative ion formation, experiments were carried out with mixtures of  $\text{NH}_3$  and the inert gases  $\text{N}_2$ , A and He. In the experiments on oxygen, such mixtures were shown to affect the rate at which electrons gained energy in the gas without changing the character of the attachment curve, its position on an  $X/p$  scale only being shifted. The results of such measurements in  $\text{NH}_3$  are shown in Fig. 4. From these curves and data of Townsend<sup>10</sup> on electron energy in gases as a function of  $X/p$ , it is possible to estimate the energy at which the formation of negative ions begins to occur. This gives a value of about 4 volts and is of the correct order of magnitude for the process suggested. Definite proof that this is the correct explanation of the phenomenon must await mass-spectrographic analysis of the products. It seems, however, strongly suggested by the present observations.

#### CARBON MONOXIDE

Carbon monoxide was prepared from pure sodium formate and concentrated sulfuric acid, all air and water vapor being removed by evacu-

<sup>9</sup> K. T. Compton, *Rev. Mod. Phys.* **2**, 231 (1930).

<sup>10</sup> J. S. Townsend, Jr., *J. Frank. Inst.* **200**, 563 (1925).

ating the reaction flask before adding the sulfuric acid. The CO so formed was passed over hot copper shot and through several liquid air traps for complete drying.

No attachment was observed in CO at any value of  $X/p$  between 0.25 and 20, the practical limits of the apparatus. The observational limit of the apparatus is a function of pressure, but one may determine probabilities of capture greater than  $10^{-8}$  at the higher pressures and  $10^{-7}$  at lower pressures (5 mm). Any attachment in CO is therefore less than these probabilities and is presumably zero.

Electron attachment in CO has been studied by Wahlin<sup>11</sup> who found a coefficient of the order of  $10^{-8}$  but suggests that the value might be zero. This agrees with the present measurements and it is therefore concluded that CO has no electron affinity and under ordinary conditions, negative ions cannot be formed in it. Since the energy required to dissociate CO is about 9.0 volts, it is probable that electrons within this range of  $X/p$  do not attain this energy. Negative  $O^-$  ions have been observed in CO at low pressure by Tate and Lozier<sup>12</sup> when the energy of the bombarding electron exceeded 10 volts. Such a process could doubtless be made to occur at ordinary pressures provided the electron energy reached the proper amount. The measurements of Townsend,<sup>10</sup> however, indicate that even at an  $X/p$  of 20, the energy is hardly 2 volts. The similarity of the electronic structure of CO to that of  $N_2$  makes quite reasonable its lack of an electron affinity.

#### NITRIC OXIDE

Nitric oxide was prepared by two different methods since the character of the results obtained showed that definite and unambiguous purity was necessary. The gas was first prepared by the decomposition of a dilute sodium nitrite solution in an air free flask with sulphuric acid. The gas so formed was passed over  $P_2O_5$  and solidified in a trap cooled with liquid air. The other means of preparation, which was simpler and equally satisfactory, was by the thermal

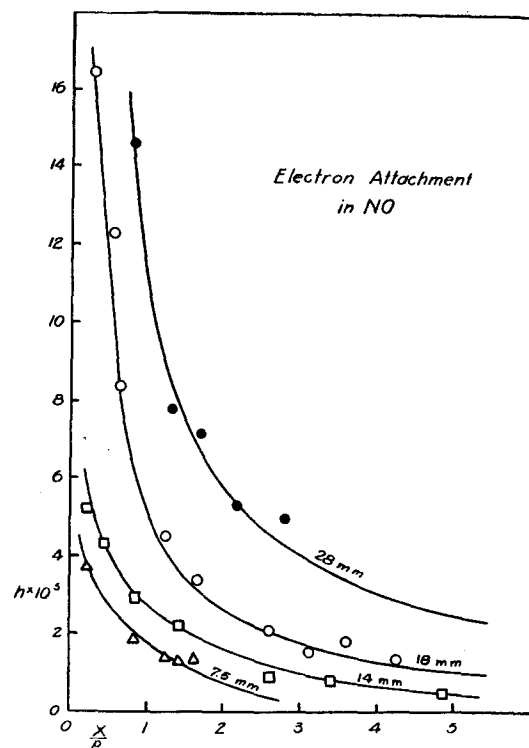


FIG. 5. Probability of electron attachment in NO. The different curves are for different pressures as shown.

decomposition of diphenyl nitrosoamine. Eastman's practical grade was employed and heated below the temperature of decomposition ( $140^\circ$ ) for some time in a vacuum. The temperature was then raised to  $140^\circ$  and the gas collected in a liquid air cooled trap. As far as could be determined, the resulting NO was extremely pure. The gas was fractionated from the solid state and passed through traps held at  $-150^\circ$  into the measuring chamber. The use of mercury cutoffs in place of ordinary stopcocks was particularly advantageous with this gas. The presence of any  $O_2$  would have been indicated by a red color from  $NO_2$  formed, and the latter gas would have been frozen out in the protecting traps.

The results obtained in this gas are shown in Fig. 5 where the probability of attachment is plotted as a function of  $X/p$ . Almost alone of all gases studied, there was here observed a definite variation of the probability of attachment with pressure. The curves indicate a marked increase in attachment with increase in pressure. To make doubly certain that the effect was not due to

<sup>11</sup> H. B. Wahlin, Phys. Rev. **19**, 173 (1922).

<sup>12</sup> J. T. Tate and W. W. Lozier, Phys. Rev. **39**, 254 (1932).

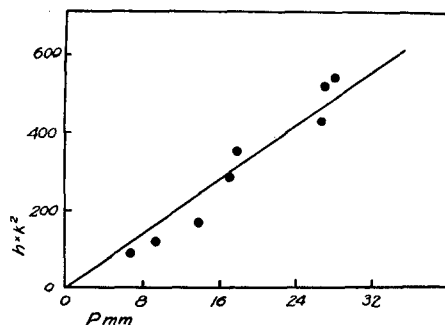
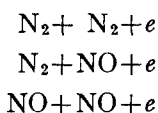


FIG. 6. Variation in the probability of electron attachment in NO with pressures. The electron energy corresponds to that for  $X/p = 1.5$ .

impurities, experiments were made on a single sample of gas which was pumped down from the higher pressures to the lower, the runs in each case being taken at the same  $X/p$ . The points so obtained were used as the basis for Fig. 6 and the data from the curves in Fig. 5 plotted there as well. It is seen that the attachment coefficient at a given  $X/p$  is a linear function of the pressure. Such a variation immediately suggests that some form of triple collision occurs since an increase in pressure increases the fraction of all collisions which are of the three body type.

Inasmuch as a three body process has often been put forward as one of the means of dissipating the energy of attachment, if was of interest to investigate the effect further in this gas. A mixture of equal parts of  $N_2$  and NO was made up and attachment investigated in this artificial gas.  $N_2$  was chosen as it is the most nearly similar in mass to NO of the inert gases. In such a mixture, three kinds of triple collisions may take place. They are:



The first of these will not result in a negative ion. *A priori*, either of the other two processes might be equally effective, and hence, if results were compared at the same pressure, the value of  $h$  for the mixture should be  $2/3$  that for NO. Actually, however, it is about  $1/3$  showing definitely that *two molecules* are involved in the attachment process and *that they are both NO molecules*.

It is, therefore, suggested that in the case of NO, we are dealing, in the primary attachment process, not with NO, but with a labile, lightly bound polymer of NO, i.e.,  $(NO)_2$ . NO is one of the well-known "odd" molecules, and, in view of the tendency of such molecules to polymerize, it has been a most interesting exception. There is, however, evidence for its association into double molecules at low temperatures, and Kassel<sup>13</sup> has calculated the energy of attraction between two NO molecules. This comes out to be as much as 0.05 volts. The electronic structure of NO has been discussed by Pauling,<sup>14</sup> and reasons have been presented why NO may not polymerize to any great extent. However, in consequence of these experiments, the character of the molecule, and its known association at low temperatures, it is suggested that lightly bound polymers of NO do occasionally occur. Negative ion formation in NO is then to be explained by the formation of  $NO^-$  from one of these temporarily existing pairs, the other molecule of NO carrying away the excess energy of the reaction. Triple collisions of the kinetic theory type when no intermolecular forces exists are probably too rare to account for negative ion formation, but the existence of slight intermolecular forces is sufficient to enormously increase their frequency. While the deviation of NO from a perfect gas is not excessively great, it is of sufficient magnitude to permit this explanation.

The rate of negative ion formation in NO has not previously been studied and there are no data with which to compare these results. Negative ions with high velocity electrons ( $\sim 10$  volts) have been observed in NO by Tate and Smith<sup>15</sup> and also Hogness and Lunn,<sup>16</sup> but the ions formed are largely atomic and due to processes involving dissociation.

#### CHLORINE AND HYDROGEN CHLORIDE

The great rapidity with which these molecules apparently attach free electrons as well as their great chemical reactivity made measurements in

<sup>13</sup> L. S. Kassel, *Kinetic of Homogeneous Gas Reactions*, p. 170, Chemical Catalog Co., New York, 1932.

<sup>14</sup> L. Pauling, J. A. C. S. **53**, 3225 (1931).

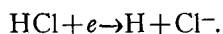
<sup>15</sup> J. T. Tate and P. T. Smith, Phys. Rev. **39**, 270 (1932).

<sup>16</sup> Hogness and Lunn, Phys. Rev. **30**, 26 (1927).

these gases extremely difficult. Attachment was so rapid that at even the lowest pressures at which the grids would function ( $\sim 2$  mm) no measurements were possible. The device of dilution with an inert gas, usually argon, was therefore resorted to since the mixture experiments had always showed that the character of the curves was unchanged under such circumstances. Under these conditions the grids functioned properly, yet the concentration of the active gas was small enough to permit measurements to be made.

Hydrochloric acid gas was prepared by dropping concentrated sulfuric acid on NaCl in a vacuum. The resulting product was frozen, any uncondensable gas pumped off, and the final product fractionally distilled. The gas was passed through traps held at  $-115^\circ$  before admission to the measuring chamber. Under these circumstances a gas of such purity and dryness was obtained that ample photoelectric currents could still be obtained from the zinc photoelectric surface. The diluting gases were purified in the usual manner with hot copper shot and liquid air cooled traps.

The results are shown in Fig. 7. In this case the values of  $X/p$  are those for the gaseous mixture of argon and HCl and must not be considered as applying to the undiluted gas. It is seen that attachment occurs in HCl for electrons even of very low energy, and that the probability of attachment increases rapidly as the energy of the electrons is increased. This latter phenomenon seems to indicate that negative ions are formed in HCl as the result of a dissociation process similar to that observed in  $\text{NH}_3$ . The reaction probably occurring would be of the form



The energy of dissociation of HCl is 4.5 volts and the electron affinity of the Cl atom, calculated by means of the Born cycle,<sup>17</sup> is about 4.1 volts. Thus energy is available for the dissociation process at even low electron energies, and the presence of negative ions in the gas, indicated by mobility experiments, at low values of  $X/p$  can be explained on this basis. As the energy of the electrons is increased, dissociation and the forma-

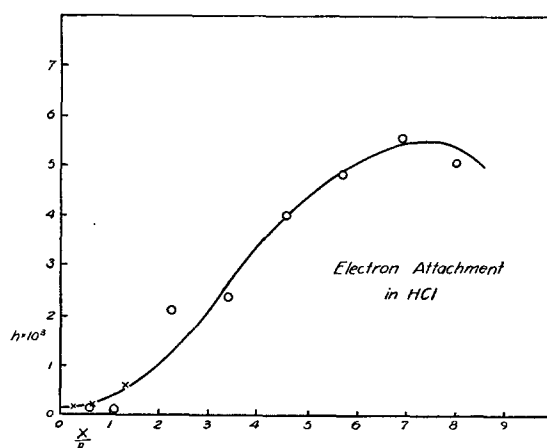


FIG. 7. Probability of electron attachment in HCl (in argon mixtures).

tion of  $\text{Cl}^-$  becomes more probable and the rate of negative ion formation increases. Such a process permits a kinetic disposition of the energy of binding, and seems to be in accord with the experimental observations. Further support for such an interpretation is found in the work of Barton<sup>18</sup> who found only  $\text{Cl}^-$  ions in HCl with even very slow electrons. It is therefore suggested that the negative ion initially formed in HCl is not  $\text{HCl}^-$  but  $\text{Cl}^-$ . These experiments are also in accord with those of Bailey<sup>19</sup> who observed attachment in HCl at high values of  $X/p$ . He found that the probability of attachment increased as  $X/p$  increased, the most rapid rise occurring at an  $X/p$  of 15. This is undoubtedly the same phenomenon as observed here.

The experiments with chlorine presented even greater difficulty than those with HCl. The gas was prepared by the thermal decomposition of  $\text{CuCl}_2$  in the manner described by Loeb<sup>20</sup> with great care to keep the system thoroughly dry. In spite of this, a considerable decrease in the photoelectric activity of the plate was observed. However, measurable currents could still be obtained, and the results of experiment with argon dilution are shown in Fig. 8. Here it is to be expected that a process of dissociation would occur since the dissociation energy of the  $\text{Cl}_2$  molecule is only of the order of 1.5 volts. There

<sup>18</sup> F. A. Barton, Phys. Rev. **30**, 614 (1927).

<sup>19</sup> V. A. Bailey and W. E. Duncanson, reference 4.

<sup>20</sup> L. B. Loeb, Phys. Rev. **35**, 184 (1930).

<sup>17</sup> J. Sherman, Chem. Rev. **11**, 93 (1932).



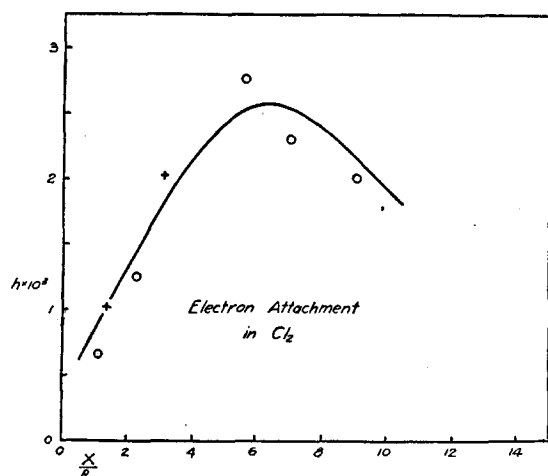


FIG. 8. Probability of electron attachment in  $\text{Cl}_2$  (in argon mixtures).

is thus available ample energy to dissociate the molecule with the formation of  $\text{Cl}^-$ , and the character of the curve, rising with increase in electronic energy substantiates this interpretation. This is also in accord with the observations of Hogness and Harkness<sup>21</sup> on the formation of negative ions in  $\text{I}_2$  at very low pressures. They observed as a primary process only the formation of  $\text{I}^-$  even at very low electron energies. A similar behavior would be expected in  $\text{Cl}_2$ . The only quantitative measures of the probability of attachment in  $\text{Cl}_2$  are those of Wahlin<sup>11</sup> who found an approximate value of  $10^{-3}$  in good accord with the present measurements.

### DISCUSSION

As has been indicated, one of the greatest problems of negative ion formation is the means of dissipation of the energy of binding. Three *a priori* possibilities are available for this. They are: (1) radiation; (2) three body collision; (3) dissociation and simultaneous attachment. Of these three processes, (2) and (3) are not essentially dissimilar since both involve the removal of the energy as kinetic energy by a third body.

<sup>21</sup> Hogness and Harkness, Phys. Rev. 32, 784 (1928).

Various attempts have been made to observe the radiation emitted in the formation of negative ions, but the experiments have been complicated by a lack of intensity or other factors. Oldenburg<sup>22</sup> attempted to observe an electron affinity spectrum from the iodine atom but without success. However, in certain cases, notably  $\text{O}_2$  and  $\text{SO}_2$ , there seems to be fairly definite evidence that an  $\text{O}_2^-$  or an  $\text{SO}_2^-$  ion is formed. In such a case there is no process except radiation which can carry off the excess energy. Since the probability of attachment *increases* for very *slow* electrons, the energy of the electron cannot play any part in a dissociation process, and the energy of attachment cannot be as much as the 5.4 volts necessary for dissociation. Other considerations as well seem to point to the existence of an  $\text{O}_2^-$  ion. Erikson<sup>23</sup> has found that the mobilities of newly formed positive and negative ions were the same, and Luhr<sup>24</sup> has shown that even in a glow discharge, 95 percent of the positive ions formed are  $\text{O}_2^+$ . The aging experiments thus point to an initial equality of mass and hence to an  $\text{O}_2^-$  ion. The question cannot be settled definitely, however, without mass-spectrographic analysis.

Of the three types of attachment process, all apparently can and do occur. That of dissociation and attachment in a single elementary process, in which the energy is carried off by the particles themselves, is apparently the most common and readily occurring. It occurs in NO though here the electron affinity is sufficient to break the apparently weak binding forces, and the kinetic energy of the electron plays no part other than to decrease the probability of attachment as its energy increases. Further examples of the more common type of curve, where the probability of attachment increases with increasing electronic energy, and which is interpreted as a dissociation process, will be discussed in Part II.

<sup>22</sup> O. Oldenburg, Phys. Rev. 43, 543 (1933).

<sup>23</sup> H. A. Erikson, Phys. Rev. 30, 339 (1927).

<sup>24</sup> O. Luhr, Phys. Rev. 44, 459 (1933).