

The Formation of Negative Ions in Gases Part II. CO₂, N₂O, SO₂, H₂S and H₂O

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The Formation of Negative Ions in Gases

Part II. CO₂, N₂O, SO₂, H₂S and H₂O

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The study of electron attachment has been extended to the gases CO₂, N₂O, SO₂, H₂S and H₂O. No negative ions were observed in CO₂. In N₂O, below $X/p=2$, no negative ions were formed, and the N₂O molecule apparently has no electron affinity. For values of $X/p>2$, the electrons possessed sufficient energy to dissociate the molecule and negative ions, probably O⁻, were formed in increasing numbers. SO₂ showed an electron affinity forming negative ions with electrons of very low velocity. The probability of attachment decreased as X/p increased until an X/p of about 13 when an increase in probability of formation

was noted. This is probably due to dissociation and formation of SO⁻. No negative ions were observed in H₂S below an X/p of 6. For greater values of X/p negative ions were formed in increasing amounts presumably by a dissociation process with the formation of HS⁻. A similar behavior was observed in H₂O at an $X/p=10$, with the formation of OH⁻. Negative ion formation in H₂O was also observed at low X/p and varied with the pressure of the gas. This is explained as being due to negative ion formation from small molecular aggregates existing near the point of condensation of the water.

THE formation of negative ions by electron attachment in the common diatomic gases has been reported in the preceding paper. It was possible, there, to interpret the characteristics of the observed attachment processes in terms of known molecular constants and properties. Extensive experimental work in both electron bombardment and band spectroscopy of such molecules has made available a great amount of pertinent data, thereby greatly simplifying the analysis of the energy relations in negative ion formation. The study of electron attachment in ammonia, however, showed that it was possible to interpret the phenomena occurring fairly satisfactorily, even where detailed knowledge of the electronic properties of the molecule was lacking. It was, therefore, of great interest to extend the data to include the common triatomic inorganic molecules. The results given here were taken with the same apparatus and methods described in Part I.

NITROUS OXIDE

Nitrous oxide was obtained from a commercial tank of the gas of high purity. The gas was solidified in a trap cooled with liquid air, and any uncondensable gases pumped off. This process was repeated and the resulting product twice fractionated with liquid air. The middle third of the final sample was retained for use.

In all these experiments, it was generally found that physical methods of purification were not only simpler than chemical means, but lead to a purer product.

The results of the experiments are shown in Fig. 1 where the probability of electron attachment at a single collision, h , is plotted as a function of X/p , the field strength in volts/cm divided by the pressure in millimeters of Hg. It is seen that no attachment occurs for small values of X/p , and that therefore, the N₂O molecule *has no electron affinity*. However, at an X/p greater than 2, negative ions are formed in the gas and continue to be formed in increasing numbers as the value of X/p is increased. This is a type of process which has been observed in NH₃ (Part I) and it has been shown that dissociation is apparently typified by such an attachment curve. The most interesting feature of this case is the low energy at which the process seems to occur.

Electron attachment has been studied in N₂O by Bailey and Rudd,¹ and though they do not carry their curve to a very low value of X/p , the general behavior is the same as that reported here, a probability of attachment increasing with increasing X/p . They also find that at very high X/p of the order of 25 the probability of attachment decreases somewhat. This observation was beyond the range of the present apparatus.

* National Research Fellow.

¹ Bailey and Rudd, *Phil. Mag.* **14**, 1033 (1932).

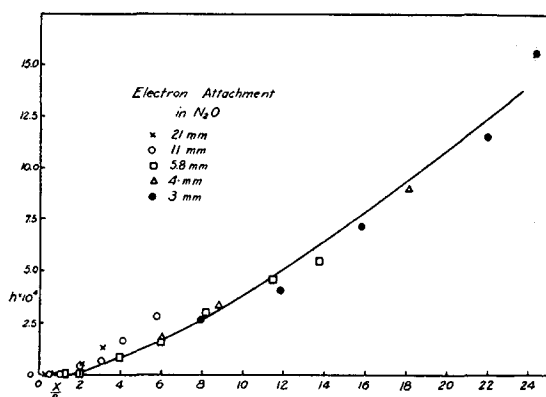
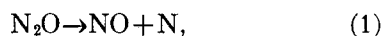


FIG. 1. Probability of electron attachment in N_2O . Data taken at different pressures as shown.

The decomposition of N_2O , by both thermal and photochemical means, has been extensively studied, though the results are not highly concordant. Two processes are possible for the decomposition:



The energy required for reaction (1) is 4.7 volts and that for reaction (2) is 1.8 volts. The first reaction has been shown to occur for the photochemical process by Dutta² who observed continuous absorption to set in at 2750Å and this interpretation is further supported by observations of Wulf and Melvin³ who found NO bands appearing in irradiated N_2O . On the other hand, the thermal reaction has been definitely shown⁴ to follow (2) with a slightly higher energy of activation.

To determine which of the reactions occurred in the present case, the expedient of mixing N_2O with inert gases was tried. The results are shown in Fig. 2. It is seen that for low energies at least, electrons gain energy in N_2 at much the same rate as in N_2O . It is then possible to determine from data of Townsend⁵ on electron energies in N_2 , the approximate energy at which attachment begins to occur. This is approximately 1.7 volts for the foot of the curve, a value which is

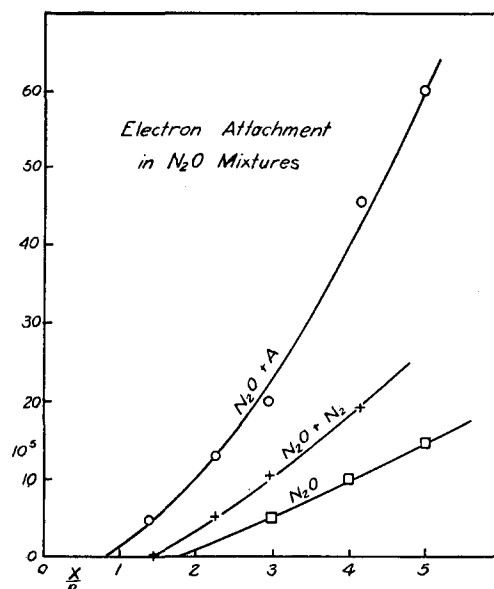
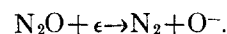


FIG. 2. Probability of electron attachment in mixtures of N_2O with equal parts of the inert gases, N_2 and A.

in excellent agreement with the value for reaction (2) above.

Hence the most probable mechanism for negative ion formation in N_2O is a reaction of the type



Since N_2 does not form negative ions, at least in the unexcited state, it is probable that the initial ion formed is O^- . The subsequent character of the ion can be determined only by other methods. This is, apparently, another example of simultaneous attachment and dissociation and the products of the reaction are available to carry off the excess energy. It may be noted in both this experiment and in that with NH_3 that the electronic reaction is not necessarily the same as the photochemical reaction. Where two types of dissociation are possible, that of the lower energy may first occur with electron bombardment when it does not appear photochemically.

CARBON DIOXIDE

Carbon dioxide was obtained from a commercial tank of anhydrous CO_2 and purified in a manner similar to N_2O . Solid CO_2 snow was kept on all traps during the course of the experiment to condense Hg vapor.

² A. K. Dutta, Proc. Roy. Soc. **A138**, 84 (1932).

³ Wulf and Melvin, Phys. Rev. **39**, 180 (1932).

⁴ L. S. Kassel, *Kinetics of Homogeneous Gas Reactions*, p. 227, Chem. Catalog Co., New York (1932).

⁵ J. S. Townsend, J. Frank. Inst. **200**, 563 (1925).

No attachment was observed in CO_2 even at the highest X/p which could be studied. Since the lowest energy required for the dissociation of CO_2 into $\text{CO} + \text{O}$ is 5.5 volts, it seems probable that electrons, at moderate values of X/p , do not easily attain this energy. This conclusion is supported by Townsend's data for CO_2 . Negative ion formation has been studied in CO_2 by Loeb⁶ and Wahlin.⁷ Loeb found values as low as 10^{-7} , but the value varied with the age of the gas indicating the presence of contamination from the walls of the chamber. It therefore seems reasonable to assert that the probability of attachment in CO_2 must be less than 10^{-8} and that apparently CO_2 does not form negative ions.

SULFUR DIOXIDE

Sulfur dioxide was obtained from a commercial tank of the anhydrous gas. It was first passed through a long tube of P_2O_5 and then condensed at low pressure in a trap cooled with liquid air. Any residual gas was then pumped off and the process repeated after remelting the sample, which was then fractionated in the usual manner. CO_2 cooled traps were employed before the tube and for further drying, though they required that the experiments be made at pressures of SO_2 less than 4 mm.

The results for SO_2 are plotted in Fig. 3 where the probability of attachment is represented as a function of X/p . In SO_2 , as in oxygen, attachment definitely occurs for electrons of low energy and increases rapidly as the energy of the electrons decreases. This indicates that the SO_2 molecule must have an electron affinity and that some radiative process occurs for the dissipation of energy. As the electronic energy increases, the probability of attachment at first decreases, and then begins to increase. A similar phenomenon was noted in O_2 . This increase may be due either to a dissociation process or to an inelastic impact (as in O_2), reducing the electron energy to zero with consequent increased probability of capture.

To determine at approximately what energy the rise in the probability of attachment occurred, mixture experiments were made with

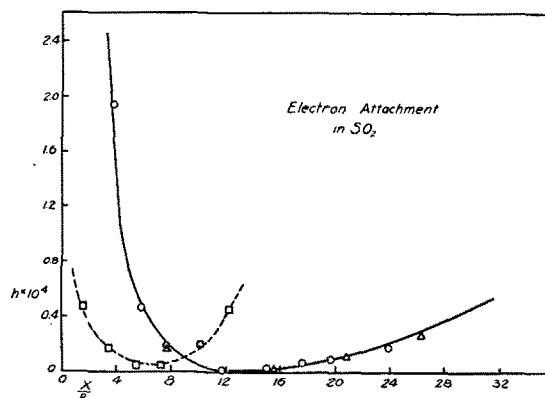
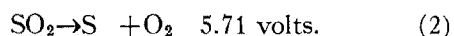
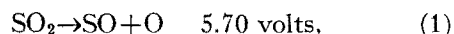


FIG. 3. Probability of electron attachment in SO_2 . The dotted curve is the probability of attachment in a mixture of equal parts of SO_2 and argon.

argon and the X/p of the minimum points extrapolated to zero concentration of SO_2 . This, using Townsend's tables, gives only a rough estimate of the electron energy, but determines, at least, an order of magnitude. The value so obtained is 4–6 volts for the electron energy at which the probability of attachment begins to increase.

There is very little spectroscopic, photochemical, or electronic data with which to compare this value. The energy of dissociation of SO_2 , calculated from spectroscopic data, is given by Franck⁸ for the two possible cases as:



Obviously, with energies so nearly equal it is impossible to determine which reaction, if either, occurs. Comparison of the observed and calculated energies seems to indicate, however, that dissociation is occurring, though from these data alone it is impossible to determine which of the four possible initial ions is formed. Reaction (1) seems the most probable in the light of all evidence and SO^- is suggested as the ion initially formed at values of $X/p > 14$.

HYDROGEN SULFIDE

Hydrogen sulfide was first obtained from a commercial tank of the gas and purification

⁶ L. B. Loeb, Phys. Rev. **17**, 89 (1921).

⁷ H. B. Wahlin, Phys. Rev. **19**, 173 (1922).

⁸ Franck, Spomer and Teller, Zeits. f. physik. Chemie **B18**, 88 (1932).

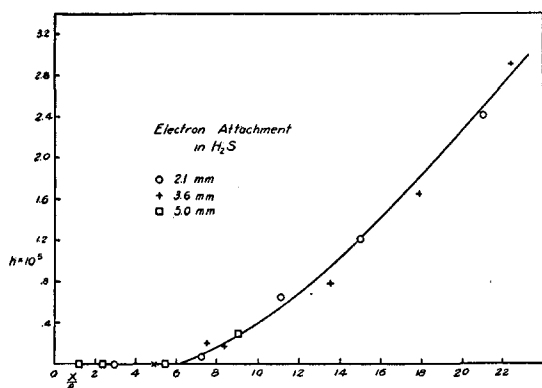
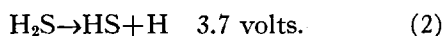
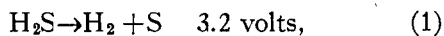


FIG. 4. Probability of electron attachment in H_2S . The data were taken at different pressures as indicated.

attempted in the usual manner. Experiment, however, showed that even after fractionation, the gas obtained was not entirely pure. The gas was therefore prepared by the cold hydrolysis of Al_2S_3 which gave a product of high purity.

The results of the experiment are shown in Fig. 4. It is seen that no attachment occurs for low values of X/p , and consequently the H_2S molecule has no electron affinity. However, at an X/p of 6, negative ions begin to be formed in the gas and are formed with increasing probability as the energy of the electrons increases. This again is most easily interpreted as a dissociation process of which two types are possible. They are:



The photochemical decomposition of H_2S has been studied by Stein,⁹ but he was unable to interpret his results unambiguously. The present experiments cannot discriminate between two reactions which require so nearly equal amounts of energy. However, from analogy with water, in which the OH^- ion has been observed in electron bombardment experiments, it is probable that the same type of dissociation occurs here, and the initial ion formed is SH^- according to reaction (2) above. This energy is in accord with that determined from argon mixtures.

The formation of negative ions in H_2S has not been studied directly, but some experiments of Loeb¹⁰ are interesting in this connection. In

⁹ N. O. Stein, Trans. Far. Soc. 29, 583 (1933).

¹⁰ Loeb and Du Sault, Proc. Nat. Acad. Sci. 14, 192 (1928).

studying the mobility of negative ions in highly purified samples of H_2S , he observed that at certain values of the field strength he obtained only free electrons in the gas. For higher fields negative ions were again observed and also for lower fields. The effect was transient and greatly dependent on the purity of the gas. These results are easily explained by the present experiments.

The formation of negative ions at low fields was presumably due to slight traces of impurity which is not improbable in view of the difficulty of completely purifying this gas. (Similar effects were observed with the tank samples of gas in the present experiments.) At moderate values of X/p (~ 4) no ions were obtained, and at values greater than 6, negative ions were formed by the dissociation indicated above.

WATER VAPOR

Samples of distilled water were difficult to purify owing to the presence of dissolved gases which were hard to remove completely. It was found more satisfactory to prepare water vapor from carefully purified hydrogen and pure copper oxide which had been drastically heated in vacuum. The water thus prepared was frozen with liquid air and any excess hydrogen pumped off. Since hydrogen does not attach electrons, its presence in very small amounts would be harmless, while, as will be seen later, the oxygen or CO_2 dissolved in distilled water would have seriously affected the results.

The probability of the formation of negative ions by electron attachment in water vapor is plotted in Fig. 5. Owing to the similarity of their electronic and chemical properties, H_2O and H_2S would be expected to show similar behavior in forming negative ions. At low pressures this prediction is verified. For higher pressures, however, there is definite attachment and formation of negative ions even at low values of X/p . The explanation for this deviation from the character of the process observed in H_2S is simple, and is due to the fact that at the moderate pressures and room temperature water vapor is approaching condensation. Hence, there may exist large numbers of small aggregates and these should be very effective in forming negative ions. Otherwise, at lower pressures, where such groups will

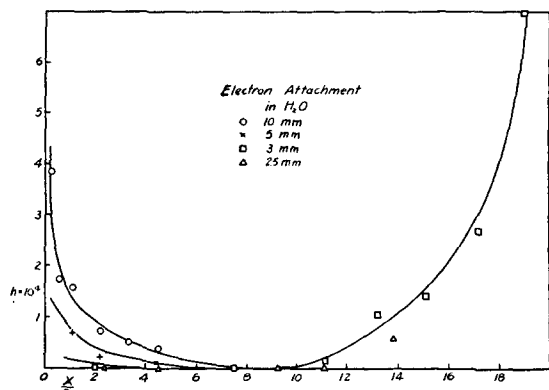
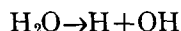


FIG. 5. Probability of electron attachment in H_2O . The various curves are for different pressures as shown.

be far fewer, the water molecule behaves as does the H_2S molecule and shows no electron affinity.

At higher values of X/p , there is distinct evidence of a dissociation process similar to that observed in H_2S . The energy required for the reaction



is about 5.4 volts, a value which is reasonable in these experiments and which was substantiated by the usual argon mixtures. Hence, the probable elementary process occurring in the formation of negative ions in water vapor at high X/p is that given by the above process with the formation of OH^- . This ion has been observed by Smyth and Mueller¹¹ and others and certainly does exist. H^- has also been observed, but the conditions for its formation are so unique that it is doubtful if it occurs here.

Cravath¹² has briefly reported some interesting results on the effect of water vapor on the attachment process in oxygen. For water vapor alone he found a probability of attachment not greatly different in order of magnitude from that of oxygen. Under the circumstances of his experiment, he was undoubtedly studying the low X/p portion of the curves at the higher pressures given in Fig. 5. He also found that when water vapor and oxygen were mixed, more attachment was obtained than with either alone. Since mixture experiments with argon had given no indication of such an effect, other gases were tried. In order not to complicate the results, only gases

which did not form negative ions were studied in the mixtures. Nitrogen was found to behave normally. CO_2 , on the other hand, was found to produce many ions when mixed with water vapor. The explanation, then, of these results and those of Cravath must be that in the case of O_2 and CO_2 considerable intermolecular forces exist between these molecules and water molecules. Their solubility in water is an indication of this. It has been seen that whenever strong intermolecular forces exist, and polymers and compounds result (as apparently in NO and water) ready attachment to such compounds may occur. In general, it can be predicted that the effect of water vapor will be greatest in those gases which are highly soluble in water.

Bailey¹³ has studied the formation of negative ions in H_2O and has found a probability of attachment which rises very rapidly from an X/p of 12. He did not investigate it at lower electron energies, but his observations are in agreement with the present experiments.

CONCLUSIONS

Of the triatomic molecules studied, SO_2 alone apparently has a real electron affinity. Mulliken¹⁴ has suggested that both N_2O and CO_2 are linear molecules of similar electronic structure. It is therefore reasonable that if one of these molecules has no electron affinity, that the other should lack it as well. H_2S and H_2O behave in similar fashions, and would probably show identical behavior if H_2S were studied near its point of liquefaction. In all this work the fallacy of attempting to describe the electron affinity of a molecule from experiments in a single energy range has been very evident. As a result, a true electron affinity of a stable molecule is a much rarer quality than has been commonly supposed, though negative ions do exist in a large number of gases under certain conditions. A study of the mobility of some of these ions for very short ages might prove of considerable interest.

It is a pleasure to acknowledge indebtedness to the Massachusetts Institute of Technology for the facilities of their laboratories and to the staff of the department of physics for many helpful suggestions.

¹¹ Smyth and Mueller, *Rev. Mod. Phys.* **3**, 384 (1931).

¹² A. M. Cravath, *Phys. Rev.* **33**, 605 (1929).

¹³ V. A. Bailey and W. E. Duncanson, *Phil. Mag.* **10**, 144 (1930).

¹⁴ R. S. Mulliken, *Phys. Rev.* **40**, 60 (1932).