a coulometer, the number of coulombs passed while the boundary sweeps through a measured volume. Since an enlarged apparatus was necessary, heating effects were encountered which diminish the usefulness of the method. The values for the transference numbers, however, agree with those previously obtained by this method.

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[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY, UNIVERSITY OF WISCONSIN]

A STUDY OF IONIZATION PRODUCED IN CERTAIN GASEOUS REACTIONS[1]

BY A. KEITH BREWER

RECEIVED MARCH 20, 1924

Is chemical action accompanied by ionization? This question, important as it is, has not been answered definitely in the case of gaseous reactions. A complete answer will help to explain the mechanism of chemical reaction. It is believed that electrons are transferred from one atom to another during chemical reaction, and it is likely that they are loosened at the moment of transfer. The displacement of these electrons should result in ionization. Although the evidence for ionization in reacting gases has been unsatisfactory, the present investigation shows that ionization may be detected in every reaction studied, if proper precautions are observed.

Improvements which have made possible a greater precision are (1) a chamber of special design in which electrical leakage is eliminated; (2) a sensitive electrical system which makes possible the measurements of currents as small as 5×10^{-15} ampere; (3) a construction which permits heating the chamber to red heat in order to diminish the adsorption of gases on the electrodes; (4) a 2200-volt battery.

J. J. Thomson[2] was one of the first to investigate this problem. Using a small gold-leaf electroscope in the reacting gases he concluded that no ionization is produced. Reboul[3] failed to detect ionization in gaseous reactions. Haber and Just,[4] using a galvanometer sensitive to 10^{-9} ampere per scale division found that a metal emits electrons when it reacts with a gas. In all the experiments the quantities of electricity emitted were much less than the Faraday equivalents. Bloch[5] found that no ionization was produced, except in the oxidation of phosphorus.

Pinkus[6] carried out extensive experiments in which the change in the rate of fall

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[1] A portion of a thesis submitted to the Graduate School of the University of Wisconsin in partial fulfilment of the requirements for the degree of Doctor of Philosophy. A preliminary report was published by Brewer and Daniels in (a) *Trans. Am. Electrochem. Soc.*, **44**, 257 (1923).

[2] Thomson, *Proc. Cambridge Phil. Soc.*, 11, 90 (1901).

[3] Reboul, *Compt. rend.*, **149**, 110 (1909); **151**, 311 (1910).

[4] Haber and Just, *Z. Elektrochem.*, **20**, 783 (1914).

[5] Bloch, *Compt. rend.*, **150**, 694 (1910); *Ann. phys. chim.*, **22**, 370, 441 (1911).

[6] Pinkus, *J. chim. phys.*, **16**, 201 (1918); **18**, 366, 412 (1920). *Helvetica Chim. Acta*, 1, 141 (1918).

of an electroscope leaf was measured when the reacting gases were admitted to the chamber. He failed to detect ionization in the oxidation of nitric oxide, but obtained some evidence of ionization in the action of chlorine on nitric oxide and in certain other reactions. For example, in the decomposition of ozone 6 out of 21 experiments showed slight ionization. Whenever ionization was detected, his curves showed that only an instantaneous current was obtained, although the investigation was confined to comparatively slow reactions. The charge on the electroscope amounted to only 70 volts.

J. J. Thomson[7] has proposed an hypothesis for electron behavior during chemical reaction which is based on the assumption that no ionization is produced.

In the light of the following experiments it is probable that these investigators failed because the voltage was low and the apparatus for measuring current comparatively insensitive and because adsorption of gases on the electrodes was not prevented.

Much of the confusion in the literature on the subject of the liberation of ions during the process of a chemical reaction has resulted from the fact that the various investigators, with the exception of Pinkus, have been dealing with reactions which were complicated by physical changes which in themselves might produce ionization. To avoid these difficulties this work has been limited to purely gaseous reactions, yielding only gaseous products. Unfortunately, reactions of this type are few in number.

Apparatus

In detecting ionization, the reactions were allowed to take place between two perfectly insulated electrodes. One electrode was charged to any desired potential by means of a bank of dry cells. The other electrode was connected to a high sensitivity quadrant electrometer. The presence of ionization was noted by the deflection of the electrometer. The electrometer was grounded through a high resistance of the radioactive type. The sensitivity of the electrometer and the value of the resistance being known, the current was calculated directly by Ohm's law. The arrangement of the apparatus is shown in Fig. 1.

The deflection of the Compton quadrant electrometer was read by reflecting the image of a straight filament light on a ground glass screen placed one meter from the mirror.

The electrometer was capable of a sensitivity of 20,000 mm. per volt. However, it was found in practice that a sensitivity of 7,000 mm. was more satisfactory as the drift at this sensitivity was very small.

The resistance of the radioactive leak was due to ionized air between sides of a copper box (15 × 7 × 4 cm.), which could be charged to any desired potential, and a copper plate placed within the box, but perfectly insulated from it. This plate was in turn connected to the electrometer circuit. The air was ionized by means of pitchblende.

The plate connected to the electrometer was charged through the ion-

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[7] Thomson, "The Electron in Chemistry," *J. Franklin Inst.*, **195**, 593, 737 (1923); **196**, 1, 145 (1923).

ized air to any desired potential by placing a suitable potential on the outside copper box. This was accomplished by means of a 22,000-ohm bridge with 4.5 volts across its terminals. It was necessary only to change the resistance of the bridge in order to shift the zero point to any desired position on the scale. A difference of about 100 ohms on the bridge corresponded to a deflection of 30 cm.

In order to determine the resistance of the leak it was necessary to know the capacitance of the leak, the switch, the electrometer, and the leads. This capacitance was determined by charging the system to a known voltage and measuring the rate of discharge through the leak. After the rate of discharge had been accurately determined a known capacitance was added to the system, and the rate of discharge again determined between the same fixed points. In this manner several known capacitances were added and the rates of discharge noted. From these data the capacitance, C, of the system was calculated to be 1.96×10^{-10} F.

The resistance, R, of the radioactive leak was calculated from the equation, $R = t/[C\ ln\ (V_1/V_2)]$, in which t is the time required for the charge on the system to fall from voltage V_1 to voltage V_2. The resistance was found to be 8.85×10^{10} ohms.

The potential was supplied by 100 Burgess radio B batteries, of 22.5 volts each. The gift of these batteries by Dr. C. F. Burgess, President of the Burgess Battery Company, Madison, Wisconsin, is gratefully acknowledged.

The entire electrical set-up was placed upon a grounded metal plate and housed in a metal cage. Openings through the cage were made as small as possible and were fitted with screen doors. All the metal parts were carefully soldered together, using rosin in alcohol as the soldering flux. The switchboard and all outside electrical connections were covered with grounded metal plates. Induction effects of the alternating current used in heating the furnace and lighting the electrometer lamp were eliminated by means of twisted lamp cord. A carefully constructed outside ground was essential.

A Reaction Chamber

Several reaction chambers were designed before a successful type was evolved. It was found that the following principles of construction were necessary for the measurement of small ionization currents: (1) the incoming gases must react between the electrodes; (2) the products of the reaction must be removed immediately; (3) the movement of the gases must not produce frictional charges; (4) the electrodes must be so placed that a high potential gradient is maintained throughout the period of reaction; (5) short circuiting between the electrodes must be eliminated; (6) the electrodes must not be attacked by the reacting gases; the chamber must contain no organic matter, nor glass, exposed to the reacting gases; (7) the chamber must be enclosed in a furnace which permits the removal of adsorbed gases.

The reaction chamber used in the early work has been described.[1a]

The construction of the chamber used in the final work is shown in Fig. 1.

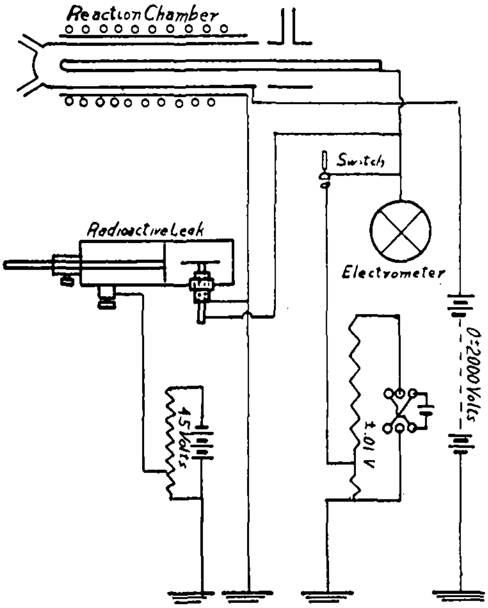


Fig. 1.

The outer wall of the chamber was a gold tube 16 cm. in diameter, connected to the batteries. The gases were admitted at one end of the tube through two gold tubes 1 cm. long and 4 mm. in diameter. They were so placed that the two gases met at about 1 cm. from the end of the chamber. Connection was made to the gas train by special Pyrex tubes. The inner electrode, which was connected to the electrometer, was a gold tube 0.5 cm. in diameter and 18 cm. in length, closed at one end. It was held in position by a quartz rod running down the center, supported on an ebonite frame. Electrical contact was made by gold wires, welded to the electrodes. The outer electrode was supported at each end by asbestos boards which were in turn mounted on an ebonite stand. Two grounded metal plates were placed between the ebonite supports holding the outer and inner electrodes. The outer electrode was surrounded by an alundum tube at a distance of about 2 mm. from the gold. Around this No. 20 Ni-chrome wire was wound. The furnace could be maintained at any temperature up to a white heat. No effect of temperature on the operation of the chamber was noted until a red heat was reached. A thermo-ionic effect then developed which made it impossible to make determinations above that temperature. In order to eliminate disturbing effects from the alternating current, the chamber was heated by grounding one terminal of the lighting circuit through the furnace. The gold electrodes were treated for two days with nitric acid to remove impurities.

Experimental Procedure

The reaction chamber was treated with nitric acid and rinsed before making a series of runs. The chamber was heated to redness by the surrounding electric furnace, while a stream of dry air was blown through it. The resistance in series with the furnace was then increased and the chamber allowed to cool to the desired temperature. The grounding switch was then opened and the radioactive-leak bridge was adjusted so that the electrometer stood at a suitable zero on the scale. When the electrometer had come to rest at the desired zero point the reacting gases were allowed to flow into the reaction chamber. The rate of flow was noted. As soon as the gases had time to reach the reaction chamber, the electrometer showed a deflection indicating that the inner electrode had acquired a charge of the same sign as that of the outer electrode. When a charge was built up on the inner electrode of such a magnitude that the leak through the radioactive resistance equalled the charge transmitted through the gas to the electrode, the further deflection of the electrometer ceased. The deflection was then noted and the reacting gases were shut off. The electrometer again returned to the original zero.

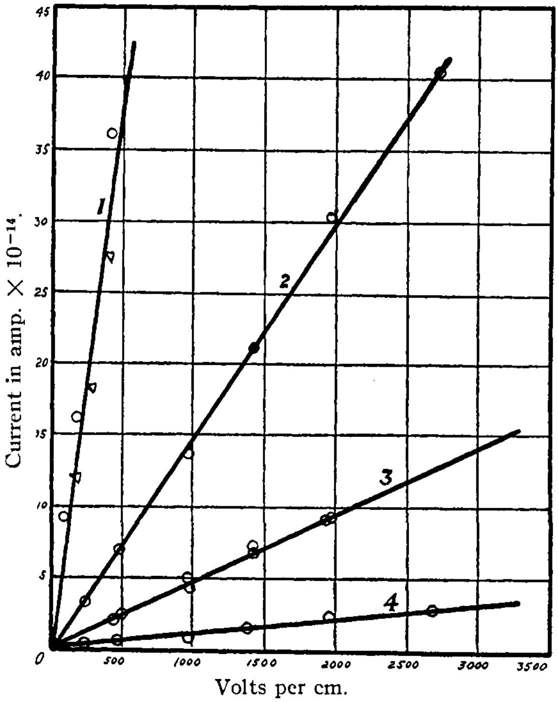


Fig. 2.—Line 1. Nitric oxide-oxygen reaction; 100°; NO, 80 cc. per min. (O) Gold reaction chamber. (Δ) Platinum reaction chamber. Line 2. Nitric oxide-oxygen; 385°; NO, 80 cc. per min. Line 3. Decomposition of ozone; 220°; 5.4 cc. per min. Line 4. Nitric oxide-oxygen; 385°; 5.4 cc. per min.

Duplicate readings were taken for all deflections; these readings usually checked within 5 mm. or less, depending largely on the constancy of flow of the reacting gases.

Elaborate precautions were taken to make sure that the current obtained was due to the gas phase reaction and not to other causes. It was shown by experiments described in the preliminary paper[1a] that the currents measured were not caused by friction of the gases, nor by heating effects nor by contact potentials.

Results

The Oxidation of Nitric Oxide by Oxygen

The first series of results were obtained by using a glass reaction chamber sputtered with platinum similar in design to the gold chamber. The chamber was kept at 100° during the course of the reaction. The results which were obtained with this chamber were presented in the preliminary paper. It was shown that the nitric oxide-oxygen reaction is accompanied by ionization which is proportional in amount to the number of molecules reacting and to the potential drop through the chamber; also, that the ionization current was slightly larger when the outer electrode was charged negatively than when it was charged positively. The final results obtained with the gold chamber described above are shown in Figs. 2, 3 and 4.

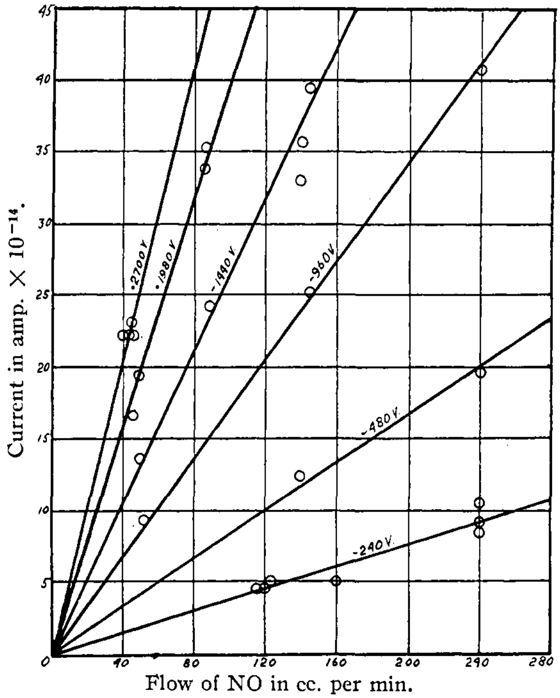
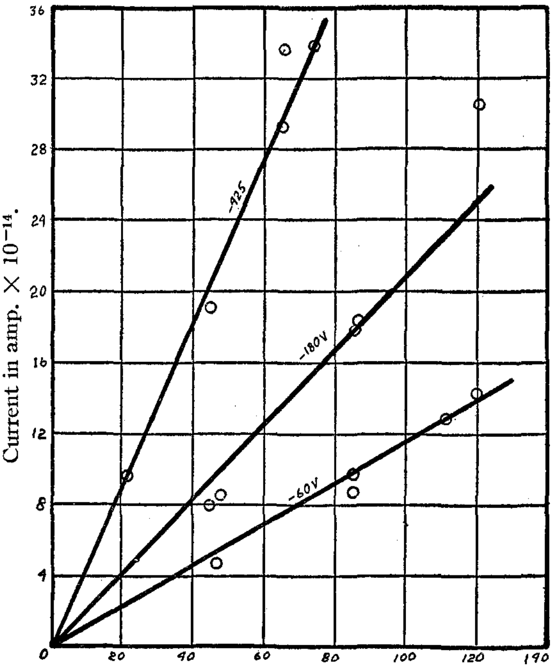


Fig. 3.—Nitric oxide-oxygen reaction; 385°.

Fig. 3 is representative of a series of experiments carried out with this chamber. During these determinations the temperature of the reaction chamber was maintained just low enough to prevent a thermo-ionic effect, at about 385°. At this temperature the adsorption of gases on the electrodes was very small. During all of the experiments a constant flow of 650 cc. of oxygen per minute was carefully maintained. The flow of nitric oxide was varied from 0 to 240 cc. per minute. The fall of potential through the chamber was varied from 0 to 2700 volts per cm. It is evident that the degree of ionization is directly proportional to the amount of reaction taking place. In no case is there a tendency toward a maximum current.

The relationship between current and voltage is shown by curves 2 and 4 in Fig. 2, which were derived from the data in Fig. 3. It will be seen that the current is directly proportional to the voltage up to 2700 volts per cm., and that there is no tendency to reach a saturation current.



Flow of NO in cc. per min.

Fig. 4.—Nitric oxide-oxygen reaction; 100°.

In order to compare the results obtained with the gold chamber and the platinized chamber a series of experiments shown in Fig. 4 was carried out. The temperature of the two chambers was nearly the same (100°). It is evident that the results in the two cases are practically identical.

It is seen by comparing Lines 1 and 2 in Fig. 2 that a greater current was obtained at lower temperatures than at temperatures just below red heat. Experiments at room temperature were unsatisfactory and those at 100° were not quite as consistent as those at higher temperatures. At room temperatures, with large quantities of nitric oxide, there was a tendency for the electrometer needle to swing out to a maximum and then drift back to the other side of the zero. For very small quantities of nitric oxide the drift back was scarcely noticeable, but it increased rapidly with small increases in the nitric oxide concentration. In recording the data the maximum deflection was taken as a measure of the current through the chamber.

From the data presented in Fig. 3 it was possible to calculate the ratio of the number of reacting molecules to the number of ions which reach the electrodes, as shown in the preliminary paper. This ratio, which ranges from 1.4×10^{14} at 240 volts per cm. to 1.2×10^{12} at 2700 volts, is of no significance in determining the relation between molecules and ions in the reaction, because the vast majority of the ions recombine before the electrodes are reached. A similar calculation showed that for each volt per cm. 700 electrons reached the electrodes for each cubic centimeter of reacting gas. These calculations were made from the data of Line 2, Fig. 2.

From Line 1 and Line 2 in Fig. 2 the effect of temperature is readily shown. At 100° the number of electrons per volt per cc. of nitrogen dioxide formed is 6.37×10^3. At 385°, counting the reaction but 64.5% complete, the number of electrons per volt per cc. of nitrogen dioxide formed is 1.4×10^3. The volumes are measured at room temperature.

The Decomposition of Nitrogen Dioxide

Since ionization has been shown to exist in the synthesis of nitrogen dioxide it was thought desirable to see whether the decomposition is accompanied by ionization. Since the decomposition is endothermic, a detection of ionization in the latter case would completely rule out the possibility that ionization was due to thermal effects. It was possible to operate the reaction chamber between 385° and 400°, at which temperatures a very appreciable decomposition of nitrogen dioxide occurs, amounting to 35.5%[8] at 390°.

A current of dry air was passed continuously into the reaction chamber through one of the inlets. A volume of about 200 cc. per minute was admitted. Nitrogen and nitrogen dioxide were admitted through the opposite arm. The nitrogen was bubbled through liquid nitrogen peroxide (N_2O_4) at 0°, at which temperature the vapor pressure is 257 mm.

The observations were made as in the previous case with nitric oxide and oxygen. To make sure that any deflection which might exist was due to the decomposition of nitrogen dioxide and not to the gas itself, a

[8] Richardson, *J. Chem. Soc.*, **51**, 397 (1887).

series of experiments was first made with the reaction chamber at room temperature. Although in some cases a small momentary deflection of about 5 mm. was noted, it was concluded that nitrogen dioxide in the cold does not give rise to measurable ionization.

The chamber was then heated up to 400° and a series of experiments was made as before. The fall of potential through the chamber was varied from 960 to 2100 volts. The quantity of nitrogen dioxide entering the chamber per second was varied by changing the rate of flow of the nitrogen. When the nitrogen dioxide was first admitted to the chamber the electrometer was deflected, showing that the inner electrode was being charged with the same sign as that existing upon the outer electrode. After the deflection in the usual direction, however, the beam of light drifted back, crossed the zero and registered a deflection on the other side of the scale. After a still longer time the light slowly returned nearly to its original zero. This same phenomenon had been detected to a less extent in the case of the nitric oxide-oxygen reaction at low temperatures with larger quantities of the nitric oxide. The effect was much more pronounced in the present experiments because of the greater quantities of nitrogen dioxide present. Since constant deflections could not be obtained, it was impossible to plot accurate volt-current or flow-current curves. It was evident, however, that an increase in either the voltage or flow of nitrogen dioxide increased the amplitude of the deflection of the electrometer in both directions.

With all of the reaction chambers except the gold it was necessary to wash and dry the electrodes carefully before making a series of runs, in order to obtain concordant results. With the gold chamber satisfactory measurements could be obtained only when the reaction chamber had been heated to redness and then cooled to the desired temperature. Whenever the chambers were prepared for use by either of the above methods an excessively large ionization current was always obtained for the first reaction. After this first large deflection, the concordant results as plotted were obtained. It was not possible to measure accurately these first erratic currents, as they were somewhat more than that necessary for full scale deflection. Before the radioactive bridge could be adjusted to balance the current the electrometer would be drifting back. It was evident, however, that these larger currents seldom, if ever, were of the same value. The obvious explanation of these phenomena is that the heating or washing removed an adsorbed film from the surface of the electrodes. The postulate of Schuster[9] of an adsorbed layer of gas of high specific inductive capacity to explain the variations in the sparking potentials for small gaps would help to explain, according to Anderegg,[10]

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[9] Schuster, *Phil. Mag.*, **29**, 197 (1915).

[10] Anderegg, *Trans. Am. Electrochem. Soc.*, **44**, 349 (1923).

changes in potential distribution across the tube. These changes in potential distribution would materially change the size of the ionic current flowing through the chamber.

Decomposition of Nitrogen Pentoxide

Nitrogen pentoxide decomposes into nitrogen dioxide and oxygen; this decomposition is very rapid at 100°, and at 385° it is practically instantaneous.[11] At this temperature it is still further decomposed, however, into nitric oxide and oxygen to the extent of about 35%. The nitrogen pentoxide decomposition goes on with very little heat change.

Method of Procedure.—The method employed in this case was precisely the same as that used in the case of nitrogen dioxide. A steady stream of air was passed through one arm of the reaction chamber. Nitrogen pentoxide[12] was blown into the chamber by passing a known volume of nitrogen over the crystals. As in the previous cases, the gases were carefully dried by passage over phosphorus pentoxide. An all-glass drying train was used. The quantity of nitrogen pentoxide admitted to the chamber was calculated from its vapor pressure, and the volume of nitrogen used. The U-tube containing the crystals of nitrogen pentoxide was surrounded by a water-bath maintained at 8°. The vapor pressure of nitrogen pentoxide at this temperature was 120 mm. The quantity of nitrogen pentoxide admitted per minute was varied by changing the flow of nitrogen.

When the reaction chamber was maintained at 100° during the course of the reaction no concordant results were obtained. In practically every case the electrometer charged up slightly with the proper sign only to reverse the charge as stated in the cases mentioned before. Apparently the adsorption of nitrogen dioxide was very pronounced at this temperature.

The results obtained by the decomposition of nitrogen pentoxide at 385° are shown in Fig. 5. Line 1 represents the volt-current curve obtained when nitrogen pentoxide is admitted to the system at the rate of 13 cc. per minute. Line 2 represents 24.3 cc. per minute. Although the points do not fall exactly upon the line, it will be noted that the current is in general proportional to the voltage. For small flows of nitrogen pentoxide the current was also approximately proportional to the flow. The discrepancy for larger flows was doubtless due to the fact that the nitrogen in passing over the nitrogen pentoxide did not become saturated. Calculations similar to those given for the other gases showed that 450 ions for each volt per cm. difference in potential were produced for each cubic centimeter of nitrogen pentoxide decomposed. The same number

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[11] Daniels and Johnston, THIS JOURNAL, **43**, 53 (1921).

[12] Prepared according to directions given by Daniels and Bright in *ibid.*, **42,** 1131 (1920).

was calculated with a flow of 13 cc. of nitrogen pentoxide per minute as with a flow of 24.3 cc.

The values just tabulated are not due to the composition of nitrogen pentoxide alone. At this temperature the nitrogen pentoxide is decomposed into nitrogen dioxide which is still further decomposed into nitric oxide and oxygen to the extent of about 35.5%. Since some ionization is produced when nitrogen dioxide is decomposed, the values obtained in these experiments may come, in part, from the decomposition of the nitrogen dioxide. The ionization currents obtained for the decomposition of nitrogen dioxide would appear, on averaging, to be of practically the same order of magnitude as those noted for the nitrogen pentoxide. The vapor pressure of nitrogen dioxide at 0° is 257.5 mm., while the vapor pressure of nitrogen pentoxide at 8° is but 120 mm. From this it would appear that for the same flow of gas, over twice as many molecules of the dioxide as of the pentoxide were admitted to the chamber per second. Since the currents were about the same in both cases, approximately half of the ionic current must have come from the decomposition of the nitrogen pentoxide.

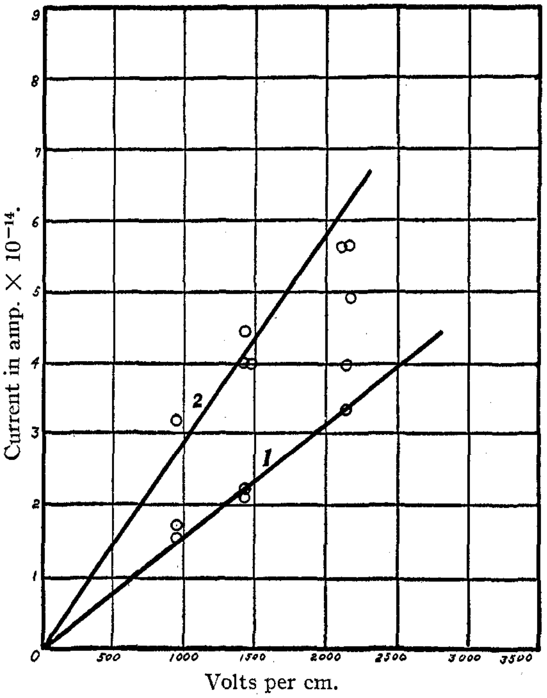

Fig. 5.—Decomposition of nitrogen pentoxide; 385°. Line 1. N_2O_5, 80 cc./min. (hot). Line 2. N_2O_5, 150 cc./min. (hot).

The Decomposition of Ozone

Ozone decomposes very slowly at room temperature even in the light. Its decomposition is instantaneous at temperatures approaching red heat. In the experiments carried out, the temperature of the reaction chamber was maintained at 200°. The rate of decomposition at this temperature is very rapid. Previous investigators who were unable to change the temperature of their reaction chambers used chlorine or some other catalyst to speed up the rate of decomposition; but it was not necessary to do so in these experiments.

Ozonized oxygen was prepared by means of the silent electric discharge and stored in a large Kipp generator filled with distilled water. From the generator the ozone passed through a wash bottle of sulfuric acid, and thence through 3 U-tubes filled with phosphorus pentoxide into the reaction chamber. The concentration of the ozone was determined by passing a known volume of the gas through a solution of potassium iodide. Titration showed that the oxygen contained 2.4% of ozone. During these determinations one arm of the reaction chamber was closed. Oxygen was allowed to flow through the other arm at the rate of 225 cc. per minute. After the electrometer had been adjusted to a suitable zero, the supply of oxygen was suddenly shut off and the ozonized oxygen from the Kipp generator allowed to flow in at exactly the same rate of speed. The deflection of the electrometer was noted as in previous experiments. In all of the experiments the flow of ozone was kept constant and only the chamber voltage was varied.

The results obtained from the decomposition of ozone are shown in Line 3, Fig. 2. It will be noted that the ionization is proportional to the voltage, as in all the previous cases.

The measurements were very satisfactory and showed no tendency for the current to diminish or change direction as the reaction continued. This fact supports the hypothesis that the reversal noted in the previous cases was due to the adsorption of nitrogen dioxide on the electrodes. With a flow of 5.4 cc. of ozone (calculated as 100% ozone) 2.44×10^{18} molecules of ozone decomposed per second. For a potential gradient of 480 volts per cm. the corresponding current was 2.4×10^{-14} ampere, and at 1980 volts per cm. it was 9.7×10^{-14} ampere. This gives a ratio of 4×10^{12} molecules decomposing to one ion reaching the electrodes at the higher voltage. It corresponds to the formation of 3500 ions at the electrodes for each cc. of ozone for each volt per cm. potential gradient.

The Nitric Oxide-Ozone Reaction

At ordinary temperatures nitric oxide is oxidized directly to nitrogen pentoxide by ozone, without the formation of any brown fumes. The speed of the reaction is not materially different from that for the reaction nitric oxide plus oxygen. It was thought that the adsorption of nitrogen pentoxide on the electrodes might be much less than that of nitrogen dioxide. The experimentation was carried out in a manner identical with that described for nitric oxide and oxygen. A steady stream of ozone was allowed to pass through the reaction chamber. The deflection of the electrometer was read when the nitric oxide was admitted. The flow of ozone was kept constant throughout the experiments while the voltage and flow of nitric oxide were varied. Since the maximum flow of ozone that could be readily obtained was 5.4 cc. per minute, the nitric oxide was, in some cases, diluted with eight to one and sixteen to one parts of nitrogen in order to have the ozone in excess.

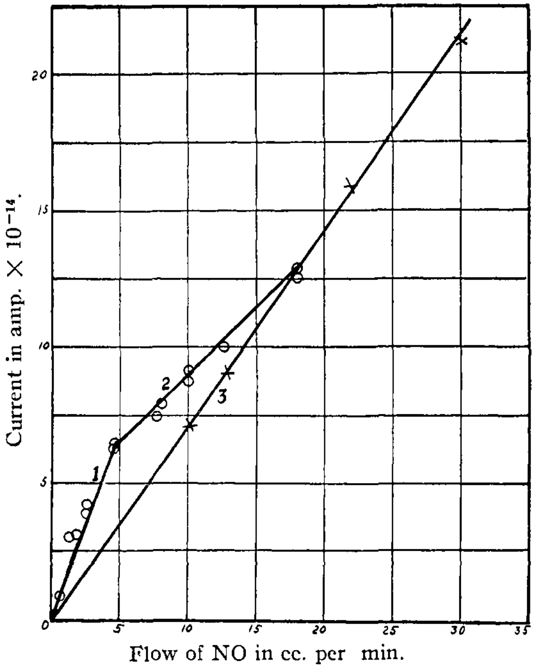

Fig. 6.—Line 1. Nitric oxide-ozone; ozone in excess. Line 2. Nitric oxide-ozone; insufficient ozone. Line 3. Nitric oxide-oxygen.

Fig. 6 represents the data obtained from the reaction of nitric oxide and ozone. To contrast the reaction with that obtained with nitric oxide and oxygen a series of experiments was run with the two gases at the same temperature, that is, the reaction chamber was just warm. The results obtained with nitric oxide and oxygen are shown on the straight line (3) in Fig. 6 and are marked by (x). The first half of the upper line (1) represents the curve for the nitric oxide-ozone reaction where the concentration of ozone was in excess. The last half (2) represents a condition where there was an excess of nitric oxide. The two coinciding points at the bend in the upper line were obtained with the same quantity of nitric oxide, in one case pure and in the other, diluted with eight parts of nitrogen. All points on the first part of the upper line were obtained with the nitric oxide diluted eight to one, except the first point where the dilution was sixteen to one. The points on the second part of the upper line were obtained with undiluted nitric oxide. Throughout the determinations the potential applied to the reaction chamber was 980 volts per centimeter, with the outer electrode negative as usual.

From the diagram it appears that the ionization produced in the nitric oxide-ozone reaction is about twice that produced with oxygen. When the nitric oxide was oxidized by the ozone and oxygen together, an intermediate ionization was obtained. When the concentration of the ozone became small compared to that of the oxygen, the ionization followed the nitric oxide-oxygen curve.

The action of nitric oxide on ozone is shown by the following equations: $2NO + O_2 = 2NO_2$; $2NO_2 + O_3 = N_2O_5 + O_2$. Taking the conditions at the break in the upper curve as a representative experiment, there were 0.075 cc. of nitric oxide, 0.037 cc. of oxygen, 0.038 cc. of ozone, and 0.075 cc. of nitrogen dioxide, or a total of 0.225 cc. of gas, reacting per second. A current of 6.4×10^{-14} ampere, or 4×10^5 electrons per second, flowed through the chamber. Since 5.48×10^{18} molecules were reacting per second, the number of reacting molecules per electron reaching the electrode was 1.37×10^{13}.

Nitric oxide reacts with oxygen according to the following equation: $2NO + O_2 = 2NO_2$. For the same quantity of nitric oxide only half as many molecules were reacting as in the nitric oxide-ozone reaction. For the same quantity of nitric oxide used as in the previous case the total number of molecules reacting per second was 2.74×10^{18}. The current flowing through the chamber is 3.7×10^{-14} ampere or 2.33×10^5 electrons per second. The number of reacting molecules per ion reaching the electrode was 1.18×10^{13}.

One cubic centimeter of reacting gas gave, for each volt of applied potential, 2780 ions in the nitric oxide-ozone reaction, and 2070 ions in the nitric oxide-oxygen reaction.

Conclusions

For the sake of comparison Table I is compiled on the basis of ions reaching the electrodes for each cubic centimeter of reacting gas for a potential gradient of 1 volt per cm.

The most important result of the investigation lies in the fact that ionization has been detected in every gaseous reaction studied. The measurements are reproducible and great care has been taken to eliminate all secondary phenomena which might be mistaken for ionization currents.

TABLE I

Reaction	Ions per cc.
Nitric oxide + oxygen (385°)	710
Nitric oxide + oxygen (50°)	2100
Nitric oxide + ozone (50°)	2800
Nitrogen pentoxide—decomposition (385°)	450
Ozone decomposition (200°)	3500
Nitrogen dioxide decomposition (385°) about	1500

Since ionization has been observed in every case without exception, it does not seem unlikely that ionization will be found to accompany every chemical reaction if suitable precautions are observed. The experimental evidence supports very strongly the modern theory of the structure of the atom, which assumes a positive nucleus surrounded by negative electrons. Although this theory is so firmly established that it scarcely needs further support, it is gratifying that the simplest chemical reactions (gaseous) offer direct evidence of its validity.

Two other results of the investigation are of almost equal importance. It has been found in every case that the current obtained is directly proportional to the number of molecules reacting, and directly proportional to the fall of potential through the reacting gases.

The fact that the currents are very small leads to interesting speculations. In every case about 10^{13} molecules reacted for each ion that reached the electrodes. The very low ratio of ions to reacting molecules can be explained in a number of ways; several hypotheses seem worthy of discussion.

An explanation based on a possible photoelectric effect on the electrodes does not seem likely. No ionization could be detected except during a chemical reaction and there was no evidence of the emission of light from the reaction. In fact, one of the reactions was endothermic. If a photoelectric effect is the cause of the ionization, a saturation current should be reached at comparatively low voltages; but no evidence of such a saturation current could be found even up to 2700 volts per cm. Furthermore, the current was practically the same for gold as for platinum electrodes, a fact which renders a photo-electric explanation unlikely.

Again, a possible explanation for the low value of ions to molecules lies in the fact that only those molecules in actual contact with the electrodes at the moment of reaction become ionized. Since only a very small portion of the molecules react in immediate contact with the electrodes, this hypothesis might account for the small ratio of ions to molecules. This hypothesis does not explain why the current is proportional to the voltage. If electrons are liberated only from those molecules in contact with the electrodes a saturation current would be expected at comparatively low voltages.

According to another hypothesis it is reasonable to suppose that certain molecules come together in such a position at the moment of reaction that an electron is completely removed from the sphere of attraction of the parent molecule. In this case the molecule is *completely* ionized. In the majority of cases the force of attraction between the valence electrons and their respective nuclei is materially lessened, but does not completely disappear. In this case the molecules are only *partially* ionized. The rate of recombination is therefore very rapid. The application of a potential field tends to draw the electrons farther away from the nuclei and thus complete the ionization, in proportion to the potential gradient.

Finally it may be assumed that all the reacting molecules are ionized, but only those ions which are formed in the immediate neighborhood of the electrodes ever reach the electrodes. The vast majority of reacting molecules are situated farther away from the electrodes; they give rise to ions which immediately combine without ever affecting the electrometer. Since the current through the chamber is proportional to the applied voltage, the magnitude of the current is probably a matter of ionic velocities. When the voltage is increased, the velocities of the ions are increased proportionally. Only those ions can be detected which are formed so near the electrodes that the time required to reach the electrodes is less than the time required for recombination. Only a very small number of ions are ever able to reach the electrodes, since the rate of recombination is extremely rapid. Also the adsorption of gases on the surface of the electrodes materially limits the ability of the ions to reach the electrodes. At low temperatures this adsorption of certain gases may be so pronounced as to prevent the ions from reaching the electrodes, thus making the reacting gas a nonconductor.

In conclusion the writer wishes to express his very great indebtedness to Dr. Farrington Daniels for the continual advice and encouragement which he has so freely given throughout the course of the work.

Summary

1. An apparatus for the study of ionization in gaseous reactions has been constructed, which permits the measurement of currents as small as 5×10^{-15} ampere at temperatures up to 400° and at potentials up to 2700 volts per cm. Elaborate precautions have been taken to eliminate all disturbing influences.

2. Ionization currents have been obtained in every gaseous reaction investigated. The reactions are: (1) nitric oxide and oxygen; (2) nitric oxide and ozone; (3) the decomposition of ozone; (4) the decomposition of nitrogen pentoxide; (5) the decomposition of nitrogen dioxide.

3. In every case the current was directly proportional to the voltage and directly proportional to the number of reacting molecules.

4. The ratio of ions to reacting molecules was in every case exceedingly small, about 1 pair of ions for 10^{13} molecules reacting. It is likely that ionic recombination prevents all but a minute fraction of the ions from reaching the electrodes.

5. The experimental facts which have been obtained substantiate the electronic hypothesis for the constitution of matter and the electron theory of chemical bonds. It is apparent that at the moment of reaction there is an electronic rearrangement wherein the fall of potential between certain electrons and their parent nuclei has materially changed.

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THE INTERNAL PRESSURES OF SOLIDS

By Theodore William Richards

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Everything points toward the existence of very great internal pressures in solids. These pressures appear to be caused by chemical affinity and cohesion; they must be intimately connected with the circumstances which determine the very existence of solids and also of liquids. Although they give little obvious outward indication of their presence, they are nevertheless of great importance and interest in their direct bearing upon any theory of atomic structure, as well as in their indirect bearing upon most of the chemical and physical properties of matter. The present paper briefly outlines a recent attempt to add to the knowledge of this subject; it is a sketch rather than a finished picture.

Both the chemical affinity and the cohesion which are assumed to cause these pressures may well be due, at least in part, to electrical attractions and repulsions, as current theories demand. No attempt is made in the present sketch, however, to seek the ultimate source of the agencies involved, or to define how the atomic domain is filled. The effort has been rather to discover how internal pressures behave—to trace their effects on some of the cardinal properties of matter.

One of the first desiderata in the study of these pressures is the discovery of the hitherto unknown laws which determine the relation of the volume of liquids and solids to external pressures, as well as to the great internal pressures which exist within them. Any such study, like any other attempt to solve an entirely unsolved problem of this type, must depend upon the determination of the facts concerned, and must proceed inductively from these facts. Hence the very valuable experimental investigations