[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS.]

AN ATTEMPT TO PREPARE NITRO-NITROGEN TRICHLORIDE. II. THE CONDUCT OF MIXTURES OF NITROGEN AND CHLORINE IN A FLAMING ARC.

BY WILLIAM ALBERT NOYES.

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Eight years ago[1] an account was given of experiments designed in the hope of preparing a nitro-nitrogen trichloride in which the chlorine atoms would be negative and which would hydrolyze normally to hydrochloric and nitrous acids in contrast with the ordinary nitrogen trichloride in which the chlorine atoms are positive and show a tendency always to separate in such a manner as to be replaced by hydrogen, while the chlorine atoms have twice the oxidizing power of the atoms of free chlorine.[2]

Since that article was published evidence for the composite nature of chemical atoms has accumulated rapidly and chemists seem ready to accept the view that atoms are composed of electrons and positive nuclei held together by either static or dynamic electrical forces or by a combination of the two. The distinction between nuclear electrons, which remain unchanged in their relation to the nucleus of the atom, and valence electrons, which take part in some manner in reactions between atoms, seems also to be universally accepted by those who discuss questions of this character at all.

Three more or less distinct hypotheses have been proposed to account for the mechanism by which valence electrons hold atoms in combination.

1. J. J. Thompson,[3] who was the first to state the concept of valence electrons clearly, proposed the hypothesis that atoms consist of a sphere of positive material with electrons inside and valence electrons transferred completely from one atom to the other in chemical combination. Nearly all of the purely chemical discussion by Falk and Nelson, Fry, Jones, Stieglitz and others has made use of this simple notion of the transfer of electrons.

2. Ramsay[4] suggested that an electron might serve as a connecting link between atoms. In almost or quite the last paper that he published[5] he described an apparatus designed to show that atoms may be held in combination by the magnetic attraction between rotating electrons. Bohr[6] also supposed that atoms may be held in combination by elec-

[1] THIS JOURNAL, **35**, 767 (1913).

[2] For recent evidence for this point of view see *ibid.*, **42**, 2167 and 2173 (1920).

[3] J. J. Thompson, *Phil. Mag.*, **7**, 237 (1904).

[4] Ramsay, *J. Chem. Soc.*, **93**, 774 (1908).

[5] Ramsay, *Proc. Roy. Soc.*, **92A**, 451 (1916).

[6] Bohr, *Phil. Mag.*, **26**, 1, 476, 857 (1913).

trons rotating about the line joining the centers of the atoms, the attraction being static rather than magnetic. Parson[7] has also developed an elaborate magneton theory

3. G. N. Lewis,[8] in an hypothesis which has been elaborated and brought to the attention of a wide circle of chemists by Irving Langmuir,[9] makes the following suppositions.

(*a*) Every atom has a central kernel composed of positive units and electrons, the latter being, of course, the nuclear electrons referred to above. X-rays seem to be emitted from these nuclear electrons.

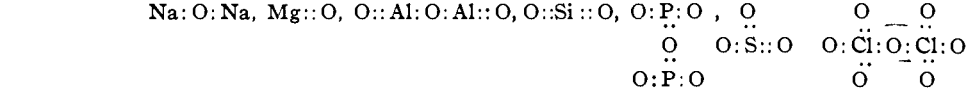
(*b*) The central kernel is identical with the atom and has a zero charge for elements of the zero group. It has a unit positive charge for hydrogen and an excess of positive charges varying (by whole units) from 1 to 7 for other atoms. The words in parenthesis are not included in the statement of Professor Lewis but seem to be justified by the experimental evidence.

(*c*) Neutral atoms have an outer shell of electrons varying from 1 to 8. The positive charge of the kernel is exactly balanced by the negative charges of these electrons.

At the April meeting of the National Academy of Sciences, R. A. Millikan gave evidence from the spectrum lines beyond the ultra-violet which affords very strong support for this part of the hypothesis and which seems to prove that these electrons of the outer shell are very far from the center of the atom in comparison with the nuclear electrons which emit X-rays. It seems evident that the electrons of the outer shell are the valence electrons.

(*d*) Atoms may give up electrons from the outer shell, forming positive ions, or take electrons from other atoms, forming negative ions, 7 or two atoms may hold 2 (or 4) electrons in common forming "non-polar" compounds.

(*e*) It seems to follow from the hypothesis as stated that no atom can be in direct union with more than 4 other atoms. It is at this point that the hypothesis differs most radically from theories of valence previously current. It does not seem to agree very well with the existence of such compounds as PCl_5, SF_6, $S(OH)_6$, etc., though Langmuir has attempted an explanation of some of these.[10] It does not give a very satisfactory picture of the apparent regular increase of valence from 1 to 7 in the series of oxides Na_2O---Cl_2O_7 and in the corresponding acids. According to the hypothesis of Lewis this series of oxides is represented as follows:



An examination of these formulas makes it clear that in phosphorus pentoxide and in sulfur trioxide two of the double unions of the older formulas have become single unions while in chlorine heptoxide three double unions have become single unions.

The hypotheses of Bohr and of Lewis agree with the evidence of the scattering of α-particles by thin films presented by Rutherford.[11] He

[7] Parson "A Magneton Theory of the Structure of the Atom," *Smithsonian Inst. Pub.*, **65**, No. 11 (1915).

[8] Lewis, THIS JOURNAL, **38**, 762 (1916).

[9] Langmuir, *ibid.*, **41**, 868 (1919).

[10] I understand that Lewis assumes a higher value than 4 in some cases but I do not know that such a statement has been published.

[11] Rutherford, *Phil. Mag.*, **21**, 669 (1911).

considers that this evidence has demonstrated that the positive nuclei of atoms have a volume very small in comparison with the effective size of the atoms. J. J. Thompson's hypothesis of a sphere of positive material with embedded electrons has, therefore, been abandoned. The question whether there is a transfer of an electron from one atom to another in all forms of chemical combination or whether this occurs only in the so-called "polar" compounds, and the question whether atoms are held together by a single electron or by pairs of electrons may well be considered as still open.

Nitrosyl chloride, NOCl, hydrolyzes to nitrous and hydrochloric acids. According to the hypothesis of Professor Lewis, the two electrons which hold the atoms of nitrogen and chlorine together remain with the chlorine atom in the decomposition of the nitrosyl chloride, but they remain with the nitrogen atom in the decomposition of nitrogen trichloride, or of chloroamine, NH_2Cl. The difference in conduct may be explained as due to the oxygen atom in the nitrosyl chloride but, if it were possible to prepare an isomeric nitrogen chloride in which the chlorine would tend to separate as a chloride ion, the hypothesis that there is a pair of electrons between the atoms would become far less probable. The question seems one of sufficient theoretical importance to justify the considerable amount of time which has been spent on the experiments described in this paper.

Nitrogen and oxygen combine at a very high temperature to form the endothermic compound, nitric oxide, in which the nitrogen is usually assumed to be positive and the oxygen negative. It seemed possible that a nitrogen dichloride in which the chlorine would be negative might be formed in a similar manner. So far as the writer is aware no one had ever tried the experiment. The first experiments, in which an ordinary induction coil and heavy platinum wires were used, were begun about 7 years ago and the study of the problem has been continued at intervals up to the present. The final result of the investigation is negative and it is unnecessary to describe in detail a dozen or more different modifications of the apparatus used.

The two forms which were longest used and which seem to be best adapted for such a purpose are shown in the figures.

The air was displaced by nitrogen passed in from the top and liquid chlorine was condensed in the small bulb at the bottom. The apparatus was then closed and a circulation of the nitrogen mixed with chlorine, at the vapor pressure of liquid chlorine at the temperature of carbon-dioxide snow mixed with alcohol, was produced by the heat from the discharge in the bulb and by cooling the side tube with ice. The electrodes were attacked by the chlorine and it was never possible to continue the experiments more than a few hours before they were perforated. In a considerable number of experiments the periods of operation were from 1 to 3 hours

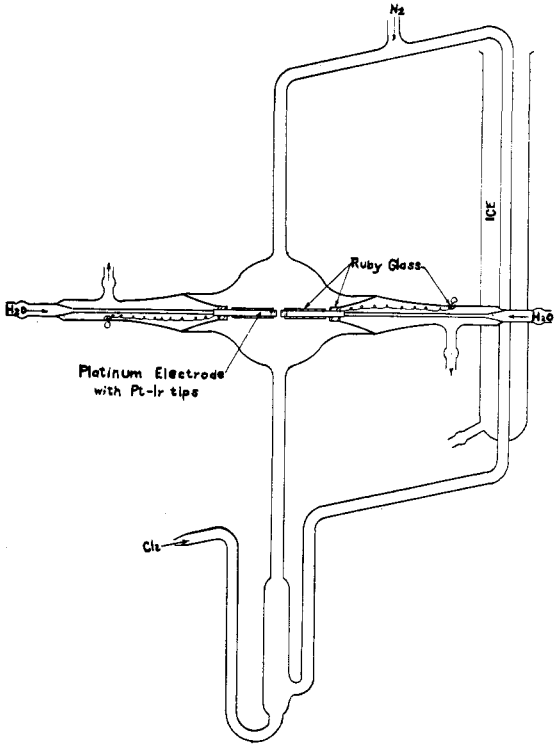


Fig. 1.

Fig. 1 shows a bulb with a capacity of about 350 cc. Two hollow platinum electrodes with heavy platinum-iridium tips were used. Between these electrodes an alternating discharge was produced by a Thorardson transformer rated at 110/10,000 volts. The electric flame was spread to an area of 4 to 5 sq. cm. by a very powerful electro-magnet having the poles properly placed on the two sides of the bulb.

and in two experiments for 8 and 10 hours respectively. At the close of the run the chlorine was allowed to evaporate and pass through water to hydrolyze the product and the gases remaining in the apparatus were driven through the water by nitrogen or air. The nitric acid formed in this way was determined by reduction to ammonia.

Careful blank tests for compounds of nitrogen were run on the mixture of the two gases placed in the tube in the usual manner, as well as on the water used for hydrolysis, with absolutely negative results. The first four runs with this apparatus lasting from 1 to 4 hours have values for combined nitrogen ranging from 0.5–1.0 mg. The next two of 3.5 and 2 hours duration gave 0.2 and 0.3 mg; while in the seventh run lasting 8 hours, analysis indicated only 0.07 mg. From the well-known difficulty in removing moisture from glass it seems probable that the yields

were due to interaction between nitrogen in the arc with either oxygen or hydrogen from decomposed moisture. With the gradual elimination of this absorbed water the yields decreased. In the eighth run 2 or 3 drops of water were added to the chlorine forming a small visible lump of ice. The vapor pressure of the ice is small at the temperatures used, below 0°, so that but little escaped, and during a 10-hour run only 0.17 mg. of nitrogen was brought into combination.

In the endeavor to "freeze out" any compound of nitrogen and chlorine that might be formed, an apparatus was made where the arc, spread as before, was allowed to strike between platinum-iridium electrodes close to the surface of liquid chlorine in an atmosphere of chlorine and pure nitrogen. A quartz tube protected the glass walls from the heat of the arc. Four completed runs were made lasting from 1 to 2.5 hours with the formation of no appreciable amount of nitrogen compound. Other forms of apparatus designed to bring the gases after leaving the arc more quickly into contact with a cooled surface gave negative results with a spread arc. A silent discharge likewise gave negative results.

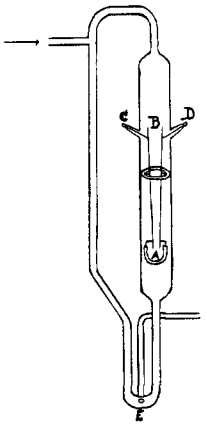


Fig. 2.

The last form of apparatus to be used, and the most satisfactory, is shown in Fig. 2.

Two platinum wires, A B, 18 cm. long and 0.5 mm. in diameter, but made heavier at the top by putting 3 or 4 pieces of the wire together, were supported from the platinum connections C and D and held in place by the circular rod of Pyrex glass bearing platinum wires welded to the longer wires and by a U-shaped rod of Pyrex glass at the bottom.

By this arrangement contact of the electric flame with the glass supports was completely avoided. The wires were placed about 4 mm. apart at the bottom and 15 mm. apart at the top. These distances were fixed by careful preliminary experiments. The distance at the bottom must be such that a discharge from the Thorardson transformer will pass between the wires and immediately begin to travel up the wires as the gases above the discharge become heated. If the distance is too great the discharge will not pass and if too small it remains at the bottom and soon melts the ends of the wires. The distance at the top is such that when the discharge reaches that point a flaming arc is produced. In a part of the experiments (1–10) recorded in the table (p. 1780), wires 50 cm. long, 4 mm. apart at the bottom and 20 mm. apart at the top, were used. With this form of apparatus the arc would break when it reached the top, and start again at the bottom. This was more difficult to regulate than the stationary arc. Dr. Rideal suggested this form of apparatus and we understand that it has been used in commercial practices.

The nitrogen was prepared by passing a mixture of air and purified hydrogen, from a Kipp generator, through a hard glass tube about 80 cm. in length placed in a combustion furnace. The tube was filled at first with copper oxide, and about half of this was reduced to metallic copper. It is easy to regulate the rates for the hydrogen and air so that the relative amounts of copper and copper oxide remain nearly constant; and if these are moderately hot it is impossible for either oxygen or hydrogen to pass beyond the tube. The nitrogen was dried with conc. sulfuric acid and phosphorus pentoxide. Chlorine was prepared by warming a mixture of sodium dichromate and hydrochloric acid and was condensed in a bulb surrounded by carbon-dioxide snow and alcohol and introduced through a side tube sealed to the tubes between the sulfuric acid bottle and the phosphorus pentoxide tube.

All parts of the apparatus were sealed together. In the last experiment where the negative result was most conclusive, a current of nitrogen was passed through the apparatus at first for 5 hours and it was then surrounded with asbestos and heated from below to 100° or 130° while the current of nitrogen was continued and the arc maintained for 18 hours longer. The chlorine was then introduced and condensed in the lower bend of the apparatus by surrounding this with carbon-dioxide snow and alcohol. Nitrogen was again passed through the apparatus for some time and the arc was operated for 51 hours. The upright tube at the left side of the apparatus was about one cm. in diameter, and during the operation of the arc the circulation of the gases through the system was sufficiently rapid so that the tube on the right through which the cold gases rose into the larger tube became covered with frost.

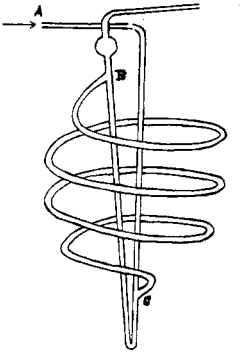


Fig. 3.

At the close of the experiment the carbon dioxide snow was removed and the chlorine was allowed to evaporate and pass through the hydrolysis tube shown in Fig. 3. The spiral tube is 185 cm. in length and only 2 mm. in diameter. If 2 or 3 cc. of water is placed in the apparatus, gas entering at A pushes short columns of water around the spiral to B, from which point the water is returned through the upright tube to C. This secures a very effective contact between the gas and liquid with the use of a very small amount of water.

If any nitro chloride of nitrogen were formed it would be converted to nitric acid by the chlorine passing the hydrolysis apparatus with it. $NCl_3 + Cl_2 + 3H_2O = HNO_3 + 5HCl$, or $2NCl_2 + 3Cl_2 + 6H_2O = 2HNO_3 + 10HCl$. The ratio of nitrogen to chlorine, irrespective of the composition of the nitrogen chloride, would be 1:5. It was shown that pure chlorine left only the merest trace of combined chlorine in the water when it was passed through the spiral and followed by nitrogen or air.

If nitrosyl chloride were formed in the apparatus because of the pres-

ence of a trace of oxygen or of moisture the ratio of nitrogen to chlorine would be 1:3 : $NOCl + Cl_2 + 2H_2O = HNO_3 + 3HCl$.

If the vapor of ordinary, ammono-nitrogen trichloride is passed through the spiral tube it was demonstrated that practically no hydrolysis occurs. On the other hand, if the vapor is passed through conc. hydrochloric acid, ammonium chloride and chlorine[12] are formed. The products formed in the arc were tested in that way with negative results.

After the completion of an experiment the water in which the products were hydrolyzed was diluted to a standard volume and the combined nitrogen and chlorine were determined in aliquot portions. The nitrogen was determined by reduction in an alkaline solution with Devarda's alloy, and the chlorine by precipitation with silver nitrate. The results of 13 experiments were as follows.

Expt.	No. of hours arc was operated.	Mg. atoms. N.	Mg. atoms. Cl.
1	10	1.54	4.20
2	20	0.11	0.113
3	18	0.96	2.96
4	20	0.44	1.05
5	30	0.66	2.80
6	14	0.12	0.35
7	10	0.20	0.60
8	10	0.05	0.18
9	6	0.02	0.05
10	8	0.01	0.07
11	38	0.06	0.22
12	53	0.05	0.57
13	51	0.006	0.024

In the earlier experiments, in which the extreme care of the later experiments to remove traces of oxygen and moisture was not observed, appreciable amounts of combined nitrogen were formed, but the ratio of nitrogen to chlorine was much less than 1:5 and in those cases where most nitrogen was formed approximated 1:3. It seems quite certain that the compound present in these cases was nitrosyl chloride. The evidence of the later experiments seems practically conclusive as demonstrating that if nitrogen and chlorine combine at all in the flaming arc the compound is decomposed as it escapes from the zone of heat.

In all of the experiments with platinum electrodes a grayish-brown deposit was formed on the walls of the tube. Expts. 6 to 10 of the table were carried out consecutively. The solution obtained by washing the apparatus out with water, contained 0.75 mg. atoms of combined nitrogen. The wash solutions from Expts. 11 and 12 contained 0.33 mg. atom, while that from the last experiment contained only 0.02 mg. atom of combined nitrogen.

[12] Noyes, THIS JOURNAL, **42**, 2173 (1920).

The ratio of platinum to chlorine was also determined in the solutions. In the last experiment the atomic ratio was 1:3.6, indicating a mixture of platinic chloride, $PtCl_4$, with a little platinous chloride. In two earlier experiments the atomic ratios were 1:5.76 and 1:5, indicating the presence of chloroplatinic acid. The hydrochloric acid to form this probably came from the interaction of moisture, chlorine and nitrogen: $N_2 + 2Cl_3 + 2H_2O = 2NOCl + 2HCl$.

Several experiments were tried with carbon electrodes. The results were similar, but appreciable amounts of a white solid and of a colorless liquid were formed, doubtless carbon hexachloride and carbon tetrachloride.

To test the efficiency of the apparatus a run was made with air passing through it at the rate of 3.6 liters per hour. The oxides of nitrogen condensed almost completely in the lower part surrounded by carbon-dioxide snow and alcohol, as colorless crystals of nitrogen tetroxide, with only a little blue nitrous anhydride. About 30 mg. atoms of combined nitrogen were obtained in 2 hours—250,000 times as much as was obtained in the same time in the last experiment with nitrogen and chlorine.

Experiments were also tried with a very efficient ozonizer of Pyrex glass, consisting of two concentric tubes 55 to 60 cm. long and 2.8 and 3.7 cm. in diameter, respectively. The inner tube was filled with a solution of sodium sulfate and the outer tube was surrounded with the same electrolyte. A copper spiral running to the bottom of the inner tube and another wound around the larger tube furnished the connection with the terminals of the Thorardson transformer. When the latter was connected with the 110 volt circuit, quantities of ozone were produced in air passed between the tubes but no combined nitrogen was found. With 220 volts there was a crackling sound with a blue glow, and a large number of streamers appeared between the walls of the tubes. Under these conditions air passed through the apparatus gave 0.15 mg. of combined nitrogen in 30 minutes but a mixture of nitrogen and chlorine passed for 6 hours gave no combined nitrogen. A negative result was also obtained with the conditions which gave ozone but no combined nitrogen.

When active nitrogen prepared by Strutt's method was passed over chlorine at the temperature of liquid air no combination occurred.

Summary.

1. It has not been found possible to prepare either a nitro-nitrogen chloride or ordinary nitrogen trichloride by passing a mixture of nitrogen and chlorine through a flaming electric arc.

2. So far as negative results have value, the experiments favor Professor Lewis's hypothesis that electrons are held jointly by two atoms

rather than the view that electrons are transferred from one atom to the other when atoms combine.

I wish to express my appreciation of the valuable assistance of L. C. Johnson, B. R. Honovski, F. O. Anderegg, A. B. Haw, and G. H. Coleman in carrying out the experiments described in this paper.

URBANA, ILL.

[CONTRIBUTION FROM THE EXPERIMENTAL STATION OF E. I. DU PONT DE NEMOURS AND COMPANY.]

VAPOR PRESSURES OF AQUEOUS SOLUTIONS OF NITRIC ACID.

BY WILLIAM C. SPROESSER AND GUY B. TAYLOR.

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The partial pressures of water and nitric acid vapors in equilibrium with all concentrations of aqueous nitric acid possess scientific interest and are practically useful to the acid industry. Burdick and Freed[1] have recently supplied data for concentrations ranging from 24% to 70% nitric acid at 25°, 50°, and 75°. The present investigation had as its object the extension of similar data to 100% nitric acid and over a wider temperature range. The dynamic method chosen did not prove suitable for concentrations above 80%, owing to thermal decomposition of nitric acid vapor. The measurements covered the range from 20 to 90% at temperatures from 0° to 80° and, therefore, considerably extend the range, making it possible to draw a series of curves showing the acid composition of minimum vapor pressure within these temperature limits.

Experimental.

The apparatus is shown in Fig. 1. Water from the reservoir A was siphoned into the calibrated bottle B, displacing a known volume[2] of air and forcing it through the dryer C, the carbon dioxide-remover F, the three saturators D, and the absorbers E. The dryer C was a Friedrichs "spiral" gas-wash-bottle containing conc. sulfuric acid. The U-tube F was filled with soda lime. The saturators D were special forms of spiral wash-bottles. In the last bottle a small accurate Anschutz thermometer, 3, was sealed to record the temperature, which was maintained constant to ±0.1°. The three saturators were filled with nitric acid of known composition, fused together, and placed in the Freas constant-temperature oven G. The ground-glass joint, 4, connected the absorbers E to the rest of the system. The whole apparatus was always set up so that nitric acid, liquid and vapor, came in contact with glass only. To avoid condensation in the tube and ground joint protruding from the oven, an electrically heated wire-spiral was placed about the ground joint, 4, to keep the joint warm. The U-tube E, filled with solid sodium hydroxide and followed by two or more such tubes (not shown) containing as well, layers of phosphorus pentoxide on glass wool, was used to absorb the effluent vapors.

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[1] Burdick and Freed, THIS JOURNAL, **43**, 518 (1921).

[2] Calculated from the volume of the bottle, temperature and pressure within the bottle, and the barometric pressure.