cated by mechanical stirring through gases or by rotation or other movement of the anode. The change of chemical behavior of the metals is, therefore, due only indirectly to the magnetic field and the conclusion cited previously in this article is still valid.

Further, the examination of the phenomena of passivity shows it to be influenced by the following factors: *a*, character and condition of the metal; *b*, temperature; *c*, electrolyte employed; *d*, density of current; *e*, time of passage of current; *f*, character and extent of movements of the electrolyte.

In view of these variables and the examination of the literature t no longer is surprising that no satisfactory explanation is at hand; since, so far as we know, during any investigation, no adequate attempt has been made to control more than two factors. If, therefore, a correct conclusion has been reached it is perhaps more accidental than otherwise.

Why stirring an electrolyte should delay the establishment of passivity does not seem clear to us. If passivity is due to an adhering layer of oxygen or to the formation of an oxide it may be argued either that rotation of an anode should spread evenly, and, therefore, complete the film more readily; or that friction would delay the same result. Again stirring with oxygen would apparently facilitate the formation of such a film and with hydrogen would hinder the same. Both gases produce like effects. Again, such ought not to be the case if passivity is the natural state of iron and activity is due to the catalytic action of occluded hydrogen, as suggested by Graves.[1]

In short we are only prepared to repeat a previous statement, "no explanation of the phenomena of passivity even approximately satisfactory has yet been produced—we have none to offer. When the experimental development warrants it, we confidently expect the cause of passivity to be found in an altered state of the metal itself, this alteration, whatever its character, being produced," or prevented, "by any one of a number of different agencies."

UNIVERSITY OF WASHINGTON.

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

AN ATTEMPT TO PREPARE NITRO-NITROGEN TRICHLORIDE, AN ELECTROMER OF AMMONO-NITROGEN TRICHLORIDE.[2]

BY WILLIAM A. NOYES.

Received April 24, 1913.

The idea, first proposed in its modern form by Arrhenius,[3] that electrolytes are more or less completely separated in aqueous solutions into

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[1] *Loc. cit.*

[2] Presented in abstract at the Milwaukee Meeting of the American Chemical Society, March, 1913.

[3] *Z. physik. Chem.*, 16, 4116 (1895).

electrically charged ions, which recombine on the evaporation of the solution or combine readily with other ions in the same solution, has furnished the basis for an accurate quantitative treatment of many of the phenomena of solutions. It is now accepted, at least as a working hypothesis, by nearly all active workers in this field. An application of a similar principle in the discussion of a reaction between substances ordinarily considered as non-electrolytes was, so far as I can discover, first made by Ostwald[1] in an attempt to explain the formation of ozone by the action of oxygen on moist phosphorus. Several years later, in conjunction with Mr. Lyon,[2] the author of this paper showed that the primary reaction between ammonia and chlorine gives nitrogen trichloride as well as nitrogen,

$$3NH_3 + 6Cl_2 = NCl_3 + N_2 + 9HCl.$$

In discussing this reaction the suggestion was made that the chlorine molecules may separate into positive and negative ions, Cl^- and Cl^+, in the reaction and that some of the nitrogen and hydrogen atoms were temporarily positive and others were negative while reacting. Stieglitz[4] very shortly after stated that similar notions had been presented by him in the class-room for some years before this, especially to explain such reactions as that of chlorine on water:

$$Cl^- + Cl^+ + H^+ + OH^- = HCl + ClOH.$$

In 1904, J. J. Thompson[3] proposed the hypothesis that atoms may consist of a shell of positively charged matter containing within groups of electrons, or atoms of negative electricity, and suggested that the transfer of electrons may be the cause of chemical combination and of the valence of the elements. About the same time Abegg[4] developed the closely related idea of normal and contra valences—the sum of the two kinds of valence being eight for a given atom. Thus nitrogen has five normal, positive valences which it may develop in combining with negative oxygen and three contra, negative valences developed in combining with hydrogen. Chlorine has seven normal, positive valences and only one contra, negative valence. In his discussion of the question Abegg suggests[5] a possible connection between his hypothesis and the electron theory. It may be mentioned, in passing, that, as a corollary of his view Abegg explains the fact that silver trinitride, AgN_3, and iodine trinitride, IN_3, do not react with each other by assuming that the silver and iodine are both positive.[6] In 1908, Ramsay[7] discussed a theory of chemical com-

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[1] THIS JOURNAL, 23, 463 (1901).

[2] *Ibid.*, 23, 797 (1901).

[3] *Phil. Mag.*, March, 1904.

[4] *Z. anorg. Chem.*, 39, 342 (1903).

[5] *Loc. cit.*, p. 343.

[6] *Handbuch der anorg. Chem. Bd.*, 5S, 214.

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

bination in which the electrons are supposed to furnish the bond of union between the atoms of compounds, though by a mechanism somewhat different from that supposed by Thompson. Falk and Nelson,[1] Fry[2] and others have discussed the electron theory as a basis for the explanation of various phenomena of organic compounds, the fundamental conception being that each union between atoms is positive on one side and negative on the other and that atoms are held in combination by electrical forces.

In 1892, Seliwanow[3] pointed out that chlorine may be positive in some compounds and negative in others. He refers also to similar ideas proposed by Schützenberger.[4] A few years later Stieglitz discussed some reactions of compounds containing chlorine and bromine combined with nitrogen in which the halogen atoms are clearly positive.[5]

During the fall of 1911, my attention was directed again to the anomalous conduct of nitrogen trichloride. When titrated with a solution of arsenious acid, one molecule of the trichloride is equivalent to *six* atoms of available chlorine. This indicates that the nitrogen of the compound is negative and the chlorine positive and that it hydrolyzes, as a reversible reaction:

$$N^{---}\ Cl_3^{+++} + 3H^+\ O^{--}\ H^+ = N^{---}\ H_3^{+++} + 3Cl^+\ O^{--}\ H^+.$$

It then occurred to me that there ought to be another nitrogen trichloride in which the nitrogen would be positive and the chlorine negative and which would hydrolyze normally, as the chlorides of other non-metallic elements do.

$$N^{+++}\ Cl_3^{---} + 3H^+\ O^{--}\ H^+ = H^+\ O^{--}\ N^{+++}\ O^{--} + H^+\ O^{--}\ H^+ + 3H^+\ Cl^-.$$

In accordance with its conduct ordinary nitrogen trichloride might be called ammono-nitrogen trichloride while the other, if found, would be properly designated as nitro-nitrogen trichloride.

Experimental Part.

The method of possible preparation which first suggested itself was by the action of phosphorus pentachloride on nitrosyl chloride, NOCl. Nitrosyl chloride hydrolyzes normally to nitrous and hydrochloric acids and its nitrogen is evidently positive. On heating nitrosyl chloride with phosphorus pentachloride in a sealed tube there was no apparent reaction till comparatively high temperatures were reached and then the products seemed to be nitrogen and chlorine, but the reaction and analyses were not carried out very carefully by this method because of the difficulty of working with more than small quantities of materials and of separating a complex mixture of gaseous products. Some experiments were also

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[1] *School of Mines Quart.*, **30**, 179 (1909); THIS JOURNAL, **33**, 1140 (1911).

[2] *Z. physik. Chem.*, **76**, 385, 398; 591 (1911).

[3] *Ber.*, **25**, 3617 (1892).

[4] *Ann.*, **120**, 113.

[5] *Am. Chem. J.*, **18**, 756 (1896).

tried with nitrosyl chloride, sulfur dichloride, S_2Cl_2, and chlorine, but these were not carried through to any positive result. At the temperature used the sulfur dichloride was not completely oxidized. It seems unnecessary to give the details of a large number of experiments, many of which have given results entirely negative or results too close to the errors of analysis to furnish any satisfactory evidence of the existence of the compound sought.

The method of experiment which has given most satisfactory results, thus far, consists in passing a mixture of nitrosyl chloride and phosphorus pentachloride through a tube heated to a high temperature. The mixture was obtained by heating a mixture of one mol of sodium nitrite with about two mols of phosphorus pentachloride. The reactions desired are:

$$NaNO_2 + PCl_5 = NOCl + POCl_3 + NaCl$$

and

$$NOCl + PCl_5 = NCl_3 + POCl_3.$$

In addition to these reactions a large part of the nitrosyl chloride remains unchanged and chlorine and silicon tetrachloride are formed.

In the earlier experiments a tube of Jena difficultly fusible glass, heated to as high a temperature as possible in a combustion furnace, was used. Then in two experiments an electrically heated tube of fused silica was employed, but in the second of these the walls of the tube were eaten through. In the latest experiments a porcelain tube, heated electrically to 1000°–1100°, has been used.

The arrangement of the apparatus for these last experiments is shown in Fig. 1.

The tube B contains the mixture of sodium nitrite, 11 to 14 grams, and phosphorus pentachloride, about 70 grams. It is placed in an iron trough lined with asbestos paper and heated gradually, beginning at the end towards A. The porcelain tube A is heated electrically by means of a platinum

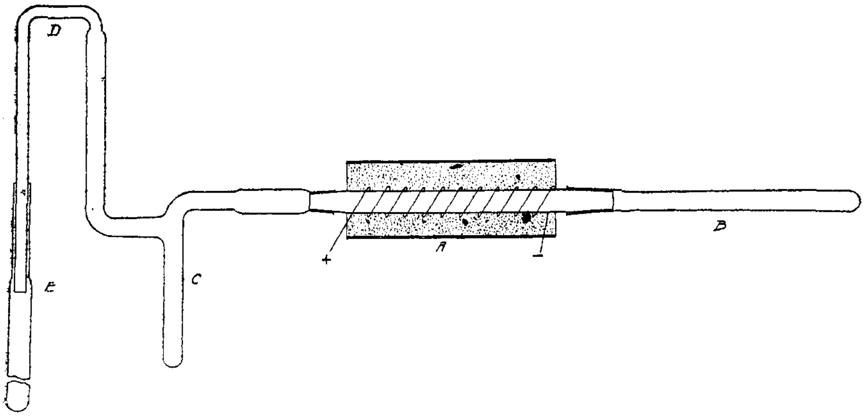

Fig. 1.

wire wrapped around it and is surrounded with amorphous silica as a heat insulating material. With a current of 110 volts it is found that the tube reaches a temperature of 1000° in about 30 minutes, and a temperature of 1000°–1100° can be maintained indefinitly with a suitable rheostat for external resistance. The porcelain tube is connected by ground joints to the generating tube B, and the receptacle for phosphorus oxychloride C. The joints were rendered a little more perfect by the use of a little "float" graphite. The tube D is about one centimeter in diameter to avoid its closing with sublimed phosphorus pentachloride. The bulb E fits closely over the end of D and is cooled, sometimes with a freezing mixture of ice and hydrochloric acid, sometimes with liquid air. In the latter case it must not dip too deeply in the liquid air or the end of D may be closed by frozen nitrosyl chloride and chlorine.

The tube B is heated slowly so that two or three hours are required to pass the mixture of nitrosyl chloride and phosphorus pentachloride through the porcelain tube. At the end of the operation the liquid collecting in C is heated to boiling for a few minutes to drive nitrosyl chloride and other volatil products absorbed by the phosphorus oxychloride and phosphorus pentachloride over into E.

The products condensed in E were distilled and the mixtures gaseous at ordinary temperatures were analyzed. It soon became evident that portions which remain liquid at 25°–35° retain no appreciable amount of nitrosyl chloride or of nitro-nitrogen trichloride after one or two distillations. It was also shown by repeated analyses that products distilling at 0°, or slightly above, do not contain more than 0.001 to 0.002 milligram atoms of phosphorus in a volume of 70 cc. of the gases. This is an amount which may be neglected in comparison with the other quantities involved.

For analysis the mixed gases were allowed to evaporate upward through a bulb having a capacity of about 70 cc. When the air had been displaced, the capillary tubes at the ends of the bulb were sealed, using care to avoid warming it. The bulb was weighed with a small counterpoise of about the same volume before filling and again after sealing and cooling. The weight of air contained in the bulb at the first weighing was, of course, easily calculated from the temperature of the balance case and the barometric pressure.

After weighing, the bulb was cooled by evaporating a little ether on its surface and the tip was broken off under a standard solution of potassium hydroxide. Some gas, which proved to consist mainly, or exclusively of nitric oxide, was left unabsorbed. This was converted into nitrite by forcing in oxygen under pressure and shaking the gas quickly with the alkalin solution. Under these conditions the nitric oxide is almost exclusively converted into nitrite.[1] In most cases the contraction was

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[1] Baudish and Klinger, *Ber.*, 45, 3231 (1912).

pretty closely five-fourths of the volume of the gas left in the bulb, as it should be in accordance with the reaction:

$$4NO + O_2 + 4KOH = 4KNO_2 + 2H_2O.$$

When the agreement was not close a correction was made for the air corresponding to the residual nitrogen left in the bulb.

The amount of potassium hydroxide solution was determined by weighing the bulb again and after transferring the solution to a 100 cc. flask, the volume of the bulb was determined by filling it with water and weighing it.

The amount of unneutralized potassium hydroxide was determined in an aliquot part of the solution by titration with 0.1 *N* hydrochloric acid, then 2 or 3 cc. of methyl alcohol and an excess of hydrochloric acid were added and the nitrous acid expelled as methyl nitrate.[1] By titrating back with 0.1 *N* potassium hydroxide the amount of nitrite present was obtained. In the residual solution the amount of nitrate was determined by Ulsch's method of reduction to ammonia in acid solution with reduced iron. The ammonia was distilled and titrated after the addition of an excess of sodium hydroxide. In most cases the nitrous acid was also determined by titration with potassium permanganate and the nitrate determined in the oxidized solution. In another portion, the chlorine was precipitated and weighed as silver chloride. In another, larger portion, the silica was determined, as usual, after evaporation with an excess of hydrochloric acid. In a number of cases the phosphorus was determined with molybdic solution after evaporating the filtrate from the silica with an excess of nitric acid. The amount found was always too small to be of importance for the present purpose.

It has been found convenient to calculate the results, in the form of milligram mols and atoms. As a volume, this is, of course, 22.4 cc. at 0° and 760 mm.

In the latest experiment the products of the reaction were condensed by means of liquid air. The bulb containing the condensed gases was then connected with a series of U tubes sealed together as shown in Fig. 2.

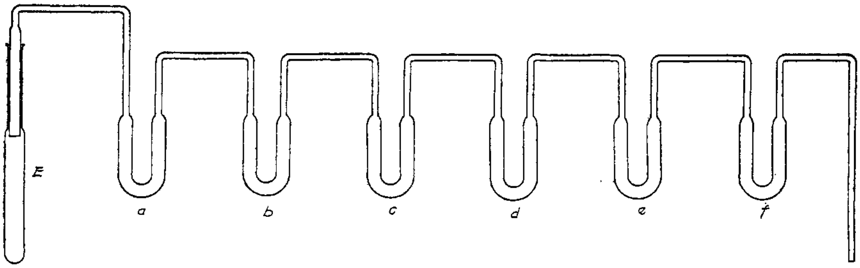

Fig. 2.

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[1] Fischer and Steinbach, *Z. anorg. Chem.*, 78, 134 (1912).

The liquid in E was allowed to boil with the use of a boiling capillary[1] while the U tubes were placed in ice water, a freezing mixture of ice and hydrochloric acid or liquid air. In four consecutive distillations the arrangement was as follows:

	a.	b.	c.	d.	e.	f.
1.	Ice water	Freezing mixture	Liquid air			
2.	Air	Ice water	Freezing mixture	Liquid air		
3.	Air	Ice water	Freezing mixture	Freezing mixture	Liquid air	
4.	Air	Air	Air	Freezing mixture	Freezing mixture	Liquid air

At the end of the operation each U tube was sealed off and the contents analyzed after conversion to the gaseous form.

The results of the analyses were, in milligram-atoms:

	c.	d.	e.	f. Less volatil.	f. More volatil.
Volume (cc. ÷ 22.4)....	2.27	2.67	2.88	0.63	2.81
Acid (in equiv.).......	5.16	5.63	5.97	1.26	....
N as NO_2............	1.70	1.62	1.66	0.12	....
N as NO_3............	0.47	0.73	0.89	0.27	1.36
Chlorine.............	3.01	3.28	3.54	0.83	4.30
Silicon...............	0.10	0.03	0.02	0.01	0.01
Weight.............	0.1733 g.	0.1849 g.	0.1987 g.	0.0437 g.	0.1929

The results are in fairly satisfactory agreement with the following composition in milligram mols for the mixed gases. The calculations are based primarily on the amounts of nitrogen, chlorine and silicon present. They are checked further by the calculated weight of gases corresponding to the composition given and the amount of acid which should be formed by the hydrolysis of such a mixture. The amount of nitrate present is dependent on the amount of free chlorine, the amount of nitric oxide formed during the absorption of the gases, the amount of dissolved oxygen in the absorbing solution and on the presence of a small amount of air in some cases. An exact agreement with the theory is not to be expected, but the amounts of nitrate and nitrite found are inconsistent with the supposition that the nitrogen trichloride indicated could have been the ammono-trichloride. They are also inconsistent with the supposition that $NOCl_2$ or $NOCl_3$ might have been present. Indeed Tilden[2] and Goldschmidt[3] have shown conclusively that these compounds do not exist in gaseous form.

[1] Scudder, THIS JOURNAL, **25**, 163 (1903).

[2] *J. Chem. Soc.*, **27**, 630; see also van Heteren, *Z. anorg. Chem.*, **22**, 277 (1900).

[3] *Ann.*, **205**, 372 (1880).

	c.	d.	e.	f.	f.
NOCl	1.95	2.19	2.41	0.39	1.36
NCl_3	0.22	0.16	0.14	0.00	0.00
Cl_2	0.00	0.29	0.31	0.23	1.44
$SiCl_4$	0.10	0.03	0.02	0.01	0.01
Calculated wt.	0.1712 g.	0.1884	0.2002	0.0435 g.	0.1931
Calculated acid	5.18	5.72	6.08	1.28	....

Twelve different experiments have been carried out in various ways and 30 gaseous mixtures have been analyzed. Of these mixtures twelve, obtained in six different experiments, have given evidence of the presence of from 0.12 to 0.22 milligram mols of nitro-nitrogen trichloride in a volume of about 70 cc. The analyses have indicated the following compositions for the mixtures:

NOCl	2.22	2.27	2.08	2.53	2.51	2.46	2.37	2.25	2.15
NCl_3	0.17	0.16	0.14	0.13	0.12	0.14	0.15	0.20	0.13
Cl_2	..	..	..	..	..	0.18	..	0.25	0.47
$SiCl_4$	0.07	0.16	0.25	0.05	0.14	0.04	0.19	0.07	0.05

The results which are bracketed are each two analyses, one of the more volatil and the other of the less volatil portion of the condensed gas from the same experiment. The less volatil portion contains, of course, more silicon tetrachloride than the other.

It seems probable that the nitro-nitrogen trichloride, if it can be obtained pure, will have a quite low boiling point.

When these preliminary results were communicated to the meeting of the Chicago Section in March and again in Milwaukee, the suggestion was made, especially by Professor Bancroft, that ferric chloride or aluminium chloride might prove better than phosphorus pentachloride for the preparation of the new nitrogen trichloride. Experiments made by heating mixtures of anhydrous aluminium chloride and sodium nitrite show that nitrosyl chloride can be easily obtained in this way but the results thus far indicate that the nitrogen trichloride is not formed.

Conclusions.

1. Some evidence has been secured which seems to indicate the existence of a nitro-nitrogen trichloride differing from the ordinary ammono-nitrogen trichloride in that its nitrogen is positive and its chlorine negative while in the ammono-nitrogen trichloride the nitrogen is negative and the chlorine positive. The evidence thus far obtained can not, of course, be considered as conclusive and is given at the present time with reserve and because the difficulties encountered make it seem likely that considerable time may elapse before more positive results can be secured.

2. The discovery of such a compound would make it seem probable that the electrical charges of atoms persist in compounds and are not merely

formed during the ionization of compounds in solutions. This would give support also to the hypothesis that atoms are held in combination by electrical forces.

URBANA, ILL.

THE EFFECTS OF SULFATES ON THE DETERMINATION OF NITRATES.

BY W. P. KELLEY.

Received April 26, 1913.

Introduction.

As is well known, the determination of nitrates in the sanitary analysis of water is generally made with the aid of the phenoldisulfonic acid reagent. During recent years this reagent has found extensive application in soil investigation, particularly in studies on nitrification. The chemistry of the reactions involved in this determination has been extensively studied, and, as shown by Chamot and Pratt,[1] the yellow color that is produced depends upon the formation of the tri-salt of the phenoldisulfonic acid. It is not the purpose of this paper, however, to discuss the chemistry of this reaction, but rather to present some data bearing upon the effects of sulfates on the nitrate determination.

Natural waters, as well as the solutions obtained from soils, frequently contain various salts. Among these are the chlorides, carbonates and sulfates. The effects of chlorides and carbonates on the determination of nitrates have been studied in detail, especially the former; but the fact that the phenoldisulfonic reagent contains free sulfuric acid, which upon neutralization gives rise to sulfates has caused chemists to neglect to study the effect of sulfates.

Recently, Lipman and Sharp[2] published some investigations on this subject in which chlorides, carbonates and sulfates were studied. They found, in common with previous studies, that chlorides caused an apparent loss of nitrates, but, contrary to previous observations, carbonates have no effect. They further found that considerable loss of nitrate took place upon evaporating a nitrate solution containing sodium sulfate. The addition of dry sodium sulfate to the dry nitrate residue, however, occasioned no loss of nitrate. From these observations the claim is made that sulfates cause a loss of nitrate in this determination not by interfering with the phenoldisulfonic acid reaction, but by the expulsion of nitric acid during the time of evaporation on the water bath. Hence they conclude that nitrate determinations in solutions containing sulfate must be made by the use of other methods.

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[1] THIS JOURNAL, **21**, 922; **32**, 630; **33**, 366.

[2] *Univ. Cal. Pub. Agr. Sci.*, **1**, No. 2, pp. 21–37.