Summary

1. The velocity of hydration of acetic anhydride has been measured by a dilatometric method at 0°.

2. The salt effect on k_0 has been determined for a number of neutral salts in dilute solution. The medium effect of acetic acid has been measured.

3. The constants of hydrogen, acetate and formate-ion catalysis have been determined. The formate ion is a remarkably good catalyst.

4. In propionate–propionic acid and in butyrate–butyric acid buffer solutions the hydration is slower than in water alone. It is hoped to make a further study of this effect.

COPENHAGEN, DENMARK

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

THE INTERACTION BETWEEN NITROGEN TRICHLORIDE AND NITRIC OXIDE. REACTIONS OF COMPOUNDS WITH ODD ELECTRONS[1]

BY WILLIAM ALBERT NOYES

RECEIVED JULY 25, 1928 PUBLISHED NOVEMBER 6, 1928

In papers recently published,[2] the point of view has been presented that valence is a *unitary* atomic phenomenon. This is closely in accord with the original ideas of Frankland, Couper and Kekulé.

The endeavor has been made to show that for any given molecule, at any particular instant, the distinction between polar (or ionic) valences and covalences is sharp and definite. In the interest of clarity it has been proposed[3] to confine the term "polar valence" to the designation of valences which are actually ionic because of the complete transfer of an electron. The "semipolar" valences of oxygen in the sulfate radical, the amine oxides, etc., are, of course, half polar and half covalence.[4]

It has also been proposed to call those valences which have an electrical moment and which permit atoms held by a covalence to separate readily in the ionic form, "potentially polar," because the distinction between a covalence and an ionic valence is, theoretically, sharp and definite, while there may be all degrees of "potentially" polar valences.

This discussion seems to be a simple and logical development of the

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[1] In memory of Ira Remsen.

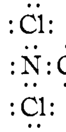
[2] (a) Noyes, *Z. physik. Chem.*, **130**, 325 (1927); (b) *Proc. Am. Phil. Soc.*, **66**, 299 (1927).

[3] Noyes, ref. 2 a, pp. 329; 26, 300.

[4] T. M. Lowry, *Trans. Faraday Soc.*, **19**, 486 (1923); *J. Chem. Soc.*, **123**, 822 (1923); Sugden, *ibid.*, **125**, 1186 (1924); **127**, 1527 (1925); Harrison, Kenyon and Phillips, *ibid.*, **129**, 2079 (1926); Noyes, THIS JOURNAL, **47**, 3027, footnote (1925); *Z. physik. Chem.*, **130**, 327 (1927).

positive and negative valences proposed, in part erroneously and vaguely in 1901[5] and 1904[6] and advocated by Professor Stieglitz,[7] Falk and Nelson,[8] Fry,[9] L. W. Jones[10] and others. It also furnishes an almost complete and satisfactory reconciliation with the octet theory of G. N. Lewis[11] and its exposition by Langmuir.[12]

If the hypothesis that a covalence is due to a pair of electrons which include the kernels of the two atoms which they unite in their orbits and that a polar valence is due to a pair rotating about the kernel of some negative atom or a deficiency of one electron in some positive atom[13] should receive further support and come to be generally accepted, the distinction between covalences and polar valences will become still more sharp than it is at present; but the distinction made in this and other papers is not dependent on that hypothesis.

Nearly all reactions of elements of low atomic weights occurring at ordinary temperatures seem to be, in reality ionic in character but we are compelled to assume odd electrons and reactions of a different type for a few compounds. For this reason, the interaction of nitric oxide, which has an odd electron, $\cdot\overset{\cdot\cdot}{\mathrm{N}}::\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{O}}}$,[14] and nitrogen tri-chloride,  $\begin{array}{l} \;\;:\overset{\cdot\cdot}{\mathrm{Cl}}: \\ :\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{N}}}:\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{Cl}}}: \\ \;\;:\underset{\cdot\cdot}{\mathrm{Cl}}: \end{array}$, an endothermic compound[15] with potentially positive[16] chlorine atoms, has proved to be of exceptional interest. Nearly all of the experiments with these compounds were carried out with a solution of the trichloride in a mixture of chloroform with enough carbon tetrachloride to prevent the mixture

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[5] Noyes and Lyon, THIS JOURNAL, **23**, 463 (1901).

[6] Noyes, *Chem. News*, **90**, 228 (1904).

[7] Stieglitz, THIS JOURNAL, **23**, 796 (1901).

[8] Falk and Nelson, *ibid.*, **32**, 1637 (1910).

[9] Fry, *Z. physik. Chem.*, **76**, 385, 398, 591 (1911); THIS JOURNAL, **34**, 664 (1912).

[10] L. W. Jones, *ibid.*, **36**, 1268 (1914).

[11] G. N. Lewis, THIS JOURNAL, **38**, 762 (1916).

[12] Langmuir, *ibid.*, **41**, 868, 1543 (1919).

[13] Noyes, THIS JOURNAL, **39**, 879 (1917); C. A. Knorr, *Z. anorg. allgem. Chem.*, **129**, 109 (1923); Sidgwick, *Trans. Faraday Soc.*, **19**, 469 (1923); Paulus, THIS JOURNAL, **48**, 1132 (1926); Grimm and Sommerfeld, *Z. Physik*, **36**, 52 (1926); Glockler, THIS JOURNAL, **48**, 202 (1926); Noyes, *Proc. Nat. Acad. Sci.*, **13**, 377 (1927).

[14] This might also be written $\cdot\overset{\cdot\cdot}{\mathrm{N}}{}^{+}:\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{O}}}:^{-}$, with a semipolar union between the oxygen and nitrogen, but Sugden, *J. Chem. Soc.*, **125**, 1187 (1924), has given good evidence, based on the parachor, that nitrosyl chloride, $:\overset{\cdot\cdot}{\mathrm{O}}::\overset{\cdot\cdot}{\mathrm{N}}:\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{Cl}}}:$, has a double covalence between the oxygen and nitrogen and it would seem quite probable that there is a similar structure in nitric oxide.

[15] Noyes and Tuley, THIS JOURNAL, **47**, 1336 (1925).

[16] Seliwanow, *Ber.*, **27**, 1017 (1894); Noyes and Haw, *Ber.*, **42**, 2167; Noyes, *Ber.*, **42**, 2173 (1920).

from freezing at −80°. A few were tried at 0°, one at −20° and two in petroleum ether at −130 to −140°.

About a hundred experiments have been performed in the endeavor to develop a satisfactory technique for separating the products formed and analyzing them to establish the course of the reaction at the different temperatures and in the different media. One hundred samples of mixed gases have been analyzed by the methods described in a previous paper,[17] $N/10$ potassium hydroxide instead of water being used to absorb the gases, which were sometimes nearly pure chlorine.

Experimental Part

Nitrogen Trichloride.—The chlorine generated by dropping 300 cc. of concd. hydrochloric acid on 60 g. of potassium permanganate was passed into 225 g. of a mixture of chloroform and carbon tetrachloride containing 10 to 20% of the latter. The mixture was in a one-liter, round-bottomed flask and had above it 600 cc. of a 10% solution of ammonium sulfate. The flask was closed with a cork stopper carrying the wide delivery tube for the chlorine and a second glass tube connected with rubber tubing to the bottom of a 2.5-liter bottle to collect a slight amount of chlorine which might escape absorption. The chloroform and ammonium sulfate solution were shaken vigorously during the half hour required to generate the gas. The solution warms somewhat but if it is cool at the beginning this does no harm. The ammonium sulfate solution was poured off and the chloroform solution transferred to a 500cc. bottle and shaken for five minutes with a 5% solution of ammonium sulfate. After separating, this was repeated. The solution was then separated sharply, dried with a few grams of powdered calcium chloride and filtered on a dry filter.

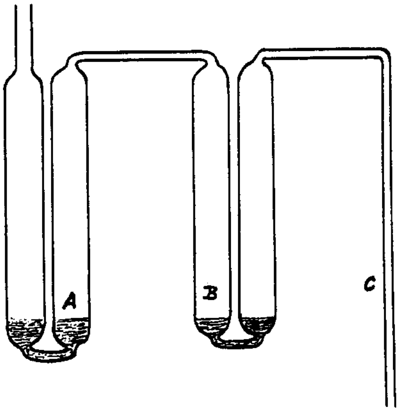

Fig. 1.

The solution prepared in this manner contains about 12% of the nitrogen trichloride, or one millimole per gram. If any unused portion is kept in the dark and in contact with a 5% solution of ammonium sulfate, there is little loss in strength for some days. It should be shaken vigorously with the sulfate solution before use.

Solutions as concentrated as 18% have been prepared and Hentschel's[18] statements seem to indicate that there is no danger of explosion in working with such concentrations.

Analysis.—Three to five-tenths of a gram of the solution was weighed in a U-tube having a capacity of less than 1 cc. and drawn out at right angles, on one side, to a small, thin capillary. The contents of the tube was transferred to A of the double U-tube shown in Fig. 1. A contained 2 cc. of concentrated hydrochloric acid and B, 0.5 cc. of water. The tube C dipped beneath the surface of 15 to 20 cc. of a 10% solution of potassium iodide. A slow current of air was passed through the apparatus until the chloroform was all evaporated and the liberated chlorine was swept out into the iodide solution.

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[17] Noyes, This Journal, **47**, 2162 (1925).

[18] Hentschel, *Ber.*, **30**, 1434 (1897).

The iodine was titrated with $N/10$ sodium thiosulfate, the hydrochloric acid solution was neutralized with 10 cc. of 30% potassium hydroxide and the ammonia distilled over into $N/10$ hydrochloric acid. The equation for the reaction is

$$NCl_3 + 4HCl = NH_4Cl + 3Cl_2$$

If the nitrogen trichloride is pure and free from chlorine, the volume of thiosulfate used will be 6 times the volume of the $N/10$ hydrochloric acid. Any excess of thiosulfate furnishes a determination of the free chlorine present.

Nitric oxide was prepared by dropping sulfuric acid (1:1) into a 25% solution of sodium nitrite[19] and the gas was kept in an aspirator bottle having a capacity of 3.5 liters.

Technique of the Experiments.—A weighed quantity of the nitrogen trichloride solution, containing in different experiments from 28 to 82 millimoles, was introduced through D (Fig. 2) into the bulb F. B was connected with an aspirator bottle containing nitrogen purified by passing it through an acid solution of chromous chloride to remove a trace of oxygen, through a tower containing soda lime and through an effective wash bottle containing concd. sulfuric acid.

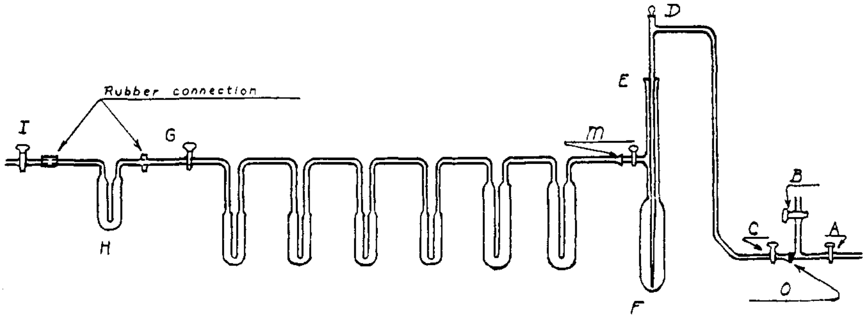

Fig. 2.—Ground glass joints at O, E and M.

After immersing F in a Dewar cylinder containing carbon dioxide-snow and acetone, the apparatus was evacuated with a good mechanical pump connected with I. By closing C and opening B, the T-tube was filled with nitrogen and after closing B and opening C this was pumped out. A few repetitions removed the small amount of oxygen remaining in the apparatus. The stopcocks m, G and I were then closed and nitric oxide was admitted through A. In many of the experiments nearly 3 liters of nitric oxide was admitted and the products absorbed without opening the stopcock m. The bottle containing the nitric oxide had been calibrated and the amount used was determined with an accuracy of 1 to 2%.

After introducing the gas, the apparatus was allowed to stand for an hour or more to permit the last of the nitric oxide to react with the nitrogen trichloride or chlorine present in the bulb. After this a variety of methods was used for separating and analyzing the products. The best of these is now thought to be the following.

The U-tube nearest to the bulb and U-tube H were immersed in liquid air, the U-tubes having all been evacuated. With the stopcocks I and G closed and m open, the nitrous oxide formed and some of the nitrosyl chloride and chlorine began to distil into the first U-tube. With the mechanical pump connected beyond I continually working, the stopcock G was opened and after closing it I was opened momentarily to allow nitrogen which had passed into U-tube H to escape. By this method a good

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[19] Noyes, This Journal, **47**, 2170 (1925).

vacuum was maintained with only a very slight loss of nitrous oxide. The solution in F was allowed to warm up to −20° and a very slow current of nitrogen admitted through B. After the nitrous oxide and some of the chlorine and nitrosyl chloride had condensed in the first U-tube, the liquid air was transferred to the second and a carbon dioxide–acetone cylinder placed around the first. When a considerable part of the chlorine and nitrosyl chloride had been distilled, the stopcock m was closed and the bulb F was cooled again to −80°.

In many of the earlier experiments the condensed gases were distilled and analyzed without contact with air in the endeavor to get evidence for the possible presence of nitrogen dichloride or monochloride. After many analyses had demonstrated that these compounds are absent or present in very small amounts, the manipulation was changed at this point and in subsequent experiments air was admitted to the U-tubes through I and G, the liquid air was transferred from the second to the third U-tube and the carbon dioxide–acetone to the second and a freezing mixture of ice and hydrochloric acid, giving a temperature of −20°, was placed around the first. By judicious use of these temperatures, it was possible to fraction the mixture through the tubes and finally secure all the nitrous oxide in U-tube H with comparatively little chlorine or nitrosyl chloride. The U-tube was disconnected, weighed quickly to about 0.01 g. (corresponding to about $^1/_4$ millimole of nitrous oxide) and the condensed gases were allowed to evaporate through an efficient wash bottle containing potassium hydroxide. The chlorine and nitrogen (from the nitrosyl chloride) were determined and by subtracting these from the weight of the contents of the U-tube the weight of the nitrous oxide was known.

The chlorine and nitrosyl chloride remaining in the U-tubes were sometimes allowed to evaporate and condense in U-tube H, weighed and then permitted to evaporate through a solution of potassium hydroxide and in other cases allowed to evaporate directly through the solution.

After this, liquid air was placed about the last of the U-tubes and the air in the tubes was removed by the pump. By opening m the remaining chlorine, nitrosyl chloride and chloroform were distilled back into bulb F. The contents of F was then hydrolyzed with ice water, the aqueous solution was analyzed for nitrogen and chlorine and the chloroform–carbon tetrachloride solution for chlorine and unchanged nitrogen trichloride. The results were calculated in milligram moles of the nitrogen trichloride which reacted or decomposed, of the nitric oxide used and in millimoles of the nitrous oxide and nitrosyl chloride and miligram atoms of the chlorine formed. In the table the results have been recalculated in ratios to one mole of nitrogen trichloride reacting or decomposed. From nearly 100 experiments, 23 performed after the technique and the methods of analysis had been pretty well developed are recorded.

The nitrous oxide, which had previously been found in a former investigation, from the action of phosphorus pentoxide on nitric oxide,[17] was identified by its effect on a glowing splinter, by condensation with liquid air and evaporation at −80° and by its molecular weight, 44.4.

The experiments with petroleum ether suggest that either an intermediate compound, $NCl_3 \cdot NO$, is formed, which decomposes directly to nitrous oxide and chlorine, or that hydrochloric acid formed by the action of nitrogen trichloride on petroleum ether[20] catalyzes the reaction

$$NCl_3 + NOCl = N_2O + 2Cl_2$$

That the second explanation is true was demonstrated by passing nitric

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[20] Coleman and Noyes, This Journal, **43**, 2211 (1921).

Table I

Molecular Ratios

Solvent, $CHCl_3 + CCl_4$

NCl_3 recovered	NCl_3 reacting	NO	N_2O	NOCl	Cl	Temp., °C.
0	1	0.59	0.06	0.44	2.45	0
0	1	0.97	.09	.79	1.91	0
0	1	1.26	.11	.63	2.05	0
0	1	0.81	.28	.11	2.30	− 20
0.43	1	1.01	.38	.35	2.05	− 80
.37	1	1.36	.51	.75	2.29	− 80
.46	1	1.69	.54	.67	2.39	− 80
.19	1	1.84	.55	.71	2.32	− 80
.04	1	2.05	.82	.86	1.97	− 80
.27	1	2.37	.89	1.19	1.66	− 80
.06	1	2.09	.90	0.93	1.86	− 80
.11	1	2.13	.83	1.06	1.90	− 80
.06	1	2.32	.85	1.28	1.74	− 80
.38	1	2.46	.89	1.13	1.53	− 80
.14	1	2.73	.91	1.28	1.00	− 80
.05	1	2.94	1.06	1.54	1.01	− 80
.09	1	2.96	0.94	1.50	0.98	− 80
0	1	3.26	1.09	1.86	1.00	− 80
0	1	3.37	1.01	1.49	1.45	− 80
0	1	3.41	1.04	2.12	0.96	− 80
Solvent, petroleum ether						
0.99	1	0.66	0.77	0	0.90	−130
.71	1	1.44	1.03	0.01	2.15	−140
.16	1	1.03	0.98	.01	2.11	− 80

oxide into a chloroform–carbon tetrachloride solution of the trichloride until the trichloride present was exhausted and removing the nitrous oxide formed. More of the trichloride solution was then added and the mixture was allowed to stand for twenty hours at −80°; 5.5 milligram moles of nitrous oxide was formed. Three-tenths g. of hydrochloric acid was now added. After eighteen hours at −80°, 10.5 milligram moles of nitrous oxide was found and the trichloride was all exhausted, demonstrating that the acid catalyzes the reaction, as had been suspected.

Discussion

A rational explanation of the results is based on the following considerations.

1. Nitrogen trichloride is an endothermic compound which decomposes readily to nitrogen and chlorine. This means that the affinities of nitrogen for nitrogen and of chlorine for chlorine are much greater than the affinity of nitrogen for chlorine. Thermodynamically, it may be stated that the energy liberated when two isolated nitrogen atoms unite to form molecular nitrogen and six isolated atoms of chlorine unite to

form three molecules of chlorine is very much greater than the energy liberated when two isolated atoms of nitrogen combine with six isolated atoms of chlorine to form two molecules of nitrogen trichloride. It may be worth while to notice that our ignorance of the reason for these relations and, indeed, of the source of the energy liberated when atoms unite is still very profound.

2. Nitrogen readily forms compounds containing odd electrons, which are stable at ordinary and even at high temperatures but which react readily at low temperatures. Nitric oxide, $\cdot\overset{\cdot\cdot}{N}::\underset{\cdot\cdot}{\overset{\cdot\cdot}{O}}$, is an endothermic compound and even at 3000° the equilibrium is far on the side toward its decomposition; but nitric oxide will combine with oxygen to form nitrous anhydride even at the temperature of liquid air. The decomposition of nitrogen tetroxide, N_2O_4, to nitrogen dioxide, NO_2 (probably $\underset{\underset{\cdot\cdot\,-}{:O:}}{\cdot\underset{\cdot\cdot}{N}}\underset{+}{:}:\underset{\cdot\cdot}{\overset{\cdot\cdot}{O}}$), begins at ordinary temperatures.

3. At 0°, 90% of the nitrogen trichloride decomposes to nitrogen and chlorine. The reaction is evidently catalyzed by the nitric oxide or the nitrosyl chloride.

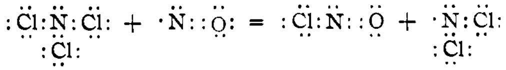
4. At −20° the reaction $NOCl + NCl_3 = N_2O + 2Cl_2$, which occurs slowly at −80° (see above), increases the amount of nitrous oxide and decreases the nitrosyl chloride present at the end.

5. At −80°, in chloroform–carbon tetrachloride, the results indicate that the normal course of the reaction corresponds to the equation $NCl_3 + 2NO = N_2O + NOCl + Cl_2$. This equation represents a trimolecular reaction and it seems much more probable that the action takes place in two stages. An intermediate stage in which nitrosyl chloride reacts with nitrogen trichloride is excluded by the slowness of that reaction at −80°, by the fact that two moles of nitric oxide are required before the trichloride is exhausted and because more than one mole of nitrosyl chloride is formed for each mole of nitrous oxide in every case except one. The excess must be due to the union of nitric oxide with chlorine.

The most probable steps seem to be the following: $NCl_3 + NO = NOCl + NCl_2$; $NCl_2 + NO = N_2O + Cl_2$.

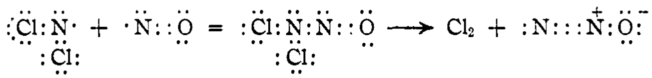
As already stated, many attempts have been made to isolate the nitrogen dichloride. The speed of the reaction between the dichloride and nitric oxide is evidently very great, as might be expected for two compounds with odd electrons.

In the primary reaction an atom of chlorine with an odd electron must separate from the nitrogen trichloride



$$:\underset{\cdot\cdot}{\overset{\cdot\cdot}{Cl}}:\underset{\underset{\cdot\cdot}{:\overset{\cdot\cdot}{Cl}:}}{\overset{\cdot\cdot}{N}}:\underset{\cdot\cdot}{\overset{\cdot\cdot}{Cl}}: + \cdot\overset{\cdot\cdot}{N}::\underset{\cdot\cdot}{\overset{\cdot\cdot}{O}}: = :\underset{\cdot\cdot}{\overset{\cdot\cdot}{Cl}}:\overset{\cdot\cdot}{N}::\underset{\cdot\cdot}{\overset{\cdot\cdot}{O}} + \cdot\underset{\underset{\cdot\cdot}{:\overset{\cdot\cdot}{Cl}:}}{\overset{\cdot\cdot}{N}}:\underset{\cdot\cdot}{\overset{\cdot\cdot}{Cl}}:$$

The second reaction may be represented electronically



$$:\overset{..}{\underset{..}{Cl}}:\underset{:\underset{..}{Cl}:}{\overset{..}{N}}\cdot + \cdot\overset{..}{N}::\overset{..}{\underset{..}{O}} = :\overset{..}{\underset{..}{Cl}}:\underset{:\underset{..}{Cl}:}{\overset{..}{N}}:\overset{..}{N}::\overset{..}{\underset{..}{O}} \longrightarrow Cl_2 + :N:::\overset{+}{N}:\overset{..}{\underset{..}{O}}:^{-}$$

The formula for nitrous oxide is supported by the following facts and considerations.

The parachors of nitric acid and nitro compounds indicate a semipolar union in these compounds;[21] the parachor of alkyl cyanides and also the hydrolysis of these cyanides to organic acids and ammonia indicate a triple covalence between carbon and nitrogen and that such a triple covalence is a stable form of combination for nitrogen; the extreme unreactivity of molecular nitrogen points to a very stable tripe covalence, $:N:::N:$. The ease with which nitrous oxide gives its oxygen to a glowing splinter indicates that the oxygen is in a reactive form and also that the molecule already approaches the structure of the nitrogen molecule; the decomposition of an alicyclic diazo compound to form nitrogen and an azo compound[22] and the ready decomposition of all diazo compounds, $R_2\underset{-}{C}:\underset{+}{N}:::N:$ or $R:\underset{+}{N}:::N:$, show that compounds whose structure approaches that of molecular nitrogen readily go over to that.

Summary

1. At 0° the interaction of nitric oxide and nitrogen trichloride results, chiefly, in the catalytic decomposition of the trichloride to nitrogen and chlorine.

2. At $-20°$, about one-fourth of the nitrogen trichloride is converted to nitrous oxide and chlorine. The comparatively small amount of nitrosyl chloride found at this temperature is probably due to the interaction of nitrogen trichloride with the nitrosyl chloride formed in the primary reaction, giving nitrous oxide and chlorine.

3. At $-80°$ the reaction proceeds chiefly in accordance with the equation $NCl_3 + 2NO = N_2O + NOCl + Cl_2$.

4. Reasons are given for believing that this reaction occurs in two steps with the intermediate formation of nitrogen dichloride, although attempts to isolate this compound have not been successful.

5. The structure of nitrous oxide is probably $:\overset{-\,..}{\underset{..}{O}}:\overset{+}{N}:::N:$, with a semipolar union between the oxygen and nitrogen atoms. Facts and considerations are given in support of this formula.

6. In petroleum ether at -130 to $-140°$ the reaction follows the course $NCl_3 + NO = N_2O + 3/2Cl_2$.

The hydrochloric acid formed by the action of the trichloride on the

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[21] Sugden, *J. Chem. Soc.*, **125**, 186 (1924).

[22] Noyes and Coss, THIS JOURNAL, **42**, 1280 (1920); Noyes and Kendall, *ibid.*, **48**, 2406 (1926).

petroleum ether catalyzes the reaction between nitrogen trichloride and nitrosyl chloride referred to in 2.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE GEOPHYSICAL LABORATORY, CARNEGIE INSTITUTION OF WASHINGTON]

RADIUM AND GEOLOGY[1]

BY CHARLES SNOWDEN PIGGOT

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This article is a brief account of the general problem of the relation of radioactivity to geologic phenomena and of some of the experimental results so far obtained by the author in this field of investigation.

As soon as the experiments of Strutt (Lord Rayleigh) and Joly had revealed the apparently universal distribution of radium and its associated disintegration products throughout the lithosphere and perhaps throughout the entire earth, and when the work of Rutherford, Curie and others had demonstrated the extraordinary properties of these substances, it immediately became a subject of speculation as to the significance of so universal and so powerful an agent on the great earth phenomena which were known to have taken place.

The general problem has three main subdivisions:

1. The determination of the radium content of, and its distribution throughout, the lithosphere, and possibly an estimation of the amount and distribution throughout the earth.
2. The heat energy made available for the melting of the sub-crustal structure and its role in mountain building.
3. The radioactive disintegration of uranium into lead and its application to the determination of geologic time.

Since the problem was taken up by this Laboratory, there has not been time for the accumulation of any great quantity of data, but a satisfactory apparatus and technique have been developed and a number of measurements made in each of the above subdivisions.

Determination of Radium in Rocks.—For measuring the radium in ordinary rocks, where the quantity is of the order of 10^{-12} grams per gram of rock, the determination was made by decomposing the rock by fusing with a flux, collecting the radium emanation thereby liberated, and determining it by means of an electroscope.[2]

Calibration was accomplished by making a number of runs on a rock alone, and then another series, identical in every respect except that a

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[1] In memory of Ira Remsen.

[2] A detailed description of the apparatus and technique, including drawings, dimensions, etc., will appear shortly in the *American Journal of Science*.