CCXXVIII.—*The Rate of Combination of Gaseous Nitric Oxide and Chlorine. Part I.*

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THE direct union of nitric oxide and chlorine was first observed in 1848 by Gay Lussac (*Ann. Chim. Phys.*, [iii], **23**, 203), who proved the composition of the orange-coloured gaseous product by measuring the contraction that took place when two bulbs containing nitric oxide and chlorine respectively were put in communication with each other. The decrease of pressure was observed by means of a mercury manometer attached to the nitric oxide bulb, but no mention was made of the rate of contraction. A repetition of this rough experiment showed that the velocity of the reaction was sufficiently slow at the ordinary temperature to be quantitatively followed.

The accurate measurement of this reaction velocity is clearly of considerable interest and importance. According to the equation:

$$2NO + Cl_2 = 2NOCl,$$

the reaction should be one of the third order. The number of gas reactions of which the kinetics have been thoroughly studied is by no means large; only a very few have been stated to be of the third order, and these are for the most part reactions which proceed at high temperatures and are subject to irregularities due to the influence of the walls of the containing vessel.* The oxidation of nitric oxide at the ordinary temperature was found by Bodenstein and Meinecke (*Zeitsch. Elektrochem.*, 1910, **16**, 876) to be a gas reaction of the third order.

The interaction of nitric oxide and chloride, being rapid at low temperatures, is likely to be "pure" and free from irregularities. Further, like many reactions in which chlorine takes part, it may be photosensitive. Briefly stated, the chief result of the experiments described in this communication is that the reaction is of the third order, when measured at the two temperatures, 0° and 14·8°.

At the time this investigation was begun (January, 1913) the authors were not aware of any recent work on the subject, and the results given in this paper formed the subject of a thesis presented in June, 1913, to the University of Birmingham. Publi-

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* See, for example, Bodenstein (combination of hydrogen and oxygen), *Zeitsch. physikal. Chem.*, 1899, **29**, 665; Bodländer and Köppen (oxidation of sulphur dioxide), *Zeitsch. Elektrochem.*, 1903, **9**, 559; Kühl (oxidation of carbon monoxide), *Zeitsch. physikal. Chem.*, 1903, **44**, 385.

cation was deferred until the work had been brought into a more complete state. Quite recently, however, the authors' attention has been called to a paper by M. Trautz (*Zeitsch. Elektrochem.*, 1914, **20**, 325, (abstract); *Sitzungsber. Heidelberger Akad. Wiss.*, Abt. A, Abh. 1, Jan., 1914), who has, it appears, also investigated the velocity of formation of nitrosyl chloride. He quotes, further, some work on the same subject by Kiss Arpád ("A nitrogen oxyd és chlor egymásra hatásának sebességéröl." *Diss.*, Budapest und Magyar Chemikusok, Lapja, 1913. Évi 7—8), whose paper has appeared in the Hungarian language only. Both of these investigators arrive at the same general conclusion as the authors, namely, that the reaction is termolecular; it appeared, therefore, advisable to publish at once the first results, reserving those of the experiments now in progress for a second communication.

EXPERIMENTAL.

In principle the method adopted was as follows: A known quantity of nitric oxide was injected very rapidly through a capillary tube into a bulb containing a known quantity of chlorine. This bulb was connected with a protected mercury manometer, so that the rate of diminution of pressure at constant volume could be readily measured. The use of a mercury manometer is, of course, rendered difficult by the fact that chlorine and nitrosyl chloride rapidly attack mercury. Protection by a short column of syrupy phosphoric acid or sulphuric acid was unsatisfactory as the liquid not only retarded the motion of the mercury but also did not completely protect it. The interposition of a cushion of nitrogen between the reaction bulb and manometer was found to afford a much better, although not a complete, protection. The best way out of this difficulty lies in the employment of a quartz manometer free from mercury, and this plan has been adopted in the most recent experiments (not described in this paper).

For the lubrication of stopcocks in contact with the reactive gases both phosphoric acid (prepared by Chapman and Gee's method, T., 1911, **99**, 1736) and a special lubricant recommended by Guye* (*J. Chim. Phys.*, 1908, **6**, 756) and by Wourtzel (*J. Chim. Phys.*, 1913, **11**, 31) were used. The latter consisted of a mixture of paraffin and stearin which had been repeatedly saturated with chlorine and heated in a vacuum; although it required fairly frequent renewal it had the advantage of allowing one to turn the stopcocks more quickly than could be done with phosphoric acid. Further, phosphoric acid was not entirely free from attack.

Preparation of Gases.—The chlorine was prepared from pure

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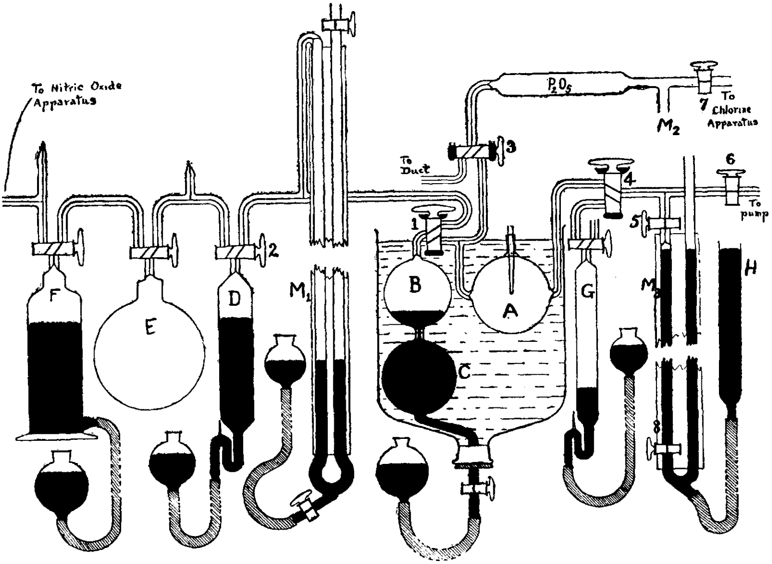
* We are indebted to Prof. P. A. Guye for a small sample of this lubricant.

potassium permanganate and hydrochloric acid, washed with permanganate solution, copper sulphate solution, and concentrated sulphuric acid, and finally dried by means of phosphoric oxide.

The nitric oxide was prepared by dropping 50 per cent. sulphuric acid into a concentrated solution of potassium iodide and sodium nitrite in molecular proportions. Acid impurities were removed by passing the gas through concentrated potassium hydroxide solution and over the solid alkali, and it was finally dried by phosphoric oxide. Owing to the impossibility of storing nitric oxide over water, with which it reacts with the formation of nitrogen (Moser, *Zeitsch. anal. Chem.*, 1911, **50**, 401), it was collected in a 3-litre glass balloon (*E*). After repeatedly exhausting the generating apparatus and balloon and washing out with nitric oxide, the gas was passed into a mercury gas-holder (*F*), from which it was forced into the balloon until the pressure in the latter was about two atmospheres.*



Description of the Apparatus.—The reaction vessel *A* consisted of a glass bulb of 240·5 c.c. capacity, at the centre of which was situated a thermocouple of platinum and platinum–rhodium alloy, the wire being completely protected by a very thin layer of glass. The couple was connected in the usual way with a sensitive moving-

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* A freshly made solution of ferrous sulphate absorbed 99·9 per cent. of a sample of this gas.

coil galvanometer, and the spot of light moved over about 20 scale divisions for a temperature difference of 1°. Although the bulb was kept in melting ice, the temperature always rose rapidly to a maximum on mixing the gases, then gradually fell again. A glance at the tables will show the general course of the temperature change. The temperature at the centre of the bulb rises somewhat higher than that at the cold walls; however, in the calculations a uniform temperature equal to that at the centre has been assumed.

The bulb *A* was connected by the shortest possible length of capillary tubing through a mercury-protected three-way stopcock 1 to a pair of glass bulbs, *B* and *C*, of which *C* was slightly the larger. The volume of *B* from the stopcock to a mark on the tube connecting *B* and *C* was 211·0 c.c. The bulb *C* was interposed between *B* and the mercury reservoir in order that the mercury entering *B* should not warm the gas above it. The bulbs *A*, *B*, *C* were completely immersed in a bath of water or melting ice, whilst the capillary between *B* and *A* was almost entirely immersed. The third arm of the three-way stopcock 1 was connected with a mercury manometer M_1, and through a three-way stopcock 2 with a reservoir *D*, which served to adjust the pressure in *B* to any desired value. *D* was further connected as shown with the balloon *E* of nitric oxide, which was joined to the auxiliary reservoir *F* and the apparatus for generating nitric oxide. For the admission of chlorine to the bulb *A*, a branch capillary led from that connecting *A* and *B* through a three-way stopcock 3 and a tube of phosphoric oxide to a mercury manometer M_2 (not drawn in the figure), protected from attack by a layer of concentrated sulphuric acid, and then to the apparatus for generating and purifying chlorine. The reaction bulb *A* was further provided with a capillary exit which served for exhaustion and for measuring the pressure of the reacting gases. It was connected with a three-way stopcock 4, one arm of which led to a reservoir of nitrogen *G*, whilst the other was joined to a mercury manometer, M_3, and a Toepler pump protected by mercury and sticks of potassium hydroxide. The manometers had a bore of 7 mm., and were provided with mirror scales. After fitting together, the apparatus was well dried by heating and long-continued washing with dry air under diminished pressure.

After exhausting, washing out with nitric oxide, and sealing off the tube connecting *E* and *D*, and filling the system *D*, M_1, *B*, *C* with mercury, nitric oxide was passed into *D*, and thence into *B*. The mercury surface was fixed at the mark on the tube joining *B* and *C*, and the pressure in *B* adjusted to the required value by moving the mercury in *D*.

Generation of chlorine was begun several hours before the commencement of an experiment; it was allowed to escape at the stopcock 3, and a sample of the gas (about 70 c.c.) taken immediately before an experiment was completely absorbed by concentrated aqueous potassium hydroxide. The bulb *A* and connecting tubes (previously well dried) were exhausted several times and washed out before finally filling with chlorine, the stopcock 5 being closed and M_3 completely filled with mercury. For the purpose of adjusting the pressure of chlorine in *A*, 4 being closed, 3 was opened, then 7 was very carefully opened until the pressure as indicated by M_2 was that desired or slightly in excess thereof; in the latter case the pressure could be reduced to the correct value by very slightly opening 4 and 6, 3 being now closed. The space between 4, 6, and 5 was then exhausted and filled with nitrogen from *G*. The pressure in *A* was finally checked by fixing the pressure of the nitrogen at the value that should obtain in *A* (5 and 8 being open), and then putting *A* and M_3 into communication through 4; no movement of the mercury in M_3 should be observed. After closing 4 the pressure above M_3 was adjusted as nearly as possible to the value that would obtain in *A* after the addition of nitric oxide and at the time observations of the diminishing pressure would be commenced. A fair approximation could be made after a little experience. The mercury meniscus in M_3 was not more than 5 mm. from the capillary continuation, so that the dead space containing nitrogen had a volume of not more than about 0·5 c.c. *B* having been filled with nitric oxide at known pressure as previously described, mercury was allowed to enter the bulb until the pressure was nearly two atmospheres. Then, at a given time signal, *B* and *A* were put into communication through 1; nitric oxide was thus very rapidly injected into *A*, and after a little practice the rising mercury in *B* could be stopped in the capillary near the stopcock, which was quickly closed.

This process of mixing occupied as a rule about ten to fifteen seconds. The "time of mixing" ($t=0$) was taken as the mean of the times of opening and closing the stopcock 1. However, this indefiniteness in the "time of mixing" became inappreciable at the time at which trustworthy pressure measurements were commenced.

Immediately after closing 1, 4 and 5 were opened, then 8 was very carefully opened slightly, the direction in which the meniscus began to move noted, and the reservoir *H* quickly adjusted until a position was found such that 8 could be completely opened without causing a movement of the meniscus of more than one or at the most two mm. from its initial position. Then, as the pressure in *A* decreased, so the reservoir *H* was steadily lowered in such a way that the mercury meniscus below 5 remained in a fixed position; this could be done quite satisfactorily after a little practice. Readings of the right-hand limb of the manometer were begun as early as possible (usually about a minute after mixing), and taken throughout at given time signals. Another observer took time and temperature readings. When the mercury meniscus began to show signs of corrosion, the gas above it was rapidly replaced by nitrogen by closing 4 and 8, exhausting, admitting nitrogen from *G*, and finally reducing the pressure to that which obtained in *A* (estimated by extrapolation). Stopcock 4 was then opened again, and pressure readings continued. This operation was usually repeated two or three times during one experiment.

In the experiments here recorded the nitric oxide and chlorine were taken in equivalent proportions (two molecules of nitric oxide to one of chlorine). The initial partial pressure of the chlorine was about a third, whilst that of the nitric oxide was about two-thirds of an atmosphere, so that the initial concentrations of the two gases from the point of view of the law of mass action were equal, namely, a third of an atmosphere. Velocity constants were calculated by means of the integrated equations for reactions of the first, second, and third orders, namely,

$$K_1 = \frac{1}{t}\log\frac{p_0}{p}\,;\ K_2 = \frac{1}{t}\cdot\frac{p_0-p}{p_0p}\,;\ K_3 = \frac{1}{2t}\left(\frac{1}{p^2}-\frac{1}{p_0^2}\right),$$

where p_0 is the initial partial pressure and p the partial pressure of the chlorine at any time t. The pressure loss π is equal to the difference between the initial total pressure (P_0) and the total pressure observed at any time (P), ($\pi = P_0 - P$), and the partial pressure of the chlorine at that time is $p = p_0 - \pi$.

In this method of procedure the validity of the simple gas law has been tacitly assumed; this introduces a slight error in the case of the chlorine, and a somewhat greater one as regards the nitrosyl chloride, but in this series of experiments they have been neglected as commensurate with the experimental errors.

The observed total pressure was corrected from the observed temperature to that of the bath before using for the calculation of the velocity constant. The following four tables give the results of three experiments at 0° and one at 14·8°. The second column gives the temperature indicated by the thermocouple, and the last gives the percentage (x) of the reaction completed ($x = 100\pi/p_0$). There is reason to believe that the results expressed in table I are somewhat less trustworthy than those that follow.

TABLE I.

Vol. of bulb A = 240·5 c.c. Temperature = 0°.
Vol. of bulb B = 205·0 c.c. Barometer = 753·4 mm.
Pressure of nitric oxide in B = 593·3 mm.
Initial pressure of chlorine in A = 252·8 mm.
Initial pressure of nitric oxide in A = 505·7 mm.

t. (mins.).	T°.	P. mm.	p. mm.	$K_1 \times 10^2$.	$K_2 \times 10^4$.	$K_3 \times 10^6$.	x per cent.
0·0	0·0	[758·5]	[252·8]	—	—	—	0
2·3	3·9	676·4	161·3	8·5	9·8	4·95	36
3·0	3·1	662·9	149·9	7·6	9·0	4·81	41
3·75	2·5	651·9	140·3	6·8	8·4	4·70	44
4·5	2·15	642·9	132·2	6·3	8·0	4·62	48
5·5	1·8	633·5	123·5	5·7	7·5	4·54	51
6·75	1·5	623·4	114·3	5·1	7·1	4·51	55
8·5	1·1	612·5	104·2	4·5	6·6	4·50	59
11·0	0·8	602·0	94·2	3·9	6·0	4·41	63
14·0	0·7	592·5	85·1	3·4	5·6	4·37	66
17·0	0·6	584·5	77·7	3·0	5·2	4·41	69
20·0	0·45	578·4	71·7	2·7	5·0	4·47	72
27·0	0·3	568·5	62·2	2·3	4·5	4·50	75
46·0	0·2	552·6	46·4	1·6	3·8	4·88	82
67·0	0·1	543·3	37·3	1·2	3·4	5·25	85

TABLE II.

Vol. of bulb A = 240·5 c.c. Temperature = 0°.
Vol. of bulb B = 211·0 c.c. Barometer = 749·1 mm.
Pressure of nitric oxide in B = 578·0 mm.
Initial pressure of nitric oxide in A = 507·1 mm.
Initial pressure of chlorine in A = 253·6 mm.

t. mins.	T°.	P. mm.	p. mm.	$K_1 \times 10^2$.	$K_2 \times 10^4$.	$K_3 \times 10^6$.	x per cent.
0·0	0·0	[760·7]	[253·6]	—	—	—	0
3·0	2·8	672·1	156·8	6·9	8·1	4·19	38
3·5	2·4	665·1	152·2	6·4	7·5	3·95	40
4·25	1·95	653·1	141·2	5·9	7·4	4·08	44
8·5	1·05	619·4	110·8	4·2	6·0	3·88	56
9·5	0·9	614·0	105·1	4·0	5·9	3·95	59
12·5	0·7	602·9	94·2	3·4	5·3	3·90	63
14·5	0·6	595·9	87·6	3·2	5·1	3·96	65
18·5	0·5	585·8	77·7	2·8	4·8	4·05	69
22·5	0·4	579·2	71·4	2·4	4·5	4·01	72
26·5	0·3	573·7	65·9	2·2	4·2	4·06	74
32·5	0·25	566·5	58·8	2·0	4·0	4·20	77
40·5	0·2	560·3	52·8	1·7	3·7	4·23	79
59·0	0·2	550·4	42·9	1·3	3·3	4·55	83
72·5	0·1	545·4	38·0	1·1	3·1	4·66	85

TABLE III.

Vol. of bulb A = 240·5 c.c. Temperature = 0°.
Vol. of bulb B = 211·0 c.c. Barometer = 751·3.
Pressure of nitric oxide in B = 584·0 mm.
Initial pressure of nitric oxide in A = 512·3 mm.
Initial pressure of chlorine in A = 255·3 mm.

t. mins.	T°.	P. mm.	p. mm.	$K_1 \times 10^2$.	$K_2 \times 10^4$.	$K_3 \times 10^6$.	x per cent.
0·0	0·0	[767·6]	[255·3]	—	—	—	0
3·0	2·75	675·1	156·2	7·1	8·3	4·27	39
3·5	2·35	666·0	148·2	6·7	8·3	4·31	42
4·5	1·80	652·0	135·2	6·1	7·8	4·37	47
5·0	1·65	647·0	130·7	5·8	7·4	4·32	49
6·0	1·35	638·5	122·8	5·3	7·0	4·25	52
8·0	1·00	624·5	109·9	4·5	6·5	4·21	57
10·0	0·75	613·8	99·7	4·1	6·1	4·26	61
12·0	0·65	605·3	91·6	3·7	5·8	4·32	64
15·0	0·50	596·3	82·9	3·3	5·4	4·35	68
20·0	0·35	584·8	71·7	2·8	5·0	4·47	72
31·0	0·20	571·0	58·2	2·1	4·2	4·51	77
57·0	0·10	555·0	42·5	1·4	3·5	4·70	83

TABLE IV.

Vol. of bulb A = 240·5 c.c. Temperature = 14·8°.
Vol. of bulb B = 211·0 c.c. Barometer = 755·3 mm.
Pressure of nitric oxide in B = 582 mm.
Initial pressure of nitric oxide in A = 510·6 mm.
Initial pressure of chlorine in A = 255·3 mm.

t. mins.	T°.	P. mm.	p. mm.	$K_1 \times 10^2$.	$K_2 \times 10^4$.	$K_3 \times 10^6$.	x per cent.
0·0	14·8	[765·9]	[255·3]	—	—	—	0
1·5	20·5	698·3	174·3	11·1	12·1	5·86	32
2·0	18·3	681·5	162·6	9·8	11·0	5·62	36
3·0	17·0	658·3	142·7	8·4	10·0	5·62	44
4·0	16·4	641·5	127·3	7·6	9·8	5·80	50
6·0	15·7	621·8	109·3	6·1	8·7	5·70	57
9·0	15·3	603·3	91·6	4·9	7·7	5·77	64
14·0	15·0	587·5	76·2	3·8	6·6	5·60	70
20·0	14·8	574·5	63·7	3·0	5·9	5·78	75
28·0	14·8	564·7	54·1	2·4	5·2	5·82	79
118·0	14·8	535·1	24·5	0·9	3·1	7·00	90

Trustworthy readings could not as a rule be made during the first third of the reaction on account of its rapidity. The values of K_1 and K_2 show a distinct drift throughout, whilst those of K_3 remain very fairly constant until about three-quarters of the reaction is over, when they begin to increase. Assuming the reaction to be of the third order, this increase in the constant indicates that the pressure in A is decreasing too rapidly; for example, in table III, at 31 minutes P(corr.) = 570·5 mm., whereas assuming $K_3 = 4{\cdot}3 \times 10^{-6}$, it should be 572 mm. This is doubtless due to attack of the mercury, which, in spite of the precautions described, could not be entirely avoided; this effect naturally became more marked in the later stages of the reaction, and the constants began to increase at about the time when the mercury showed distinct signs of attack. Further, towards the end of the reaction the walls of the manometer tube in the neighbourhood of the mercury meniscus became dirty, making it more difficult to keep the meniscus at a fixed position. Owing to these disturbances satisfactory readings for the end of the reaction could not be obtained. Combination may be assumed to proceed to completion at the low temperatures employed. Only one trustworthy set of readings was obtained at a temperature above zero, namely, at 14·8°.

The mean values of the constants may be taken to be $5{\cdot}7 \times 10^{-6}$ at 14·8°, and $4{\cdot}2 \times 10^{-6}$ at 0°, expressed in units of mm. of mercury and minutes. They may be converted into units of gram-molecules per litre by means of the equation $VP/760 = nRT$, so that n/V mol. per litre$=P/(760 \times 0{\cdot}082T)$, where P is expressed in mm. of mercury, and V denotes volume in litres. The factor for converting K into units of molecules per litre is $(760 \times 0{\cdot}082T)^2$, and in these units K has the values 1216 and 1820 at 0° and 14·8° respectively. The constant is not in agreement with that given by Kiss Arpád (*loc. cit.*), who found $K_3 = 0{\cdot}262 \times 10^{-5}$ at 18° (in units of mm. of mercury). From the above-mentioned values of K it appears that the temperature-coefficient is very small (about 1·23 for an increase of temperature of 10°), and in consequence the effect on the reaction velocity of initial rise of temperature on mixing the gases is small. Trautz (*loc. cit.*) has calculated that, according to his theory of reaction velocities, the temperature-coefficient should lie between 0·98 and 1·44, and he considers the most probable value to be 1·15, which is in fair agreement with the experimental number given above.

Further experimental work is in progress which has for its object the more accurate determination of the velocity constant under varying conditions of temperature and concentration, and a study of the effect of light, of extreme dryness, and of the walls of the vessel. Special attention has been given to the purity of the gases, which have been prepared by fractionation of the liquids, and for pressure measurements a sensitive quartz spiral manometer has been constructed.

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