104. *The Kinetics of the Reaction between Chlorine and Nitric Oxide.*

By Eric M. Stoddart.

Previous experiments have shown that this reaction is considerably influenced by surface conditions, adsorption of the nitrosyl chloride formed during the reaction inhibiting the change. The present work shows that the velocity constant of the reaction ultimately diminishes from experiment to experiment, as well as during each experiment, owing to an ageing effect of the reaction vessel. The original state of the surface cannot be recovered by mere pumping or by baking under vacuum, although the latter procedure is more efficacious than the former. Drying prevents inhibition, and it is concluded that the ageing and inhibitory effects are due to the activated adsorption or chemisorption of nitrosyl chloride on the adsorbed moisture of the wall of the reaction vessel. Such a view would satisfactorily account for the kinetic equation previously employed.

In the previous paper (J., 1940, 823) the data reported for this reaction were obtained from two reaction vessels, one packed and one empty, both of which were used until the results were in agreement amongst themselves. It was thereby clearly indicated that the chlorine–nitric oxide reaction did not obey the termolecular law under the conditions of the experiment, and it seemed that the nitrosyl chloride formed in the reaction was able to inhibit it by being adsorbed on the wall of the reaction vessel; this proves that the reaction is, at least in part, heterogeneous. During this earlier work it had been observed that, when a reaction bulb was first brought into use, it gave comparatively high velocity constants, which diminished as the bulb was used until, eventually, reproducible and concordant results were obtained. This matter has now been carefully examined.

A reaction vessel of soda-glass was sealed into the apparatus in place of the older one (see previous paper). The new vessel was then pumped out for 4 hours by means of a mercury-vapour pump backed by a " Hyvac " pump. The gases were introduced as in the previous work, and the nitrosyl chloride and excess of the reagents were removed by means of an old Geryk pump protected against attack by alkali pellets; the final removal of gas was effected by the Hyvac pump similarly protected, followed by the employment of the mercury-vapour pump acting directly on the apparatus, without such protection, as this would cause considerable restriction to pumping.

The first five experiments carried out with the new vessel gave a steady velocity constant of $12{\cdot}0 \times 10^{-7}$ at 25°; a slight decrease of the velocity constant towards the end of the reaction was noted with the next two experiments, and in the eighth, the decrease was appreciable. The tabulated results of the experiments which followed show that the velocity constants diminish from experiment to experiment as well as during each experiment. After the twentieth experiment, the results were concordant, the initial values of k being $4{\cdot}5 \times 10^{-7}$, in agreement with those of the previous paper. When this bulb was employed for experiments at 15°, the initial value of k was $2{\cdot}2 \times 10^{-7}$, also as previously reported.

This falling off of the initial value of k is presumably due to the adsorption by the wall of some of the nitrosyl chloride, and the pumping carried out between successive experiments is evidently not able to remove the whole of this gas from the wall. There comes a time when conditions are reproducible from experiment to experiment because the state of the wall is always reattained, *i.e.*, the amount of nitrosyl chloride adsorbed by the wall is essentially the same at the beginning of successive experiments, the wall being almost saturated with the gas which is scarcely affected by the pumping.

Another new bulb was employed for the fifth series of experiments, which were carried out at 15°, very similar results being obtained. The first four experiments gave $k = 10{\cdot}6 \times 10^{-7}$ over the whole time range, but further use of the vessel gave results having a distinct fall in the value of k towards the end of each experiment. The initial velocity constant ultimately fell to $2{\cdot}2 \times 10^{-7}$ and then the bulb again gave reproducible experimental data, whether the temperature was at 15° or 25°, *i.e.*, the initial values of k were $2{\cdot}2 \times 10^{-7}$ and $4{\cdot}5 \times 10^{-7}$, respectively.

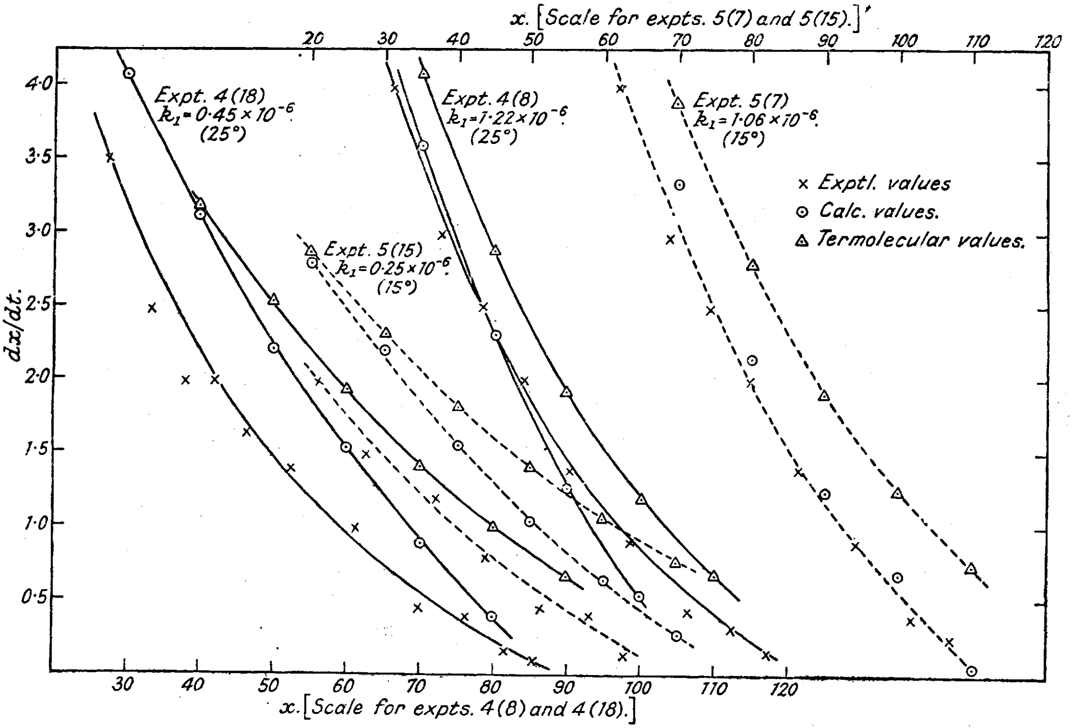
If the theory that not all the adsorbed nitrosyl chloride was removed from the wall by the pumping carried out at the end of each experiment is correct, it was thought that prolonged evacuation by means of a mercury-vapour pump, employing a vapour trap cooled to −80°, together with baking the reaction vessel until the glass collapsed slightly, might achieve complete removal of the adsorbed gas so that the initial value of the velocity constant was restored. The attempt was made on several occasions, but the effect of such treatment was always very small. The bulb used for the fifth series of experiments was treated in this fashion, the apparatus being arranged so that the thermostat bath could be lowered from the apparatus so as to allow the necessary manipulation to be carried out. Expt. 6A followed, and it is seen that baking under vacuum raised the velocity constants but did not effect complete restoration to the termolecular conditions. The bulb was then re-evacuated by means of the mercury-vapour pump for about 6 hours; baking could not be undertaken again with this bulb, since the glass was already considerably distorted. The results of expt. 6B show a general decrease in the velocity constants from those of expt. 6A, and it is clear that pumping alone is not able to effect the results achieved by baking under vacuum.

The bulb used for the fourth series of experiments was now washed out with a little dilute sodium carbonate solution to remove adsorbed nitrosyl chloride, washed with water, and dried in an oven; it was then sealed into place and evacuated by means of the mercury-vapour pump for about 4 hours. Expt. 7A which followed seemed to indicate that the alkali washing had been almost as effective as baking under vacuum. The bulb was baked before expt. 7B, carried out at 15°, whereupon it was again noted that such treatment could increase the value of the velocity constants.

The conditions at the end of each of these and the previous experiments are such as to cause the reaction to proceed very slowly. During the fourth and fifth series of experiments, it had been the practice to admit both the reactants to the reaction vessel at the end of the previous observations, and so measure the rate of reaction employing the poisoned reaction vessel with large concentrations of both reactants. It was found that the reaction velocity was not abnormally increased by the addition of more of the reactants. Rapid evacuation of the reaction vessel and admission of fresh reactants was also tried. It was found that if the evacuation can be completed in about two minutes, the velocity constant of the reaction is extremely low and of the order of that before evacuation. This clearly indicates that the inhibition is due to surface conditions existing towards the end of the reaction period and is in no way due to conditions in the gas phase.

An attempt was also made to see whether the reaction could be inhibited by either of the reactants or the resultant nitrosyl chloride. The reaction vessel was filled with one of the reactants and left for several days to attain equilibrium with the wall; the other reactant was then introduced, and the reaction velocity measured. No effect was detected when nitric oxide was introduced first, but with chlorine the effect was unmistakable. If the chlorine was allowed to enter the vessel about a week before reaction was allowed to take place, a distinct lowering of the velocity constant occurred, as shown in expts. 8A and 8B. It is evident that the adsorption of chlorine can inhibit the reaction to an additional extent, but its effect is very small compared with that of the nitrosyl chloride, since no effect is observed unless the chlorine is allowed to stand in the reaction vessel for several days before the experiment.

FIG. 1.



In the previous paper, an equation [(6), *loc. cit.*, p. 830] was deduced in order to account for the decrease of the velocity constant as the reaction proceeded, on the assumption that nitrosyl chloride was slowly and irreversibly adsorbed by the surface, the rate of adsorption being of the same order as the reaction velocity. It was interesting to see whether this equation was obeyed in the present series of experiments. If k_1 is taken as the initially observed velocity constant, it is found that nearly all the experiments in the present paper obey the equation satisfactorily, the value of k_2 being $1{\cdot}85 \times 10^{-4}$. Extremely close agreement of the experimental results with the equation is found with expts. 4(11), 4(12), 4(15), 5(7), 6A, 6B, and 7A. Fig. 1 shows the values of dx/dt for values of x calculated from the above equation, and also those obtained by assuming the reaction to obey the simple termolecular law, $dx/dt = k_1(a - 2x)^2(b - x)$. as well as the experimental values obtained in expts. 4(8), 4(18), 5(7), and 5(15). The effect of ageing the reaction vessel on the value of dx/dt is well brought out by these curves. When $x = 70$, it is seen that dx/dt is about 3·0 at 15° when a comparatively new reaction vessel is employed, but when the vessel is old enough to give reproducible results, then dx/dt is almost zero for the same value of x. The same effect can also be seen by using the value $x = 80$ for the temperature 25°. (The values of dx/dt in each of the successive experiments can be directly compared with one another, since it was arranged that the concentrations of the reactants should be approximately the same in each of these series of experiments.)

(All pressures are recorded in mm. of mercury and times in minutes.)

Time.	p	p_{NO}.	p_{Cl_2}.	$k \times 10^7$.	p.	p_{NO}.	p_{Cl_2}.	$k \times 10^7$.	p.	p_{NO}.	p_{Cl_2}.	$k \times 10^7$.
	Expt. No. 4(8).		Temp. = 25°.		Expt. No. 4(9).		Temp. = 25°.		Expt. No. 4(11).		Temp. = 25°.	
0	506	294	212	12·2	497	297	200	11·3	501	295	206	10·8
2	474	230	180	11·6	468	239	171	11·6	472	237	177	11·0
4	456	194	162	11·9	450	203	153	10·3	454	201	159	11·0
6	444	170	150	10·5	439	181	142	11·0	442	177	147	8·6
8	436	154	142	9·9	430	163	133	11·0	435	163	140	9·1
10	430	142	136	10·1	423	149	126	10·1	429	151	134	6·9
12	425	132	131	9·9	418	139	121	9·8	425	143	130	5·4
15	419	120	125	8·9	412	127	115	10·2	421	135	126	5·9
20	412	106	118	8·55	404	111	107	8·6	415	123	120	5·3
30	403	88	109	6·85	395	93	98	6·8	407	107	112	4·3
45	396	74	102	7·1	388	79	91	7·0	400	93	105	4·2
60	391	64	97	5·15	383	69	86	4·9	395	83	100	1·6
90	386	54	92	—	378	59	81	4·0	392	77	97	—
120	—	—	—		375	53	78		—	—	—	
	Expt. No. 4(12).		Temp. = 25°.		Expt. No. 4(13).		Temp. = 25°.		Expt. No. 4(15).		Temp. = 25°.	
0	492	299	193	8·6	503	292	211	7·5	520	309	211	6·5
2	469	253	170	7·8	482	250	190	7·0	499	267	190	6·5
4	453	221	154	7·2	468	222	176	6·5	484	237	175	5·6
6	443	201	144	7·6	458	202	166	5·5	474	217	165	5·1
8	436	187	137	7·4	451	188	159	5·8	466	201	157	4·7
10	430	175	131	6·9	445	176	153	5·8	460	189	151	4·6
12	425	165	126	6·1	440	166	148	3·7	455	179	146	4·4
15	419	153	120	5·9	436	158	144	3·7	449	167	140	4·0
20	412	139	113	3·7	430	146	138	2·3	442	153	133	3·8
30	405	125	106	2·8	424	134	132	1·9	432	133	123	2·9
45	399	113	100	1·7	418	122	126	1·2	424	117	115	2·4
60	396	107	97	1·0	415	116	123	0·4	419	107	110	1·2
90	393	101	94	0·69	413	112	121	0·2	415	99	106	0·7
120	391	97	92		412	110	120		413	95	104	
	Expt. No. 4(18).		Temp. = 25°.		Expt. No. 5(7).		Temp. = 15°.		Expt. No. 5(10).		Temp. = 15°.	
0	489	306	183	4·8	508	309	199	10·6	503	301	202	7·9
2	475	278	169	4·1	478	249	169	10·4	481	257	180	7·1
4	465	258	159	4·7	461	215	152	9·5	466	227	165	6·8
6	458	244	152	4·0	450	193	141	8·5	456	207	155	6·3
8	453	234	147	3·4	442	177	133	8·2	448	191	147	6·4
10	449	226	143	3·6	436	165	127	8·3	442	179	141	4·9
12	445	218	139	3·1	431	155	122	7·9	438	171	137	5·3
15	440	208	134	2·4	425	143	116	6·8	432	159	131	4·6
20	433	194	127	2·5	418	129	109	6·1	425	145	124	4·1
30	423	174	117	1·57	409	111	100	3·7	416	127	115	2·5
45	416	160	110	1·60	403	99	94	3·3	410	115	109	2·0
60	410	148	104	0·88	399	91	90	1·47	406	107	105	0·87
90	405	138	99	0·65	396	85	87	1·14	403	101	102	0·69
120	402	132	96		394	81	85		401	97	100	
	Expt. No. 5(11).		Temp. = 15°.		Expt. No. 5(12).		Temp. = 15°.		Expt. No. 5(14).		Temp. = 15°.	
0	489	303	186	5·1	511	298	213	4·3	515	313	202	3·0
2	473	271	170	4·4	497	270	199	4·0	503	289	190	2·6
4	462	249	159	4·5	487	250	189	3·3	494	271	181	2·2
6	454	233	151	3·6	480	236	182	2·6	487	257	174	2·6
8	449	223	146	3·1	475	226	177	2·2	481	245	168	1·6
10	445	215	142	2·7	471	218	173	2·8	477	237	164	2·1
12	442	209	139	2·4	467	210	169	2·4	473	229	160	2·5
15	438	201	135	2·9	462	200	164	1·97	468	219	155	1·9
20	432	189	129	2·0	456	188	158	1·44	462	207	149	1·4
30	424	173	121	1·4	449	174	151	0·99	455	193	142	1·1
45	418	161	115	1·2	443	162	145	1·1	448	179	135	0·84
60	413	151	110	0·57	438	152	140	0·44	443	169	130	0·38
90	409	143	106	0·45	434	144	136	0·38	439	161	126	—
120	406	137	103		431	138	133		—	—	—	
	Expt. No. 5(15).		Temp. = 15°.		Expt. No. 6A.		Temp. = 25°.		Expt. No. 6B.		Temp. = 25°.	
0	492	298	194	2·5	504	306	198	6·2	613	361	252	4·8
2	484	282	186	2·1	484	266	178	7·0	588	311	227	5·1
4	478	270	180	1·8	469	236	163	6·6	570	275	209	4·0
6	473	260	175	2·1	459	216	153	5·9	558	251	197	4·1
8	469	252	171	1·3	451	200	145	5·6	549	233	188	3·8
10	466	246	168	1·5	445	188	139	5·3	542	219	181	3·7
12	463	240	165	1·9	440	178	134	5·3	536	207	175	3·8
15	458	230	160	1·5	434	166	128	4·6	528	191	167	3·3
20	452	218	154	1·3	427	152	121	4·2	519	173	158	2·7
30	444	202	146	0·90	417	132	111	3·3	508	151	147	1·6
45	437	188	139	0·98	409	116	103	4·0	501	137	140	1·4
60	431	176	133	0·40	402	102	96	2·3	496	127	135	0·66
90	427	168	129	—	396	90	90	2·0	492	119	131	0·56
120	—	—	—		392	82	86		489	113	128	

Time.	p.	p_{NO}.	p_{Cl_2}.	$k \times 10^7$.	p.	p_{NO}.	p_{Cl_2}.	$k \times 10^7$.	p.	p_{NO}.	p_{Cl_2}.	$k \times 10^7$.
	Expt. No. 7A.		Temp. = 25°.		Expt. No. 7B.		Temp. = 15°.		Expt. No. 8A.		Temp. = 25°.	
0	503	197	306	5·3	587	434	153	3·28	537	327	210	3·4
2	492	175	295	4·9	571	402	137	2·73	525	303	198	3·0
4	484	159	287	4·5	560	380	126	2·67	515	283	188	2·9
6	478	147	281	4·4	551	362	117	2·25	507	267	180	3·5
8	473	137	276	4·1	544	348	110	2·30	499	251	172	3·4
10	469	129	272	4·9	538	336	104	2·04	493	239	166	2·4
12	465	121	268	4·6	533	326	99	1·96	489	231	162	2·8
15	460	111	263	4·2	527	314	93	1·81	483	219	156	2·1
20	454	99	257	3·3	520	300	86	1·47	476	205	149	2·4
30	447	85	250	2·6	510	280	76	1·02	463	179	136	2·4
45	441	73	244	2·3	502	264	68	0·73	450	153	123	1·8
60	437	65	240	1·1	497	254	63	0·28	443	139	116	0·83
90	434	59	237	0·87	494	248	60	—	438	129	111	0·41
120	432	55	235		—	—	—		436	125	109	

Time.	p.	p_{NO}.	p_{Cl_2}.	$k \times 10^7$.	p.	p_{NO}.	p_{Cl_2}.	$k \times 10^7$.	p.	p_{NO}.	p_{Cl_2}.	$k \times 10^7$.
	Expt. No. 8B.		Temp. = 25°.		Expt. No. 9A.		Temp. = 25°.		Expt. No. 9B.		Temp. = 15°.	
0	541	276	265	3·33	549	397	152	10·0	494	280	214	4·8
2	529	252	253	3·5	516	331	119	10·0	480	252	200	2·0
4	519	232	243	2·8	495	289	98	9·8	469	230	189	4·3
6	512	218	236	2·4	482	263	85	8·1	461	214	181	4·0
8	507	208	231	2·1	473	245	76	8·6	455	202	175	4·1
10	503	200	227	2·4	466	231	69	9·0	450	192	170	3·2
12	499	192	223	2·2	460	219	63	7·4	446	184	166	4·0
15	494	182	218	1·8	454	207	57	7·8	440	172	160	3·6
20	488	170	212	1·3	446	191	49	7·1	432	156	152	3·5
30	481	156	205	1·4	436	171	39	5·8	421	134	141	2·5
45	472	138	196	1·4	428	155	31	5·3	413	118	133	1·6
60	465	124	189	0·63	423	145	26	5·6	409	110	129	1·2
90	460	114	184	0·45	416	131	19	—	403	98	123	1·5
120	457	108	181		—	—	—		398	88	118	

Expt. No. 9C. Temp. = 25°.

Time.	p.	p_{NO}.	p_{Cl_2}.	$k \times 10^7$.	Time.	p.	p_{NO}.	p_{Cl_2}.	$k \times 10^7$.
0	500	297	203	5·2	15	439	175	142	3·8
2	484	265	187	4·8	20	432	161	135	3·3
4	472	241	175	4·9	30	422	141	125	3·8
6	463	223	166	5·0	45	410	117	113	3·5
8	456	209	159	4·9	60	403	103	106	2·8
10	450	197	153	4·7	90	395	87	98	2·6
12	445	187	148	4·3	120	390	77	93	

If the assumption be correct that the inhibition is due to alteration of the state of the glass surface by adsorption of nitrosyl chloride, pre-treatment with this gas should in time completely mature a new vessel. Nitrosyl chloride, prepared from a mixture of sodium chloride and nitrosylsulphuric acid and condensed in an ice–salt mixture, was dried over calcium chloride and phosphoric oxide before being introduced into the reaction vessel. New vessels were used for each of three experiments, since it is otherwise impossible to disentangle the inhibitions due to the introduced nitrosyl chloride and to the reaction products. After the gas had remained for a given time in the vessel, it was rapidly pumped out and the effect was determined by measuring the reaction velocity. The results were as follows. Expt. 9A : NOCl at 100 mm. for 1 day, $k_1 = 10{\cdot}0 \times 10^{-7}$ at 25°, k_2 being low, about $1{\cdot}0 \times 10^{-4}$; expt. 9B : NOCl at 100 mm. for 2 days, $k_1 = 4{\cdot}9 \times 10^{-7}$ at 15°, $k_2 = 1{\cdot}6 \times 10^{-4}$; expt. 9C : NOCl at 350 mm. for 5 days, $k_1 = 5{\cdot}0 \times 10^{-7}$ at 25°, $k_2 = 1{\cdot}7 \times 10^{-4}$.

The effect of drying on the reaction was also studied. Phosphoric oxide was sublimed into the storage and the reaction vessel in a stream of dry oxygen, and after the addition of approximately 10 g. of the oxide to each vessel, the apparatus was sealed, and evacuated by the mercury-vapour pump. After 3 weeks' drying, the storage vessels were filled with their respective gases, and after a further week's drying the velocity of the reaction was studied. The reaction vessel used for the experiment was one which had been thoroughly aged over a long period. It was found that the drying had caused all signs of inhibition to disappear. The velocity constant of the reaction under these conditions was $12{\cdot}6 \times 10^{-7}$ at 25° and $10{\cdot}9 \times 10^{-7}$ at 15°, the reaction obeying the termolecular law during the whole of the experiment. This result was somewhat unexpected, since drying generally inhibits a reaction. Addition of nitrosyl chloride to the reaction vessel a week before the reaction produced no effect whatsoever. A possible explanation is that the inhibition is due to the adsorption of the nitrosyl chloride on the water content of the glass surface. It is well known that the nature of a glass surface depends to a large extent upon its composition and previous history, and in consequence, such surfaces are far from being reproducible; therefore it is likely that different investigators will find differences of behaviour during the course of this reaction. The initial experiments of the present work could easily have been taken as evidence that the reaction was of the homogeneous termolecular type. It was only after a few experiments had been performed that departure from the simple law was detectable.

When a surface adsorbs gas, the physical conditions determine whether activated adsorption or van der Waals adsorption occurs. In the latter case the heat of adsorption is small, the rate of adsorption high, and the adsorbed gas is readily removed from the surface; when activated adsorption occurs, all these effects are in the opposite sense. Both kinds of adsorption occur simultaneously to some extent in most experiments involving the adsorption of gases.

The tenacity with which the nitrosyl chloride adheres to the surface, as well as the fact that the adsorption isotherm (deduced by assuming van der Waals adsorption) is incapable of quantitatively accounting for the results, indicates that in the present work, the inhibition is due to activated rather than to van der Waals adsorption. Such a view was tentatively put forward in the previous paper, in which it was assumed that the inhibition was due to a slow process of adsorption, thereby enabling an equation to be deduced which satisfactorily follows the course of the reaction.

It is suggested that at the beginning of a series of experiments, the new glass surface contains a considerable amount of adsorbed water, which can in turn adsorb the nitrosyl chloride formed during the reaction, thereby causing inhibition. It is probable that the attachment of the nitrosyl chloride to the adsorbed water is of the chemisorption type and will take place slowly. Thus it is seen that, as experiment succeeds experiment, the adsorbed nitrosyl chloride increases, leading to increasing inhibition. Baking under vacuum will tend to drive off both the adsorbed water and nitrosyl chloride, but it is well known that the adsorbed water is most tenaciously held by glass, and therefore, such treatment is only partly effective in restoring reaction velocity. On the other hand, prolonged drying in a vacuum by phosphoric oxide is an extremely efficient method of removing moisture from glass, and when this has been thoroughly achieved, the tendency for the nitrosyl chloride to be adsorbed is removed, and the reaction becomes termolecular, inhibition disappearing.

Trautz and Schlueter (*Z. anorg. Chem.*, 1924, **136**, 1) found that, according to whether a high concentration of chlorine or of nitric oxide was employed, the velocity constant increased or decreased towards the end of the reaction. Krauss and Saracini (*Z. physikal. Chem.*, 1937, *A*, **178**, 245) suggested that these fluctuations in the termolecular velocity constant were due to experimental error in estimating minute partial pressures towards the close of the experiment. This is probably the case, since in Trautz and Schlueter's experiment 19c, they started with 79·9 mm. of nitric oxide, but the experimental figures show that at least 80·46 mm. were used during the experiment. The departure from the true termolecular conditions led Trautz and Schlueter to suggest that the reaction proceeded in two stages: $NO + Cl_2 \rightleftharpoons NOCl_2$, followed by $NOCl_2 + NO \longrightarrow 2NOCl$. The author has already pointed out that the argument supporting this contention is fallacious, and since their work probably involves experimental errors which account for their conclusions, it seems that this reaction mechanism is without valid support. In these circumstances, it is justifiable to suggest that the reaction mechanism may not be very different from that of the nitric oxide–oxygen reaction, and this view was developed in the earlier paper.

If the temperature coefficient of the reaction is calculated from the initial values of k obtained with new bulbs, then $k_{25^\circ}/k_{15^\circ} = 1{\cdot}13$; but if it is calculated from the initial values of k_1 obtained from reaction bulbs which give reproducible results, then $k_{25^\circ}/k_{15^\circ} = 2{\cdot}0$. The former value is in good agreement with the values given by other workers, but it is obvious that the temperature coefficient is largely dependent upon the history of the reaction bulb.

EXPERIMENTAL.

The general procedure was the same as before, but the arrangement of the tensimeter was improved so as to increase the accuracy of the measurements. The new arrangement is shown in Fig. 2, the procedure being as follows. The reaction vessel, the tensimeter, and its jacket, and the manometer were all evacuated *via* the taps *A* and *D*. All the taps were closed except *C*, and one of the gases was then admitted to the reaction vessel. The pressure in the tensimeter jacket was adjusted by using tap *D* in order to return the needle to its null position. The correctness of the manometer reading was then checked by closing *C* and momentarily opening *B*. The lack of movement in the mercury manometer indicated correct pressure adjustment. This technique connects the reaction vessel to the manometer only, and the volume of the latter was comparatively small. Hence any small movement of the mercury manometer does not introduce a serious error into the measurements. In the earlier procedure, the jacket of the tensimeter was also connected to the reaction vessel and manometer, and since the jacket must possess a considerable volume, the error due to any movement of the manometer would be more serious.

FIG. 2.

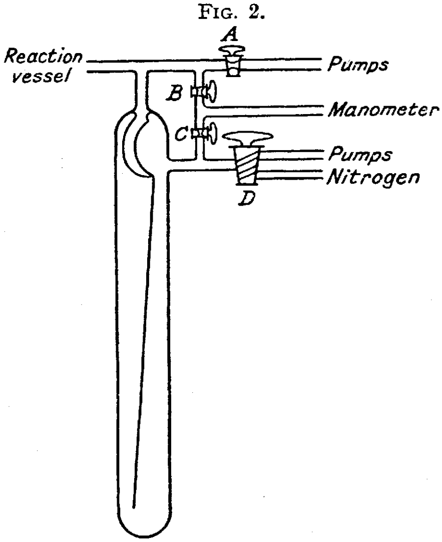
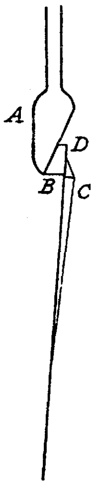


FIG. 3.



The customary method of producing a spoon tensimeter is to blow a thin glass bulb about 1—1½″ in diameter, and then to collapse one half of the bulb; gentle suction produces a "spoon" with the two walls close together. A needle about 18″ long, movement of which is observed by a lens or telescope, is attached to the tip of the spoon. A much better instrument is shown in Fig. 3. A thin bulb is blown so that its length becomes twice its diameter (1½″ and ¾″ respectively are suitable). Half the bulb is collapsed as usual; glass is removed from the collapsed film until it is thin, and then a blowpipe flame is played directly on to the film, which becomes very thin in the middle owing to surface tension thickening the glass towards the cooler edge. It is advisable to stop this thinning process before dark patches (zero interference fringes) appear, otherwise the tensimeter becomes extremely fragile. If the " spoon " is examined, it will be found that gentle suction causes the tip *B* to move in the opposite direction to the thin membrane at *D*. A thin filament of glass is fused to the membrane at a point which produces the maximum movement (*D*). A U-piece of thin glass is attached to the tip *B*, a fine thread of glass stretched between the tips of the U being the suspension. The needle used is about 18″ long, consisting of two filaments of glass bracing one another to produce enhanced rigidity. The needle is attached to the suspension, and an extension of the needle is attached to *D*. The movement of the needle is now due to the combined movements of *B* and *D*, a greater sensitivity than with the orthodox instrument thus being obtained.

For the early work, the orthodox tensimeter was used having a needle movement of 1·2 mm. per 1 mm. of mercury pressure. It was broken early in the present work and replaced by the new type of tensimeter with a movement of 2·1 mm. per 1 mm. of mercury. If these tensimeters are employed in conjunction with a telescope, accurate pressure readings can be obtained. However, in the persent work, the needle movement was observed by the unaided eye in order to make the observations more rapidly.

The zero of these instruments was relatively unaffected by temperature change. A change of 5° had no detectable result on the zero of either instrument, and therefore it was possible to use them without a thermostat. It was noted, however, that when the spoon and its jacket were simultaneously evacuated, the zero shifted as the pressure was lowered, *i.e.*, the null position depended on the pressure being measured. This difficulty was overcome by plotting the zero against the pressure. A curve was used for each instrument, and the zero checked before each experiment.

In the present experiments, it was desired to mix the gases in a definite proportion, irrespective of which gas was first introduced into the reaction vessel. This necessitated some means of adjusting the pressure in the storage vessels, so that the final desired pressure in the reaction vessel could be attained automatically. For this purpose, a pressure adjuster, consisting of a bulb fitted with a three-way tap at the top and attached to a mercury reservoir at the bottom, was inserted into the nitric oxide gas train. The gas was drawn into the bulb at atmospheric pressure, and then released into the storage vessel until the required pressure, indicated by a mercury manometer attached to the vessel, was reached. The chlorine was always stored at atmospheric pressure, as in the previous work, owing to the difficulty of using mercury in this gas train.

The apparatus was calibrated by using air in each storage vessel, so that the pressure adjustments necessary to attain given mixtures of the two gases could be determined. The first gas introduced into the reaction vessel can have its pressure in this vessel adjusted before mixing, by opening tap *A* if the pressure is to be lowered, and by introducing more gas from the train if it is to be raised. In the case of one set of storage and reaction vessels, it was found that if the gas in the reaction vessel introduced from the nitric oxide vessel was adjusted to 200, 300, or 400 mm., then admission of gas from the chlorine vessel, initially at atmospheric pressure, would introduce a further 266, 220, or 170 mm. of gas, respectively. If the gas pressure in the reaction vessel was adjusted to 266, 220, or 170 mm. when gas was first introduced from the chlorine vessel, then the pressure of gas in the nitric oxide vessel must be adjusted to 688, 851, or 1015 mm. respectively in order to introduce 200, 300, or 400 mm. respectively of gas into the reaction vessel. The desired gas mixture could thus be attained at will.

The reaction vessel was shrouded by a thin copper-foil canister, and the connecting tubes and top part of the tensimeter carrying the spoon were wrapped in black paper in order to obviate photochemical reversal. About halfway through the work, the room was blacked out; the manometer and tensimeter needle were then observed by artificial light.

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College of Technology, Leicester.

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