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

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The reaction between chlorine and nitric oxide has always been considered as a termolecular homogeneous reaction. The present work shows that the reaction velocity can be considerably influenced by surface conditions, and therefore this reaction is really heterogeneous in character. The nitrosyl chloride formed can, by adsorption on the surfaces of the reaction vessel, inhibit the reaction to such an extent that it ceases altogether, a phenomenon reminiscent of the effect of drying on chemical reactions. The evidence indicates that association of nitric oxide occurs heterogeneously, the complex being capable or incapable of homogeneous reaction with chlorine depending upon whether the complex molecule has been stabilised or not by the surface of the reaction vessel.

The author recently found (J., 1939, 5) that the reaction between oxygen and nitric oxide was inhibited by drying if mixing occurred in the oxygen-containing vessel, although it proceeded normally if mixing was effected in the nitric oxide vessel. These observations indicated the heterogeneous formation of a complex molecule $(NO)_2$ which was able to react with the oxygen homogeneously :

$$2NO \rightleftharpoons (NO)_2$$
$$(NO)_2 + O_2 \longrightarrow N_2O_4 \rightleftharpoons 2NO_2$$

the $(NO)_2$ concentration being very small, *i.e.*, dissociation of the complex being almost complete. Such a scheme would accord with Bodenstein's observation (*Z. physikal. Chem.*, 1922, **100**, 68) that the reaction is kinetically termolecular, and if the life period of the complex is assumed to decrease with rising temperature, the temperature coefficient of 0·912—0·997 can also be explained. Hasche (*J. Amer. Chem. Soc.*, 1926, **48**, 2253) showed that the reaction possessed an induction period under various surface conditions, and that the rate of reaction was reduced 20% below the normal if paraffin-coated vessels and fairly dry gases were used. These observations can also be interpreted by the above scheme, and the author inferred that the oxygen–nitric oxide reaction is not a true homogeneous reaction but a complex reaction involving concurrently consecutive changes at least one of which is heterogeneous.

As a result of this work, it was decided to investigate the inhibition kinetically. Unfortunately, the oxygen–nitric oxide reaction is complicated by the fact that the product, dinitrogen tetroxide, is dissociated, thereby making the calculations difficult and increasing the possibility of error. It was therefore decided to investigate kinetically the chlorine–nitric oxide reaction, $2NO + Cl_2 \longrightarrow 2NOCl$, the product of which is not dissociated, in the hope that this reaction would be similarly inhibited by surface conditions and that the kinetics of the inhibiting factor could be discovered. Comparatively little attention has been given to this reaction, but Coates and Finney (J., 1914, **105**, 2444) and Trautz (*Z. anorg. Chem.*, 1914, **88**, 285) found it to be termolecular and homogeneous, with a temperature coefficient about 1·2.

If a is the concentration of nitric oxide and b that of chlorine at zero time, and if x represents the change of the chlorine concentration in time t, then the velocity equation is $dx/dt = k(a - 2x)^2(b - x)$ which on integration becomes

$$kt = \frac{1}{(a-2b)^2}\log_e\frac{b(a-2x)}{a(b-x)} + \frac{2x}{a(2b-a)(a-2x)} \quad . \quad . \quad . \quad . \quad (1)$$

The velocity equation can be written in the form

$$dx/dt = k[2(a-x)]^2(b-x) = k'(a-x)^2(b-x)$$

where $2a$ is the initial nitric oxide concentration and b the initial chlorine concentration.

Trautz (*loc. cit.*) used the integrated form of this equation (in different symbols) and his velocity constant, k', is therefore four times the present constant, k.

Coates and Finney carried out their experiments under special conditions, the initial partial pressures of chlorine and of nitric oxide being about $\frac{1}{3}$ atm. and $\frac{2}{3}$ atm. respectively, and they stated 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." The velocity constant was calculated from the equation (transposed into the present symbols):

$$k' = (1/2t)[1/(b - x)^2 - 1/b^2]$$

The premise that the concentrations of the two gases were equal is incorrect; the nitric oxide concentration was twice that of the chlorine throughout the reaction since the concentration of a gas is equal to its partial pressure. Therefore the velocity equation for their experiments should be $dx/dt = k[2(b - x)]^2(b - x)$, which on integration becomes

$$k = (1/8t)[1/(b - x)^2 - 1/b^2)]$$

Their values for the velocity constant should therefore be divided by 4 to give values comparable with those in the present work.

A more important point is that for the measurements Coates and Finney used mercury manometers, protected against attack by a nitrogen cushion. They admitted that the mercury was insufficiently protected, and they believed that the attack accounted for the increase of the velocity constant towards the end of the reaction. The present work shows that the velocity constant can decrease towards the end of the reaction, and it may be that the attack of the mercury was more serious than Coates and Finney believed. In any case, the presence of mercury is undesirable. Coates and Finney also employed fine connecting tubes, and although this would not seriously hinder the functioning of their Töpler pump, it was deemed desirable in the present work to use large-diameter connecting tubes in order to decrease the time of mixing of the gases as well as to increase the efficiency of the modern pumping system.

Trautz (*loc. cit.*) carried out kinetic measurements similar to those of Coates and Finney, using quantities of the gases in various molecular concentrations. It was found necessary to use low partial pressures of the gases, since rapid reaction caused uncertainties in the manometer readings. Later, Trautz and Schlueter (*Z. anorg. Chem.*, 1924, **136**, 1) suggested that the reaction occurred in two stages: an intermediate compound $NOCl_2$, formed by the equilibrium $NO + Cl_2 \rightleftharpoons NOCl_2$, underwent a rapid but measurable change, $NOCl_2 + NO = 2NOCl$. The velocity of the second reaction was believed to determine the speed of the whole change, which is therefore termolecular in the kinetic sense. It was observed that when large partial pressures of nitric oxide were used, the velocity constant decreased rapidly as the reaction proceeded. This was explained by supposing that the large amount of nitric oxide hastened the second reaction to such an extent that the compound $NOCl_2$ was not present under the equilibrium conditions of the first reaction. Such an explanation is fallacious, since a large concentration of nitric oxide would hasten both reactions by the same relative amount. Trautz and Schlueter also noticed that in experiments where large partial pressures of chlorine were used, the velocity constant increased rapidly as the reaction proceeded, a fact for which no theoretical explanation was given. Krauss and Saracini (*Z. physikal. Chem.*, 1937, *A*, **178**, 245) confirmed the observation that the reaction obeys the termolecular law, and suggested that the fluctuations in the velocity constant reported by Trautz and Schlueter were due to experimental error.

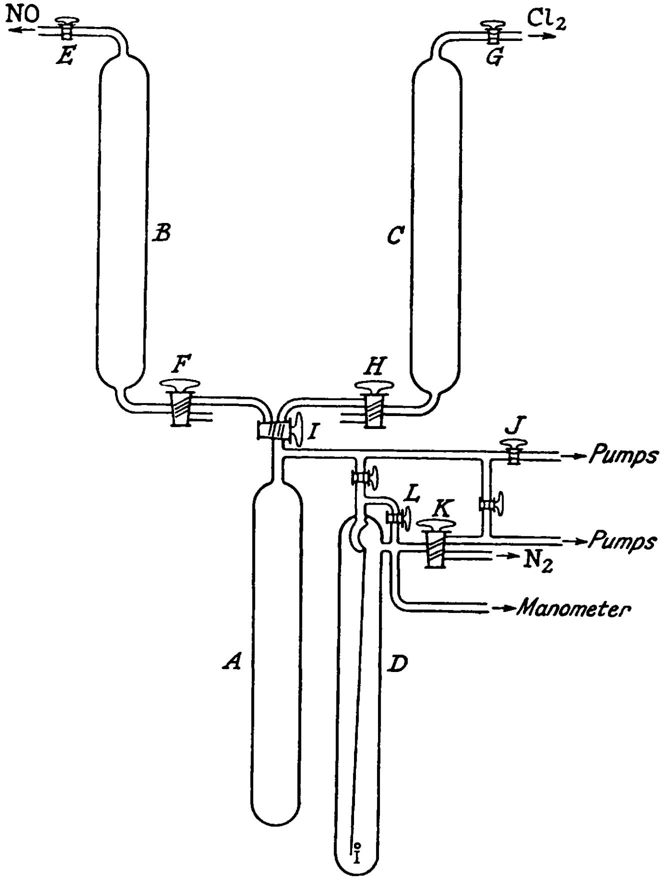
In the present experiments, the gases used were moderately dry, but the reaction vessel was exhausted for many hours before use, in order that the loosely adsorbed gas molecules could be removed, the final surface conditions thus resembling those used in the nitric oxide–oxygen investigation.

EXPERIMENTAL.

Preparation of Materials.—Nitric oxide was prepared by adding sulphuric acid to a mixture of potassium nitrate and ferrous sulphate, and was washed with water followed by concentrated sulphuric acid, which removed traces of nitrogen dioxide. The gas was evolved so quickly that a gasometer was necessary to smooth out the supply, but the gas was not stored over water, with which it reacts to form nitrogen (Moser, *Z. anal. Chem.*, 1911, **50**, 401). The chlorine was prepared by dropping hydrochloric acid on potassium permanganate and was washed with permanganate solution. The gases were dried by passing first over anhydrous calcium chloride and then over phosphoric anhydride.

Apparatus.—This was constructed throughout in soda-glass and was cleaned with alcohol–nitric acid, washed, and dried before assembly. It consisted of three vessels, *A*, *B*, and *C* (Fig. 1), each about 15″ long and of 2″ internal diameter with a capacity of about 750 c.c., immersed in an electrically controlled thermostat steady to ± 0·1° at 25°. A steadier temperature than this was not required since the reaction has a low temperature coefficient. The vessels *B* and *C* were used to contain the nitric oxide and chlorine, respectively, for the experiment, and this arrangement enabled the gases to attain a steady temperature before being introduced into the reaction vessel *A*. The last could be placed in communication with a glass-spring tensimeter, *D*, which was a sensitive spoon gauge furnished with a light glass needle 18″ long, the whole instrument being rigidly clamped to the bench. The tensimeter was used as a null instrument and enabled the pressure in the reaction vessel to be measured without allowing the gases to come into contact with the mercury manometer. The pressure in the outer jacket of the tensimeter was adjusted by the tap *K* until the instrument's needle returned to its zero position. The pressure in the vessel *A* was then that in the jacket, which was directly read off the mercury manometer. The movements of the needle over a scale were observed by the unaided eye, although the sensitivity of the instrument could be considerably increased by using a telescope. Since the experiments were conducted in such a way that very quick

FIG. 1.



determinations of pressure were necessary, it was essential to avoid all cumbersome appliances, such as telescopic readings and mirror and scale readings, and to rely upon the direct reading of the instrument. It was soon possible to estimate pressures to within 1 mm. in a matter of 5 secs. The estimated pressure was always checked by momentarily opening the tap L, which connected the reaction vessel directly to the mercury manometer: lack of movement of the tensimeter needle indicated correct pressure measurement. The volume of the connecting tubes to the tensimeter and manometer was kept small in order to increase the sensitivity of the manometer and tensimeter on opening tap L. The gas admitted to the tensimeter jacket was nitrogen, which acted as a buffer between the reactive gases and the mercury in the manometer.

The taps and tubing were of 6 mm. internal diameter throughout, except the connections of the manometer and tensimeter, which were 1—2 mm.; this facilitated rapid evacuation and rapid mixing of the gases. The taps were lubricated with Apiezon grease throughout, although trouble was often experienced after the apparatus had been in use for some time; hot water was then found sufficient to soften the grease, although it was eventually necessary to regrease the taps. The arrangement was found to be as satisfactory as the employment of special lubricants, none of which completely resists attack by chlorine and nitrosyl chloride.

Procedure.—The vessels B and C were each evacuated by a "Hyvac" pump *via* the vessel A for several hours. The respective gases were introduced, and when the vessels had attained atmospheric pressure, the taps F and H were opened to the atmosphere, and the gases streamed through the vessels for several hours. In this way pure samples of the gases were obtained in the vessels for the experiment in hand. The pressure of the chlorine could be reduced if necessary by expansion into A, and the nitric oxide pressure could be reduced or increased by a mercury gas holder inserted into the gas train.

The reaction vessel A and the side arms of the tap I, the tensimeter, and manometer were evacuated for at least 4 hours. One of the gases was then introduced into A and its pressure measured, and at a given time, the second gas was introduced. The time of mixing was usually less than 5 secs., and the total gas pressure was measured as quickly as possible. Zero time was taken as the moment at which the tensimeter was balanced to its null position, and the pressure was then noted at various time intervals.

RESULTS AND DISCUSSION.

The results of the experiments are tabulated; p gives the pressure in the reaction bulb, p_{NO} the partial pressure of nitric oxide $= a - 2x$, and p_{Cl_2} that of chlorine $= b - x$, all in mm. Cols. A and B give $k \times 10^7$ calculated respectively from equation (1) for the time interval between the successive observations, and for the interval between the current observation and the initial observation. These velocity constants fall rapidly as the reaction proceeds and it is clear that the termolecular law is not obeyed, or that the reaction is inhibited by its products or surface conditions. Trautz and Schlueter observed a decrease in the velocity constant when large concentrations of nitric oxide were used, but such conditions did not operate in the present experiments. It is possible that surface conditions inhibit the reaction due to the adsorption of nitrosyl chloride. Application of the adsorption isotherm would give the kinetic equation $dx/dt = k(a - 2x)^2(b - x)/2x$, which becomes

$$kt = \frac{2b}{(a-2b)^2}\log_e\frac{b(a-2x)}{a(b-x)} + \frac{2x}{(2b-a)(a-2x)}$$

on integration. Col. C gives the values of this velocity constant ($\times 10^5$) calculated for the interval from the initial reading. It is seen that it usually increases in the early stages of the reaction, and is then fairly constant, although a tendency to fall can often be detected in the later stages. In many experiments, this velocity constant falls very rapidly, and therefore the reaction kinetics cannot be explained by such simple theories.

The experiments show that the reaction is affected by surface conditions in a manner reminiscent of the nitric oxide–oxygen reaction, suggesting the probability that the two reactions have a similar mechanism. It is suggested that the complex molecule $(NO)_2$ plays a fundamental rôle in both reactions, the complex being formed in heterogeneous equilibrium with nitric oxide and dissociation being almost complete. The surface which brings the equilibrium about can be imagined as being in two states, part being active and the remainder inactive. When the $(NO)_2$ molecule is formed on the active surface, it is capable of reaction with chlorine; when formed on the inactive surface, it is incapable of reaction. The total number of $(NO)_2$ molecules present will not depend on the amount of surface so long as equilibrium is established, but the nature of the surface will alter as reaction proceeds, thereby altering the ratio of those complex molecules capable of reaction to the total number present, the latter being determined by the law of mass action. If these assumptions are valid, the velocity of the reaction will not be affected by increasing the amount of surface in the reaction vessel, since this will not affect either the total number of complex molecules present or the relative number capable of reaction. Moreover, as reaction proceeds, the ratio of active to total surface will always be the same no matter what the total surface happens to be. In fact, the reaction can be erroneously believed to be homogeneous. A test was made by employing a reaction bulb packed with glass tubing with a total surface of 3,500 sq. cm. and a gas capacity of 475 c.c., *i.e.*, the surface was increased ten-fold per c.c. of gas. The results are given in expts. 3A, 3B, and 3D. The velocity constants A and B differ but slightly from those of the other experiments and the effect of this increased surface is so small that that the reaction has always been reported as homogeneous. The velocity constant C is somewhat increased by the additional surface.

If the relative amount of active surface remains a constant throughout the reaction, the concentration of complex molecules capable of reaction will be proportional to the square of the nitric oxide concentration, and the velocity equation will be $dx/dt = k[NO]^2[Cl_2]$. Previous workers have found that the reaction obeys this equation and the author suggests that they have used surfaces which prevent inhibition taking place. It is not customary when investigating kinetics to evacuate apparatus to such an extent that the surfaces are denuded of all loosely held gas molecules, and under the usual conditions, inhibition would not occur since the surfaces would not be capable of further adsorption of gas.

If the surfaces of the present experiments are rendered inactive by adsorption of nitrosyl chloride, the number of complex molecules capable of reaction will decrease rapidly as the reaction proceeds. Let σ be the fraction of the total active surface which has been rendered inactive. Then $(1 - \sigma)$ will be the fraction of the complex molecules capable of reaction and the velocity equation becomes

$$dx/dt = k_1(a - 2x)^2(b - x)(1 - \sigma) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

so that dx/dt will approach zero as σ approaches unity.

If the inhibition is due to the adsorption of nitrosyl chloride, then the adsorption isotherm will apply and $(1 - \sigma)$ will be inversely proportional to the nitrosyl chloride concentration, so that $dx/dt = k(a - 2x)^2(b - x)/2x$.

Since the experiments do not obey this equation, it is supposed that the inhibition noticed in the present work is due to the slow adsorption of the nitrosyl chloride, a process requiring only a small energy of activation. The occurrence of this adsorption, and therefore the inhibition, may be prevented by protecting the surface by other gases, such as air.

Expt. No. 1A. Temp. = 15°.

Time, mins.	p.	p_{NO}.	p_{Cl_2}.	A.	B.	C.
0	498	310	188		—	—
2	490	294	180	2·20	2·20	—
4	484	282	174	2·25	2·20	0·38
6	478	270	168	2·40	2·30	0·66
8	473	260	163	2·10	2·20	0·67
10	468	250	158	2·10	2·20	0·63
12	463	240	153	2·85	2·30	0·92
20	452	218	142	1·80	2·10	1·22
30	444	202	134	1·30	1·90	1·26
45	438	190	128	0·80	1·50	1·16
60	434	182	124	0·61	1·30	1·08

Expt. No. 1C. Temp. = 15°.

Time, mins.	p.	p_{NO}.	p_{Cl_2}.	A.	B.	C.
0	463	223	240		—	—
2	458	213	235	2·40	2·4	0·92
4	454	205	231	1·80	2·1	0·18
6	450	197	227	2·15	2·1	0·18
8	447	191	224	1·80	2·0	0·32
10	444	185	221	1·85	2·0	0·33
15	437	171	214	2·06	2·0	0·53
20	432	161	209	1·89	1·9	0·75
30	425	147	202	1·30	1·8	0·68
45	418	133	195	1·30	1·6	0·85
60	413	123	190	1·10	1·5	0·88
90	406	109	183	0·92	1·3	0·93

Expt. No. 1D. Temp. = 15°.

Time, mins.	p.	p_{NO}.	p_{Cl_2}.	A.	B.	C.
0	455	252	203	2·03	—	—
2	450	242	198	2·27	2·23	0·85
4	445	232	193	1·75	2·25	0·60
6	441	224	189	1·60	2·10	0·20
8	438	218	186	1·95	1·97	0·23
10	435	212	183	1·90	1·96	0·48
15	428	198	176	1·84	1·94	0·67
20	422	186	170	1·55	1·92	0·75
30	414	170	162	1·13	1·77	0·90
45	407	156	155	1·14	1·57	0·98
60	401	144	149	0·74	1·46	0·98
90	395	132	143	0·13	1·22	0·95
120	394	130	142		0·95	0·73

Expt. No. 2A. Temp. = 25°.

Time, mins.	p.	p_{NO}.	p_{Cl_2}.	A.	B.	C.
0	565	403	162	4·40	—	—
2	544	361	141	4·80	4·40	—
4	530	333	127	3·65	4·60	1·75
6	520	313	117	3·15	4·28	1·50
8	513	299	110	3·15	4·00	2·00
10	507	287	104	4·10	3·83	2·40
12	501	275	98	4·00	3·87	2·75
15	493	259	90	3·20	3·89	3·32
20	484	241	81	2·25	3·73	3·65
30	474	221	71	1·53	3·23	3·56
45	467	207	64	0·74	2·67	3·33
60	464	201	61	0·20	2·18	2·86
90	463	199	60	0·10	1·52	2·04
120	462	197	59		1·17	1·61

Expt. No. 3A (with a packed bulb).
Temp. = 25°.

Time, mins.	p.	p_{NO}.	p_{Cl_2}.	A.	B.	C.
0	637	456	181	4·80	—	—
2	608	398	152	4·66	4·85	1·55
4	589	360	133	4·66	4·70	2·28
6	575	332	119	5·57	4·67	3·25
8	562	306	106	5·00	4·96	4 25
10	553	288	97	4·75	4 94	5·10
12	546	274	90	2·62	4·96	5·75
15	541	264	85	2·61	4·45	5·00
20	534	250	78	2·11	3·98	5·45
30	525	232	69	1·88	3·38	5·11
45	516	214	60	0·50	2·86	4·80
60	514	210	58	0·27	2·28	3·92
90	512	206	56		1·61	2·87

Expt. No. 2B. Temp. = 25°.

Time, mins.	p.	p_{NO}.	p_{Cl_2}.	A.	B.	C.
0	549	382	167	4·50	—	—
2	529	342	147	4·50	4·50	—
4	516	316	134	4·32	4·50	1·50
6	506	296	126	3·10	4·42	2·00
8	499	282	117	4·10	4·00	1·87
10	492	268	110	4·11	4·10	2·60
12	487	256	104	2·62	4·12	2·91
15	482	246	99	1·81	3·80	3·21
20	477	236	94	1·72	3·30	3·00
30	469	220	86	1·45	2·76	2·84
45	461	204	78	1·36	2·34	2·67
60	455	192	72	0·84	2·10	3·13
90	449	180	66		1·69	2·34

Expt. No. 2E. Temp. = 25°.

Time, mins.	p.	p_{NO}.	p_{Cl_2}.	A.	B.	C.
0	566	362	204	4·65	—	—
2	546	322	184	4·35	4·65	1·50
4	532	294	170	4·15	4·50	2·00
6	522	274	160	4·00	3·66	1·00
8	514	258	152	2·60	3·75	1·38
10	508	246	146	3·00	3·50	1·20
12	503	236	141	3·00	3·42	1·75
15	496	222	134	3·50	3·34	1·80
20	486	202	124	2·50	3·45	3·05
30	475	180	113	1·73	3·13	3·50
45	468	166	106	0·53	2·67	3·56
60	464	158	102	0·016	2·14	2·76
90	463	156	101	0·016	1·48	1·89
120	462	154	100		1·15	1·54

Expt. No. 3D (with a packed bulb).
Temp. = 15°.

Time, mins.	p.	p_{NO}.	p_{Cl_2}.	A.	B.	C.
0	636	474	162	2·20	—	—
2	621	444	147	2·05	2·20	—
4	610	422	136	2·30	2·13	0·35
6	601	404	127	1·84	2·18	2·10
8	594	390	120	2·27	2·04	1·00
10	587	376	113	1·67	2·15	1·45
12	582	366	108	1·83	1·97	1·31
15	575	352	101	1·32	1·95	1·47
20	567	336	93	1·32	1·79	1·00
30	555	312	81	0·66	1·63	1·63
45	548	298	74	0·41	1·30	1·47
60	544	290	70	0·13	1·08	1·28
90	542	286	68	0·02	0·77	0·94
120	541	284	67		0·58	0·69

Expt. No. 3B (with a packed bulb). Temp. = 25°.

Time, mins.	p.	p_{NO}.	p_{Cl_2}.	A.	B.	C.
0	639	352	287	4·42	—	—
2	613	300	261	4·18	4·42	0·70
4	597	268	245	4·05	4·30	2·38
6	584	242	232	3·75	4·33	2·66
8	575	224	223	3·45	4·10	3·19
10	568	210	216	3·30	3·97	3·60
12	562	198	210	3·83	3·86	3·75
15	555	184	203	3·28	3·72	4·06
20	545	164	193	2·25	3·61	4·40
30	535	144	183	1·40	3·16	4·44
45	528	130	176	0·99	2·57	3·94
60	524	122	172	0·27	2·17	3·48
90	522	118	170	—	1·53	3·56
120	522	118	170		1·15	1·92

The rate of adsorption will be proportional to the concentration of the nitrosyl chloride and the amount of adsorption which can still take place, *i.e.*,

$$d\sigma/dt = k_2(1 - \sigma)2x \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (3)$$

(this equation recalls the behaviour of activated adsorption; see Kingman, *Trans. Faraday Soc.*, 1932, **28**, 269).

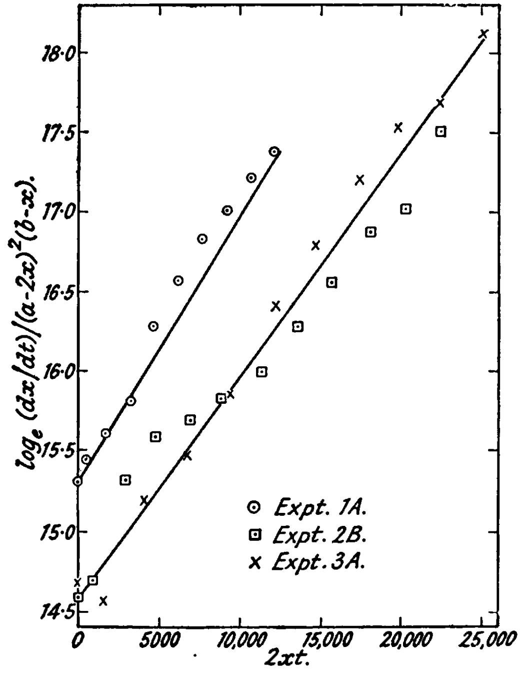
The reaction should obey equations (2) and (3) throughout the whole of its course. There are, however, two limiting cases in the reaction. It will be shown that k_2 is small; therefore at the beginning of the reaction, σ will be negligible since x is small, and equation (2) can therefore be simplified and integrated, giving equation (1). In other words, $k_1 = k$ at the beginning of the reaction. The tables show that k_1 is $4{\cdot}5 \times 10^{-7}$ at 25° and $2{\cdot}2 \times 10^{-7}$ at 15°, the temperature coefficient being 2·04, which is greater than that previously reported. At the end of the reaction, dx/dt is almost zero, *i.e.*, x is virtually a constant. If x is treated as constant, equation (3) gives

$$(1 - \sigma) = e^{-k_2 . 2xt} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

on integration, an equation similar to that of Bangham and Sever (*Phil. Mag.*, 1925, **49**, 938). Substituting in (2) and taking logarithms, we have

$$\log_e \frac{dx/dt}{(a - 2x)^2(b - x)} = \log_e k = \log_e k_1 - k_2.2xt. \quad . \quad . \quad . \quad . \quad (5)$$

FIG. 2.



If the left-hand side of this equation is plotted against $-2xt$, the result should be a straight line in the final stages of the reaction, the intercept on the $\log_e k$ axis giving $\log_e k_1$ and the slope giving k_2. The values of dx/dt at 10-minute intervals were determined graphically from the x–t curve, and the value of the logarithmic expression then calculated for these particular times. Fig. 2 shows the curves so obtained for the three experiments 1A, 2B, and 3A, the slopes approximating to give $k_2 = 2{\cdot}0 \times 10^{-4}$. Although all the experiments obey the straight-line relationship of (4) fairly well, perfect agreement with theory is only to be expected when dx/dt approaches zero, *i.e.*, when $\log_e k$ approaches $-\infty$ and when it is thus impossible to study the reaction experimentally.

The equation which would satisfy the reaction over the whole of its course is an infinite series in powers of x for a particular value of t. On combining equations (2) and (3) we have $d\sigma/dx = (k_1/k_2)(a - 2x)^2(b - x)/2x$ which on integration becomes

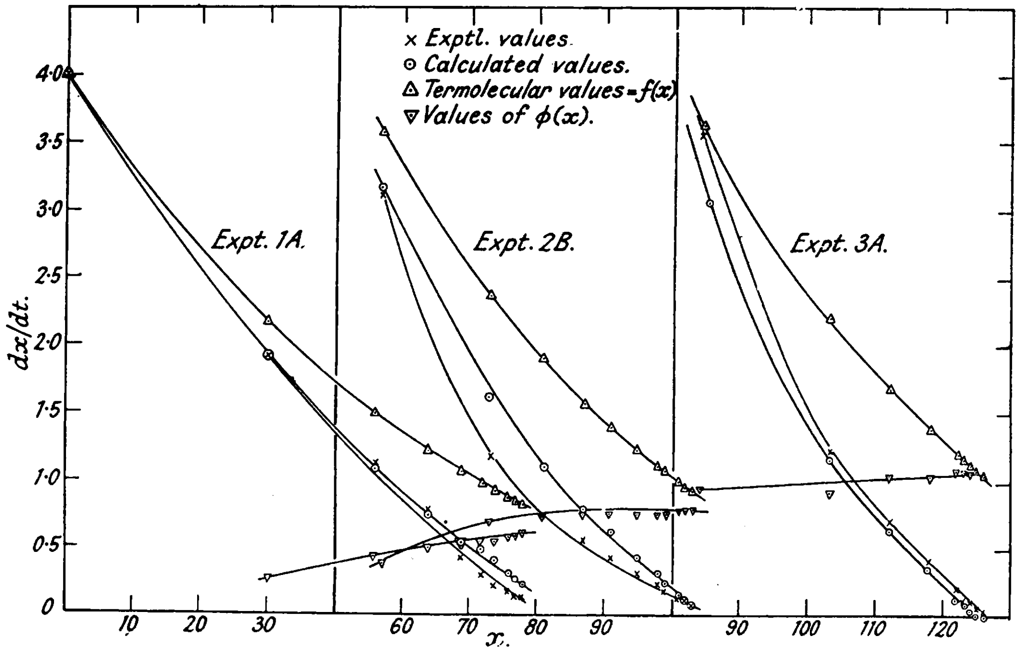
$$\sigma = \frac{k_2}{k_1}\left[\frac{2x}{(2b - a)(a - 2x)} + \frac{2b}{(a - 2b)^2}\log_e \frac{b(a - 2x)}{a(b - x)}\right]$$

Substituting in (3), we get

$$\frac{dx}{dt} = k_1(a - 2x)^2(b - x) - k_2\frac{(a - 2x)(b - x) \, . \, 2x}{(2b - a)} - k_2\frac{2b(a - 2x)^2(b - x)}{(a - 2b)^2}\log_e\frac{b(a - 2x)}{a(b - x)} \quad (6)$$

the integral of which is not a simple mathematical expression. In order to test the validity of this equation, dx/dt was calculated for various values of x and the values obtained were compared graphically with the actual values. (The tabulated data suffice for the reader to check any of the experiments in this way, and Fig. 3 gives the curves for the three experiments 1A, 2B, and 3A.) The values of the constants used for Fig. 3 were $k_1 = 4{\cdot}5 \times 10^{-7}$ and $k_2 = 1{\cdot}85 \times 10^{-4}$ at 25°; $k_1 = 2{\cdot}2 \times 10^{-7}$ and $k_2 = 2{\cdot}0 \times 10^{-4}$ at 15°. The temperature coefficient of k_2 indicates a process requiring a very small energy of activation. Fig. 3 also shows the values that dx/dt would have if the reaction obeyed the simple termolecular law, these values being calculated from the equation dx/dt $= k_1(a - 2x)^2(b - x)$. It is to be noted that in order to maintain a suitable scale for the three experiments, the values of dx/dt at $x = 0$ for experiments 2B and 3A have been omitted from Fig. 3. They are 11·0 and 16·2 respectively, and the three curves of each experiment originate at these points.

FIG. 3.



This theory would require that the reaction should be completely inhibited when

$$k_1(a - 2x)^2(b - x) = k_2\frac{(a - 2x)(b - x) \, . \, 2x}{(2b - a)} + k_2\frac{2b(a - 2x)^2(b - x)}{(a - 2b)^2}\log_e\frac{b(a - 2x)}{a(b - x)}$$

Fig. 3 shows how these two functions of x, f(x) and $\phi(x)$ respectively, approach one another as the reaction proceeds, dx/dt consequently approaching zero. In some experiments (*e.g.*, 3A, 1D, 2A, 2E, 3D, and 3B) the f(x) and $\phi(x)$ curves approach one another so closely that dx/dt should be negligible. Actually, it was so small that x was virtually a constant. This is an example of two mixed gases incapable of reaction owing to surface conditions, and is reminiscent of the author's observations on the nitric oxide–oxygen reaction, which was studied under conditions of intensive drying.

Heterogeneous reactions usually obey the adsorption isotherm. According to this, the rate of condensation is proportional to $2x(1 - \sigma)$ and the rate of evaporation is proportional to σ, these two quantities being equal and opposite, *i.e.*, the adsorbed gas is in equilibrium with the gas phase. Since these suppositions failed to give a velocity equation which would satisfy the present experiments, it has been assumed that the evaporation of nitrosyl chloride from the surface is negligible during the time of the experiment, *i.e.*, the surface and the gas phase are not in equilibrium. The rate of condensation, or the rate of covering of active surface, at a particular moment, will be proportional to $2x(1 - \sigma)$. In other words, equation (3) will express the behaviour of the surface. It is noteworthy that Maxted and Evans (J., 1938, 1228; 1939, 1750) have found that the relationship between adsorption and catalytic activity can best be accounted for by Bangham and Sever's equation, which resembles (4), the latter being deduced from (3).

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