

CXI.—*Photochemical Equilibrium in Nitrogen Peroxide.*
Part I.

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IN the course of a series of photochemical investigations with different gases, it was discovered that when nitrogen peroxide is enclosed in a water-jacketed vessel and illuminated by the rays from a quartz mercury-vapour lamp, a considerable increase of pressure is developed which is too great to be attributed to the heat effect of the absorbed radiation. For instance, with a total pressure of only 8.5 mm. of nitrogen peroxide, a pressure increase of about 3.3 mm. was obtained. For higher pressures of nitrogen peroxide, this pressure increase rapidly approached a maximum constant value of about 11.45 mm.

The development of this pressure under illumination started rapidly, but became slower and slower until it was complete in about 15 minutes: on being screened from the light, the gas gradually returned to its former pressure, at first rapidly and then more slowly, in the course of about 60 minutes (see Fig. 1).

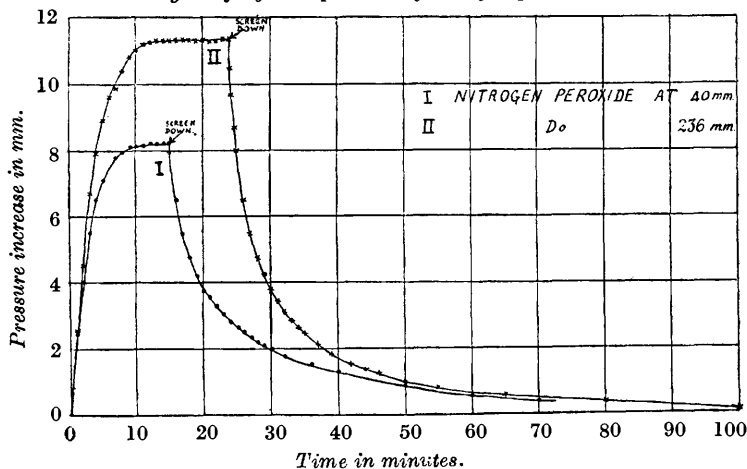
It is well known that nitrogen peroxide is a mixture of two constituents, N_2O_4 and NO_2 , in equilibrium with each other. The work of Bell (*Amer. Chem. J.*, 1885, 7, 32) and of Liveing and Dewar (*Proc. Roy. Soc.*, 1889, 46, 222) on the absorption of light by nitrogen peroxide at different pressures and temperatures leaves no doubt that the coloured constituent is the NO_2 molecule, whilst N_2O_4 (over the range of the spectrum passed by glass, at any rate) is quite non-absorbing. When the light from the mercury lamp was filtered through a plate of glass 5 mm. thick, the maximum pressure increase was only diminished by a small amount which could be partly accounted for by the loss of intensity due to reflexion at the two

glass surfaces (see Part II); it was therefore concluded that the photoactive constituent of nitrogen peroxide is the NO_2 molecule. The graph of the maximum pressure increases developed in nitrogen peroxide at various total pressures is shown in Fig. 2.

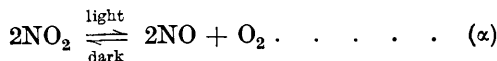
It was at first thought that the pressure increase might be explained on the basis of a shift in the equilibrium $\text{N}_2\text{O}_4 \rightleftharpoons 2\text{NO}_2$ under the influence of the light, but the slow recovery of the gas after the light had been shut off is in disagreement with this, since Argo (*J. Physical Chem.*, 1914, **18**, 438) has shown that the above equilibrium is attained instantaneously.

FIG. 1.

Effect of light on pressure of nitrogen peroxide.



Another possibility was that the results might be explained on the basis of the establishment of a photochemical equilibrium of the nature



When a steady state is reached under uniform illumination, there would be an equilibrium quantity of nitric oxide and oxygen present in the system, which would recombine according to the termolecular dark reaction investigated by Bodenstein and Lindner (*Z. physikal. Chem.*, 1922, **100**, 87).

In order to test this view, the effect of adding excess of nitric oxide or oxygen to the system was studied. The addition of increasing concentrations of either of these gases would throw back the photochemical equilibrium to a greater and greater extent until the increase of pressure due to photochemical equilibrium

FIG. 2.

Pressure changes in nitrogen peroxide on illumination.

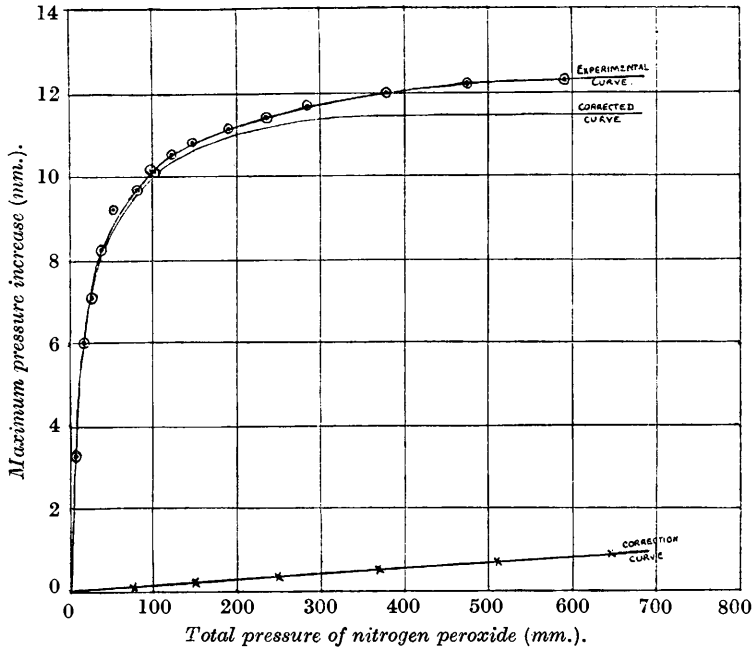
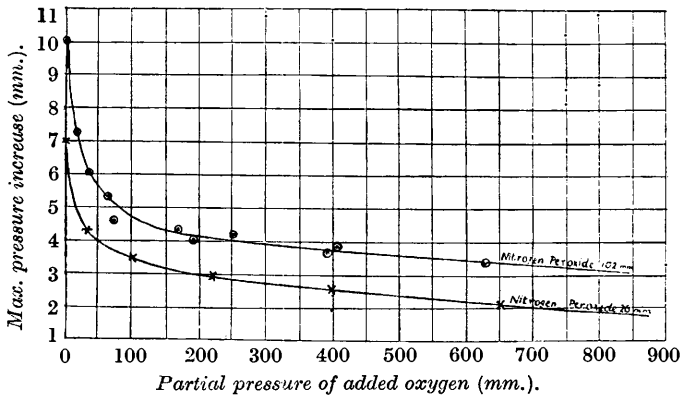


FIG. 3.

Effect of oxygen.

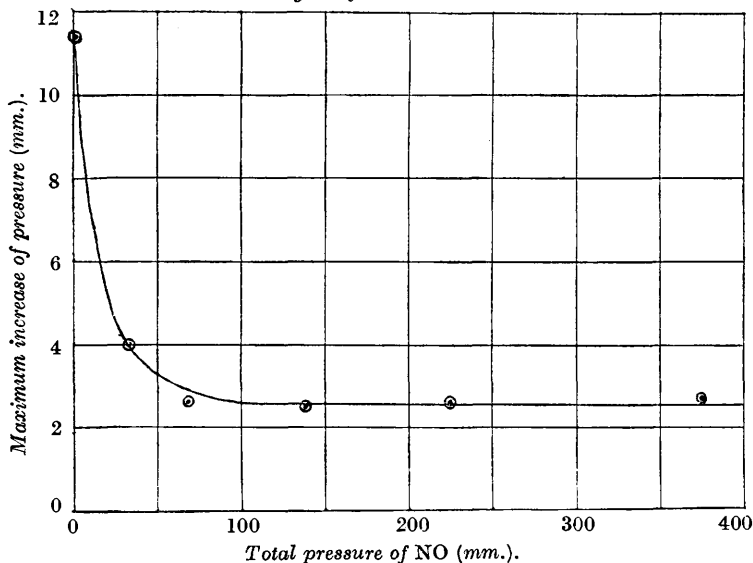


would be very small indeed. This was actually found to be the case (Figs. 3 and 4, Tables III and IV), and in accordance with the fact that the velocity of the reaction $2\text{NO} + \text{O}_2 = 2\text{NO}_2$ depends upon the square of the concentration of nitric oxide, and only on

the first power of that of the oxygen, nitric oxide was found to be the more effective in displacing the equilibrium.

The experiments with excess of nitric oxide and oxygen also showed that after the photochemical equilibrium had been completely suppressed there was still a small residual pressure increase. It will be shown later that this residual effect is proportional to the total light energy absorbed by the nitrogen peroxide, and is suitably ascribed to the sum of the heat liberated by the reverse reaction $2\text{NO} + \text{O}_2 \longrightarrow 2\text{NO}_2$ and the direct heating effect of the absorbed radiation.

FIG. 4.

Effect of nitric oxide.

Granted that the primary photochemical reaction is a decomposition of the NO_2 molecule, the order of the reaction still requires elucidation. A unimolecular reaction would require the liberation of atomic oxygen, and seems improbable in view of the high energy required to effect this. A bimolecular reaction might take place upon the collision of an active with an inactive NO_2 molecule, with the liberation of molecular oxygen. That no atomic oxygen is liberated seems to be proved by the fact that when nitrogen peroxide was illuminated in the presence of hydrogen as a depolariser, no water was formed. The hydrogen indeed slightly decreased the pressure increase (see Table II), but this seems to be simply explained as due to the more rapid loss of heat by the system con-

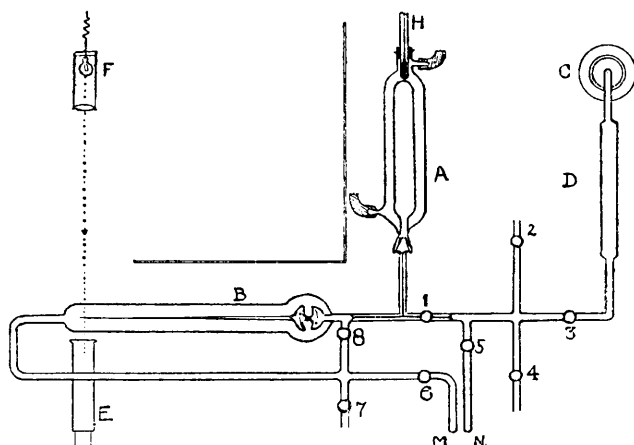
sequent upon the increased conductivity resulting from the addition of hydrogen. It may therefore, for the present, be concluded that the photochemical decomposition of nitrogen peroxide takes place by way of a bimolecular rather than a unimolecular reaction.

It is shown later that the numerical results obtained can be quantitatively explained on the basis of the above hypothesis.

EXPERIMENTAL.

The apparatus employed is shown in Fig. 5. The reaction chamber, A, a double-jacketed clear quartz vessel, was made all in one piece, and through the outer part water at a known temperature (shown by the thermometer H) could be circulated from a

FIG. 5.



thermostat by a pump. The inner part of the vessel A was 18 cm. long and 3 cm. in diameter, and was joined by the ground joint to capillary tubing which communicated with the rest of the apparatus. The pressure changes were measured by the Bourdon gauge B (see Norrish, J., 1925, 127, 2316), the deflexions of the style of the gauge being observed by a low-power microscope containing a calibrated scale in the eye-piece. A maximum pressure change of about 30 mm. of mercury could be measured by this means to an accuracy of ca. 0.05 mm., one scale division corresponding to 0.38 mm. The gauge was surrounded by an outer jacket in which the air pressure could be varied from 0 to 1 atm., thus enabling the total pressure of nitrogen peroxide and other gases which attack mercury to be measured. To effect this the pressure in B was equalised with that in A by means of the stopcock 7, the gauge pointer being brought to zero on the scale, and the pressure of the air was obtained by reading

the vertical mercury manometer, M. By means of the stopcock 8 the pressures in the inside and outside of the gauge could be equalised rapidly, in cases of emergency, to save fracture of the gauge.

The apparatus could be evacuated by way of stopcock 4, which made connexion through calcium chloride and phosphoric oxide drying tubes to a water pump and a Toepler pump, and the pressure could, if desired, be measured directly on a vertical manometer at N.

The nitrogen peroxide after purification was stored in the bulb C, and when not in use was kept in liquid air; when required, it was allowed to melt completely by removing the liquid air, and the vapour was admitted to the evacuated reaction chamber by way of the phosphoric oxide drying tube, D, and stopcocks 3 and 1.

Through stopcocks 2 and 1 pure hydrogen, oxygen, or nitric oxide could be admitted after passing through a series of drying tubes containing calcium chloride and phosphoric oxide. The contents of the quartz vessel were illuminated by a double-barrelled quartz mercury-vapour lamp, of 3000 candle power, with a burner voltage of 150 volts, and carrying a current of 2.5 amps. The lamp was placed vertically beneath and parallel to the reaction vessel A, at a distance of 5 cms. Between the lamp and the vessel A was a horizontal brass screen which could be conveniently opened against the action of a spring by means of a cord working over pulley wheels. When the cord was released the spring automatically closed the screen. In this way, the reaction vessel could be rapidly illuminated or screened at will. A glass screen also could be placed between the reaction vessel and the lamp if desired.

In carrying out an experiment, the reaction vessel, the gauge, and the bulb C were first evacuated as completely as possible by the Toepler pump. Connexion with the pump was then cut off, the nitrogen peroxide was vaporised by the method described, and admitted to the reaction chamber to the required pressure, and stopcocks 3 and 1 were then closed. The liquid-air bath was replaced on the nitrogen peroxide bulb, and the connecting tubes between stopcocks 1, 2, 3, 4, and 5 were evacuated by means of the water pump and washed out several times with any other gas, *e.g.*, pure dry hydrogen, nitric oxide, or oxygen, which could then be admitted to the reaction vessel if required. In the meantime, the lamp had been running for about 10 minutes, in order to reach a steady rate of burning, the screen being closed. The gauge pointer being accurately adjusted to zero, an exposure was now made by opening the screen, and readings of the pressure increase were taken at intervals of about 20 secs. at first, extending to several minutes when the pressure change was completed. When

the maximum pressure increase had been obtained in this way, the screen was closed, and the pressure returned slowly to its original value. It was found necessary to introduce a small and uniform correction into the readings of the pressure changes, due to a slight heating by the lamp of that part of the reaction chamber (*i.e.*, the capillary leads) which was outside the thermostat. This correction curve was determined by observations on the increase of pressure when air at different pressures was enclosed in the reaction vessel; and since the corrections could be determined as accurately as the original measurements themselves, the corrected pressures were of the accuracy (0.05 mm.) already specified. A graph of the actual readings of the pressure change in pure nitrogen peroxide is shown in Fig. 2, together with the correction curve obtained from the measurements on air. The corrected pressure changes themselves are recorded in the tables under the heading "Press. increase (obs.)."

The nitrogen peroxide was prepared by distillation of lead nitrate in a slow stream of oxygen. The evolved gas was passed through a phosphoric oxide drying tube, and condensed by means of a freezing mixture of carbon dioxide and ether. It was fractionated twice in a stream of oxygen, through drying tubes, and finally distilled into the bulb C, and attached to the apparatus (Fig. 5). When cooled in liquid air it froze to a mass of absolutely colourless crystals, which melted to a very pale yellow liquid boiling at 21.5°.

In Table I, the corrected pressure increases for the pure gas are shown; in Tables II, III, and IV, respectively, the results

TABLE I.

Pressure Change in Nitrogen Peroxide on Illumination.

Total press. of nitrogen peroxide, P .	Initial press. of NO_2 , p .	Equil. press. of NO_2 , p_1 .	Press. increase	
			(obs.), n .	(calc.), $x + y$.
8.5	7.67	2.8	3.3	3.70
19	15.6	9.4	5.95	5.80
26	20.3	14.2	7.0	6.66
40	28.6	23.1	8.15	7.91
53	35.6	30.3	9.1	8.68
81	58.3	44.4	9.55	9.57
100	56.2	52.4	10.0	9.97
102	56.8	53.2	10.0	9.99
123	64.8	60.7	10.35	10.28
146	72.6	69.3	10.6	10.53
148	73.3	70.0	10.55	10.56
193	87.2	84.7	10.8	10.85
236	99.0	96.6	11.05	11.03
286	111.7	109.6	11.3	11.17
381	133.3	131.2	11.45	11.30
476	152.7	151.4	11.45	11.38
593	173.0	172.1	11.40	11.43

showing the effects of hydrogen, oxygen, and nitric oxide, are given. All pressures are in mm. Hg, and all the experiments were at 20°.

The results of Tables III and IV are plotted in Figs. 3 and 4. From these curves the residual pressure change, remaining after the equilibrium is completely suppressed, can be deduced as described in a later section.

TABLE II.

Effect of Hydrogen.

Nitrogen peroxide at 148 mm. pressure.

Press. of hydrogen ...	0	67.5	174	368	579
Press. increase	10.55	10.15	10.1	10.05	9.8

TABLE III.

Effect of Oxygen.

Press. of nitrogen peroxide, P .	Equil. press. of NO_2 , p_1 .	Initial press. of O_2 .	Total press. change	
			(obs.), n .	(calc.), $x + y$.
102	53.2	0	10.0	10.0
102	54.6	17	7.25	6.92
102	55.3	36	6.05	5.76
103	56.1	64	5.3	5.00
102	55.9	73	4.55	4.85
103	56.6	169	4.35	4.02
102	56.3	191	4.0	3.91
100	55.3	254	4.2	3.68
102	56.5	394	3.69	3.44
103	56.7	409	3.85	3.43
102	56.6	631	3.35	3.22
26	13.3	0	7.0	6.56
26	17.7	33	4.3	3.64
26	18.1	101	3.45	2.66
26	18.6	221	2.9	2.21
26	18.9	399	2.55	2.00
26	19.4	655	2.1	1.84

TABLE IV.

Effect of Nitric Oxide.

Press. of nitrogen peroxide, P .	Equil. press. of NO_2 , p_1 .	Initial press. of NO , P_{NO} .	Total press. change	
			(obs.), n .	(calc.), $x + y$.
236	96.5	0	11.4	11.40
235	97.5	28	4.0	5.10
233	97.5	68	2.6	3.14
233	97.5	137	2.5	2.93
233	97.5	249	2.6	2.84
233	97.5	373	2.65	2.82
446	146	249	2.84	3.0
19	15.6	222	0.95	1.03

Theoretical Treatment.

In accordance with the considerations given earlier in this paper, it will now be assumed as a working hypothesis :

- (1) That the NO_2 is the photoactive constituent.
- (2) That the photodecomposition is bimolecular.
- (3) That collision between an active and an inactive NO_2 molecule may result either in chemical change, or in the degradation of the activating energy to heat.
- (4) That heat is produced both by the recombination of nitric oxide and oxygen and by the thermal degradation of the absorbed light energy.

The pressure of NO_2 present at each of the pressures used was found by the help of the equation of Wourtzel (*Compt. rend.*, 1919, 169, 1397) for the dissociation constant of nitrogen peroxide,

$$\log K_p/T = - 2810.5/T + 8.9908 \quad \dots \quad (1)$$

which gives $K_p = 71.71$ at 20° , the unit of pressure being mm. Hg.

If P be the total pressure of N_2O_4 and NO_2 , and p the partial pressure of NO_2 , then, at 20° , $p^2/(P - p) = 71.71$,

whence
$$p = \sqrt{71.71 P + 1285} - 35.85 \quad \dots \quad (2)$$

The partial pressures of NO_2 for various total pressures of nitrogen peroxide were calculated by this equation, and a curve was constructed showing the relation between p and P ; from this curve the figures shown in the column headed "Initial press. of NO_2 " were read off. This pressure of NO_2 present at the start of the experiments has now to be corrected to the pressure obtaining at equilibrium, which will in general be different on account of the photochemical decomposition which has taken place. The correction is relatively large at low pressures, but small at high pressures of NO_2 . It is obtained as follows :

If x is the equilibrium pressure increase (exclusive of heating effect) due to the reaction (α) (p. 762), then $2x$ will indicate the equilibrium excess pressure of nitric oxide present in the system. The total nitrogen peroxide present, represented entirely as NO_2 , is $2(P - p) + p = 2P - p$. When the photochemical equilibrium is established, this quantity is decreased by the amount $2x$, and if P_1 and p_1 are the new total pressure of nitrogen peroxide and partial pressure of NO_2 , respectively, then

$$2P - p - 2x = 2P_1 - p_1 \quad \dots \quad (3)$$

Also, as before,
$$p_1^2/(P_1 - p_1) = 71.71 \quad \dots \quad (4)$$

whence, solving equations (3) and (4), we obtain

$$p_1 = \sqrt{71.71P - 35.85p - 71.71x + 321} - 17.93 \quad \dots \quad (5)$$

Equation (5) gives the pressure of the photoactive constituent, the NO_2 present when the photochemical equilibrium has been established, from the known values of P and p , and from the value of x

as obtained in a later section. The values of p_1 have been calculated and tabulated in the columns headed "Equil. press. of NO_2 " in the tables.

The Photochemical Effect.

We shall now consider the photochemical equilibrium in the nitrogen peroxide. If Y represents the equilibrium concentration of active NO_2 molecules, then their rate of formation, which is proportional to the total light absorbed by the NO_2 , may be written

$$dY/dt = k_1 I (1 - e^{-kp_1}) (6)$$

where I is the intensity of light entering the reaction chamber, and $(1 - e^{-kp_1})$ is the fraction of the photochemically active light absorbed by the NO_2 .

The active molecules, according to hypothesis, collide with inactive NO_2 molecules, and cause either thermal degradation or photochemical reaction, the respective coefficients being k_2 and k_3 . Thus

$$- dY/dt = k_2 Y p_1 + k_3 Y p_1 (7)$$

From equations (6) and (7), at equilibrium,

$$Y = k_1 I (1 - e^{-kp_1}) / p_1 (k_2 + k_3) (8)$$

The rate of photochemical decomposition is therefore

$$k_3 Y p_1 = k_1 k_3 I (1 - e^{-kp_1}) / (k_2 + k_3) (9)$$

At equilibrium, this is balanced by the rate of recombination of the products, and if x is the equilibrium pressure increase, as before, and P_0 and P_{NO} are the pressures of oxygen and nitric oxide initially present in the system, then the velocity of recombination, according to Bodenstein and Lindner (*loc. cit.*), will be :

$$k_4 (P_0 + x) (P_{\text{NO}} + 2x)^2$$

whence

$$(P_0 + x) (P_{\text{NO}} + 2x)^2 = k_1 k_3 I (1 - e^{-kp_1}) / k_4 (k_2 + k_3) (10)$$

So long as the light intensity remains constant, as in the present experiments, we may write $k_1 k_3 I / k_4 (k_2 + k_3) = K$ and

$$(P_0 + x) (P_{\text{NO}} + 2x)^2 = K (1 - e^{-kp_1}) (11)$$

In the first series of experiments, pure nitrogen peroxide was used; P_0 and P_{NO} were therefore zero, hence

$$x = \sqrt[3]{K(1 - e^{-kp_1})/4} (12)$$

which gives the pressure increase due to photochemical equilibrium and exclusive of the heating effect.

The Heating Effect.

We may now obtain an expression for the heating effect. From equation (7) above, it follows that the heat evolved per second due to thermal degradation is proportional to

$$k_2 Y p_1 = k_1 k_2 I (1 - e^{-k p_1}) / (k_2 + k_3) . . . (13)$$

The heat evolved per second by the recombination of the nitric oxide and oxygen is proportional to

$$(P_o + x)(P_{No} + 2x)^2 = K(1 - e^{-k p_1}).$$

The total heat evolved per second is therefore proportional to

$$\{k_1 k_2 I / (k_2 + k_3) + K\} (1 - e^{-k p_1}) = K_1 (1 - e^{-k p_1}) . . . (14)$$

This heat is conducted away at a constant rate, independent of the total gas pressure, for the thermal conductivity of a gas does not vary between pressures of 1 and 760 mm. (Meyer, "Kinetic Theory of Gases"). It therefore follows that there will be a constant equilibrium excess quantity of heat, which we may represent by h , present in the system, and proportional to $K_1(1 - e^{-k p_1})$. The gas will therefore be at a slightly higher temperature than the thermostat, the temperature increment being given by

$$dT = k_5 h / M C_v (15)$$

where M is the total number of moles of gas present in the vessel, and C_v the specific heat at constant volume. If v be the volume of the reaction vessel, then

$$Pv = MRT (16)$$

whence, at constant volume,

$$v.dP = MR.dT = k_5 MRh / M C_v . . . (17)$$

Therefore $dP = k_5 R h / v C_v = K_0 (1 - e^{-k p_1}) . . . (18)$

where K_0 is proportional to $K_1 k_5 R / v C_v$.

The pressure increase dP due to the combined heating effect of the light and the reverse reaction is therefore proportional to the total quantity of light absorbed. We may represent it by y and write

$$y = K_0 (1 - e^{-k p_1}) (18A)$$

Determination of the Constants of Equations (11) and (18).

For the evaluation of the constants of equations (11) and (18) the data in Table III were used. The total pressure increase, n , is the sum of that due to the reaction, x , and that due to the heating effects, y . With excess of oxygen present the value of the former is

rapidly diminished as the photochemical equilibrium is suppressed, whilst the latter is only slightly changed, since the quantity $(1 - e^{-kp_1})$, upon which y depends (equation 18A), alters only to a small extent as x approaches zero (equation 5, x being always small compared with P).

Thus, as increasing quantities of oxygen are added to a given quantity of nitrogen peroxide, the magnitude of the pressure change on illumination approaches asymptotically to the value of y . This is shown quite clearly in the experimental curves (Fig. 3).

When excess of oxygen is present, the initial pressure of nitric oxide being zero, equation (11) becomes

$$(P_0 + x)x^2 = K(1 - e^{-kp_1})/4 \quad . \quad . \quad . \quad (19)$$

Now p_1 is in general different from p , the pressure of NO_2 introduced into the bulb, on account of the photochemical decomposition which has occurred, and the small correction by which the known values of p are converted to p_1 is obtained from the observed pressure change as follows.

We take the asymptote of the oxygen curve to give y when x approaches zero (*i.e.*, when the photochemical equilibrium is completely suppressed). At this point, equation (5) reduces to $p_1 = p$, and since p is known, K_0 and k can be calculated from the asymptotic values of the two oxygen curves and the known values of p by equation (18A). By this means, using the data in Table III for nitrogen peroxide at 102 mm. and 26 mm., we find $K_0 = 3.02$ and $k = 0.0267$, the asymptotic values of y being taken as 2.3 mm. and 1.3 mm., respectively.

Approximate values of x required to correct p to p_1 by equation (5) can now be obtained from the observed values of the pressure change (n) by subtracting from them the asymptotic value for y used above. Actually, of course, the value of y changes slowly as x increases, but the total variation in extreme cases is not more than 10%, and the corresponding values of x are not in error by more than 2% when this single value of y is used. The values of p_1 obtained therefrom are not affected to the extent of more than 1% by this approximate treatment, and in most cases by very much less.

From the values of p_1 so obtained, and the constants K_0 and k found above, the values of y for different oxygen pressures are next calculated. These, when subtracted from the observed total pressure change, give the "accurate" observed values of x from which, on substitution in equation (19), we find $K = 2416$. The sums of the calculated values of x and y are shown in Table III and are in good agreement with the observed values for the total increase of pressure.

With excess of nitric oxide present, the photochemical equilibrium is soon almost completely suppressed, the effect being greater than that of oxygen as anticipated (p. 763). Equation (11) now becomes

$$(P_{\text{NO}} + 2x)^2x = K(1 - e^{-kP_1}) \dots (20)$$

Calculating p_1 as before, and taking the same values for K , k , and K_0 , the values of $(x + y)$ have been calculated from equations (20) and (18A) and show suitable agreement with the observed values (Table IV).

Finally, we can now test equation (12), which applies to systems containing no added nitric oxide or oxygen (Table I). Taking the values of K_0 , K , and k already found, we have

$$x^3 = 604(1 - e^{-0.0267P_1}) \dots (12A)$$

and $y = 3.02(1 - e^{-0.0267P_1}) \dots (18B)$

Hence $x^3 = 200y \dots (21)$

Also $x + y = n \dots (22)$

where n is the total observed pressure change. The "observed" value of x can therefore be obtained from the recorded values of n by solving equations (21) and (22), and has been used in equation (5) as before to calculate values of p_1 for the different pressures of nitrogen peroxide used. From these values using equations (12A) and (18B) the values of $(x + y)$ given in the last column of the table have been calculated. It will be seen that close agreement is obtained.

In Table V are shown the experimentally determined heat effects in the presence of excess of nitric oxide or oxygen as described above; the calculated heating effect (y) obtained from equation (18B), putting $p_1 = p$ (since x is negligibly small), is tabulated for comparison. The agreement obtained can leave no doubt that the heating effect is actually proportional to the quantity of light absorbed as is demanded by the theory.

TABLE V.
Heating Effect.

Press. of nitrogen peroxide.	Press. of NO ₂ ($p_1 = p$).	Press. change due to heating.	
		(obs.).	(calc.).
19	15.6	0.95	1.03
26	20.3	1.3	1.23
100	56.8	2.3	2.36
233	97.5	2.6	2.82
446	146	2.85	3.00

The close agreement that has been obtained between the observed and the calculated values of the pressure change of nitrogen peroxide on illumination shows that the theory of the change adopted

is in agreement with the facts. It may therefore be definitely stated :

(1) That nitrogen peroxide is decomposed by the light of the mercury-vapour lamp into nitric oxide and oxygen.

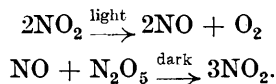
(2) That a photochemical stationary state is set up resulting in an increase of pressure in the system.

(3) That the probable mechanism is, first, the activation of an NO_2 molecule, and, secondly, the reaction of this active molecule with an inactive molecule of NO_2 to produce nitric oxide and oxygen.

In Part II of this series the photo-kinetics of this change will be further investigated and discussed.

In the light of these experiments, it is now possible to understand the experiments of Daniels and Johnston (*J. Amer. Chem. Soc.*, 1921, **43**, 72), who found that nitrogen pentoxide is apparently decomposed photochemically by blue light, but only in the presence of nitrogen peroxide, and drew from this the erroneous conclusion that the thermal decomposition of the pentoxide must also be influenced by the peroxide (Daniels, Wulf, and Karrer, *ibid.*, 1922, **44**, 2402). This was disproved by Hirst (J., 1925, **127**, 657) and later by White and Tolman (*J. Amer. Chem. Soc.*, 1925, **47**, 1240), who showed that the thermal decomposition is uninfluenced by the presence of the peroxide.

We may now assume that the photochemical decomposition of nitrogen pentoxide is a secondary dark reaction taking place according to the scheme



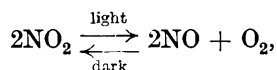
The second reaction, being bimolecular, is more likely to take place than the reverse of the first reaction, which is termolecular, so that the whole of the pentoxide will be decomposed as a result of the photodecomposition of the NO_2 .

On this view, it is obvious that the mechanisms of the photochemical and thermal decompositions of nitrogen pentoxide are entirely different, and that no effect on the latter is to be expected in the presence of NO_2 , in view of its effect on the former.

Summary.

It has been found that nitrogen peroxide undergoes a marked change of pressure on illumination by mercury light. This pressure change is too great to be accounted for on the basis of a heating effect due to the absorbed light, and has been found to be due (1) to

the establishment of a photochemical equilibrium in the system represented by the equation



and (2) to a heating effect, due to the recombination of the nitric oxide and oxygen and also to the absorbed radiation.

A reaction mechanism involving reaction between active and inactive NO_2 molecules is proposed and is in quantitative agreement with the observed results.

A simple mechanism for the photodecomposition of nitrogen pentoxide is proposed.

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