

THE REACTION BETWEEN ATOMIC OXYGEN AND
NITRIC OXIDE

BY

BEN THOBURN BRIGGS

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THE S I S

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I HEREBY RECOMMEND THAT THE THESIS PREPARED UNDER MY
SUPERVISION BY BEN THOBURN BRIGGS

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BE ACCEPTED AS FULFILLING THIS PART OF THE REQUIREMENTS FOR
THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY

W. H. Rodbruch
In Charge of Thesis
Roger Adams for W. H. Rodbruch
Head of Department

Recommendation concurred in*

B. S. Hopkins
George H. Reed
B. M. Ketchum
T. E. Phipps

Committee
on
Final Examination*

*Required for doctor's degree but not for master's.

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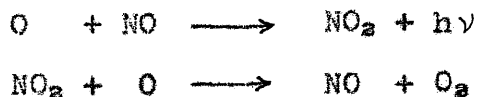
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I. INTRODUCTION

In recent years a great deal of work has been done on the kinetics of gaseous reactions. One cannot but be impressed by the number of photoreactions whose mechanisms postulate the formation and subsequent reaction of atoms in at least one step of the process. While a good deal is to be learned from photochemical studies, such methods are often difficult to interpret. Another method of attack is sometimes open, and that is the direct reaction of atoms generated either thermally or by means of an electrical discharge.

The classic example of such a study is that of Bonhoeffer¹ on hydrogen atoms. Since that time numerous investigations have been made on the various reactions of such atoms as Na, H, Cl, Br, I, O, etc.

While the visible effect of the reaction between atomic oxygen and nitric oxide here studied, i.e. its luminescence, has been known for perhaps eighty years, the first serious attempt to postulate its mechanism was made some twenty-five years ago by Strutt². More recent consideration by Spealman and Rodebush³ showed that Strutt was partially in error and indicated that the two primary reactions in the afterglow were:



It seemed desirable to do more work on the first of these reactions in order to determine its rate, and to decide whether or not it occurred by triple collision.

It seems advisable at this point to distinguish the terms "oxygen afterglow" and "nitrogen afterglow." The former is the yellowish green chemiluminescence which may be observed when oxygen containing some nitrogen is passed through a discharge tube. Its spectrum is composed of a continuum from at least $4200 \text{ \AA}$ to $6700 \text{ \AA}$ with a number of very weak, diffuse bands. On the other hand, the "nitrogen afterglow" is the brownish yellow luminescence obtained by passing nitrogen with a little oxygen, through a discharge. Its spectrum is not a continuum, but is, instead, composed of well-defined nitrogen bands.

It is not to be supposed that these gaseous mixtures are the only ones which will give their respective afterglows. Indeed, the most brilliant oxygen afterglow so far observed is that given by passing nitric oxide into a stream of partially dissociated oxygen.

II. HISTORICAL

Probably the earliest record of an oxygen afterglow is credited to Becquerel⁴. In 1859, using an oxygen discharge tube, he noted a peculiar yellowish green glow which persisted some time after the current was turned off. Soon after, Riess⁵ announced that he had in his possession a similar tube made by Geissler, who had made several tubes which gave quite strong afterglows. He claimed that the only essential difference between the ordinary oxygen discharge tube and one that glowed was that the latter contained a few drops of concentrated sulfuric acid. Morren⁶ investigated the gases which gave the afterglow and reached the conclusion that pure oxygen did not glow; that oxygen containing 40% nitrogen glowed weakly; that the intensity and life of the afterglow were greatly increased by the addition of a little concentrated sulfuric acid; and that the afterglow was caused by the formation and decomposition of an hypothetical compound, $\text{NO}_2 \cdot 2\text{SO}_2$, which he claimed to have made.

Becquerel⁴ had originally suggested the formation of ozone as the source of the luminescence. Sarasin⁷ sought to confirm this. He found that, under conditions in which ozone would be removed from the discharge as fast as formed, the glow disappeared. He decided that the light emitted came from the formation of ozone or nascent oxygen and the subsequent vigorous oxidation which these substances could cause. He could find no evidence for Morren's compound, $\text{NO}_2 \cdot 2\text{SO}_2$. His work was confirmed by de la Rive⁸.

Warburg⁹ concluded that the afterglow was occurring in the molecules of the gas and was not caused by some secondary discharge between the glass walls and the gas. His experiment consisted of

obtaining the afterglow in a long discharge chamber and then suddenly opening a stop-cock at one end of the tube. The glow was compressed in the far end of the tube. He argued that, since the luminescence was produced by a chemical action, it must involve molecules of at least two different species; and that, therefore, the afterglow could not occur in a really pure gas - a conclusion which seems to be borne out by the more precise work of recent years even if the reasoning was weak.

Dewar¹⁰ was probably the first worker to use a flow method. He passed air through a discharge tube under reduced pressure and observed an intense afterglow farther down the tube. He was evidently aware that ozone had been postulated by a number of previous workers as one of the active components of the luminescence. A little starch-iodide placed in the glow immediately darkened; another bit outside the luminous region was not changed.

J. J. Thomson¹¹ studied the spectrum of the oxygen afterglow and found it to be continuous. He also noticed that the intensity of the luminescence was weakened at higher temperatures. His work is especially important from the standpoint of the present work since it marks the introduction of the electrodeless discharge for the production of the afterglow. It appears that he was the first to notice that all oxygen-nitrogen mixtures did not emit the same spectrum after passing through the discharge. His "pure" oxygen (it must have contained traces of nitrogen) gave an afterglow, the spectrum of which was a continuum. On the other hand, a mixture rich in nitrogen showed bands.

Shortly after, Kirn¹², using an electrode discharge, confirmed Thomson's conclusion in regard to the continuous nature of

the oxygen afterglow and observed that the glow in the immediate region of the discharge had an altogether different nature.

Newall¹³, using electrodeless discharges on different gaseous mixtures, concluded that:

- (a) white phosphorescences are characteristic of oxygen and carbon compounds,
- (b) yellow phosphorescences are characteristic of oxygen and nitrogen compounds,
- (c) blue phosphorescences are characteristic of oxygen and sulfur compounds.

He also observed the continuous nature of the oxygen afterglow, but was unable to confirm Thomson's contention that a mixture of oxygen and nitrogen, rich in the latter, showed a band structure in its spectrum.

However, E. P. Lewis¹⁴ was able to photograph the spectrum of the nitrogen afterglow. It very definitely showed bands. By increasing the concentration of oxygen (using air) he got a continuum (oxygen afterglow). This work is one of the first to note that in the case of nearly pure nitrogen an increase of pressure could cause the glow to disappear.

Gehlhoff¹⁵ thought that the afterglow was at least partly a fluorescence phenomenon.

Most of the work outlined so far was of a more or less unrefined nature. In fact, it is hard to tell in some cases whether the nitrogen afterglow or the oxygen afterglow is being described.

However, the work of Thomson was sufficiently precise to permit subsequent workers to draw a sharp distinction between the

two.

In 1910, Strutt (Lord Rayleigh)^{2,16,17,18} started publishing papers on the oxygen and the nitrogen afterglows. One of the first questions he had to answer was, "What causes the oxygen afterglow?" His conclusion was that the emission came from a vigorous oxidation of nitric oxide by ozone, both of which might be formed when mixtures of nitrogen and oxygen passed through the discharge. It is important that his reasons for postulating ozone be listed in order that it may be seen that the mechanism to be maintained in this paper (not involving ozone) will explain each observation just as well as the older theory does. His experimental facts were these:

- (1) The glow disappeared when the tube was heated to about 300°C. There was sometimes a slight tendency for the glow to reappear downstream.
- (2) The glow was destroyed on passing through a liquid air trap.
- (3) The glow disappeared on passing over cupric oxide or manganous oxide, but survived passage through glass wool.
- (4) Silver gauze was oxidized in the afterglow and the glow was quenched.
- (5) Silver gauze was not affected by the gas stream beyond the afterglow region.
- (6) Paper impregnated with thallous hydroxide was turned dark by the afterglow.
- (7) Hydrocarbons were oxidized by the glow.

- (8) "Activated" oxygen (itself glowless) remained glowless when mixed with nitrogen (either activated or not).
- (9) Nitrous oxide, when added to the "activated" oxygen, gave no afterglow.
- (10) Nitric oxide, on the other hand, gave a very intense glow which proved to be a continuum from 4200 - 6700 Å. The latter fact shows that the glow thus produced was identical with that observed by Thomson in the case of nearly pure oxygen (oxygen afterglow).
- (11) The "active" oxygen, condensed in a liquid air trap, gave a weak flash with nitric oxide after having been vaporized.
- (12) Ozone produced in the usual way at either atmospheric or reduced pressures did not glow when nitric oxide was added. This observation was changed in a later experiment¹⁷ in which pure ozone at atmospheric pressure was added to nitric oxide. In this case he observed a momentary flash.

In one of his articles¹⁸, Strutt lists a number of ways of producing the oxygen afterglow. Among them are:

- (1) Mixtures of oxygen and nitrogen, rich in the former, passed through the discharge.
- (2) "Active" oxygen plus nitric oxide.
- (3) "Active" oxygen plus nitrogen dioxide.

The most luminous afterglow is obtained by adding nitric oxide to

"active" oxygen.

An observation which has since caused some confusion was that, while pure oxygen carefully dried is glowless, the presence of moisture causes a white afterglow. This particular experiment was made with an electrodeless discharge.

Strutt's assumption that ozone was the active species present is not to be wondered at, since at the time of his work, the existence of relatively long lived atoms had not yet been considered.

About the time that Strutt began his experiments, Zenneck and Strasser¹⁹ published some interesting results on the emission spectrum of nitrogen dioxide flowing through a long electrode tube at one millimeter pressure. The glow produced could be divided into four regions, each characterized by a different color. Beginning at the upper end of the tube, where the nitrogen dioxide entered, and proceeding downstream, the regions were:

- A. Yellow tinged with orange (NO_2)
- B. Violet-blue (?)
- C. Greenish yellow (NO)
- D. Bright red (N_2)

The different regions were studied spectrographically, and by comparison with the emission spectra of nitric oxide, nitrogen dioxide, and nitrogen, they concluded that the molecules shown in parentheses were the active species present. They then studied the spectrum emitted by the afterglow produced by nitrogen dioxide and found that it consisted of a continuum from about $4000 \text{ \AA}$ to at least $6680 \text{ \AA}$ (oxygen afterglow) upon which the band spectrum of nitrogen was lightly superposed. Their conclusion in regard to this afterglow

was that it had the appearance of arising from a mixture of regions A and C with a little of D.

This work must not be taken too seriously. It was done by passing nitrogen dioxide through an electrode discharge - a procedure much more violent and more difficult to control than that used in the present work. However, it did serve to confirm Strutt's view that the afterglow was produced by the vigorous oxidation of nitric oxide to some higher oxide.

Practically the same work was repeated by Duffieux^{20,21} and Kneser²², both of whom reached the same conclusion as Zenneck and Strasser in regard to the active species present in the afterglow.

Herzberg²³, using an electrodeless discharge, investigated the effect of the walls on the production of the oxygen afterglow. He found that, in a vessel thoroughly baked out so as to rid the walls of all adsorbed matter, the afterglow was much shorter-lived than in one whose walls were covered by adsorbed water. This perhaps throws some light on the observation of many early workers that a little sulfuric acid improved the intensity of the afterglow and lengthened its life.

He reported that in a mixture containing twenty per cent oxygen and eighty per cent nitrogen by volume he was able to obtain two entirely distinct afterglows by varying pressure: the nitrogen afterglow at 0.2 mm. pressure and the oxygen afterglow at pressures greater than 1 mm. This possibly accounts for the variation in color of the air afterglows reported by early workers.

About the same time Majewska and Bernhardt²⁴ published their results on the effect of walls on the afterglow. They

showed that the adsorbed gas which helped the afterglow was not oxygen, ozone, nitric oxide, or nitrogen dioxide.

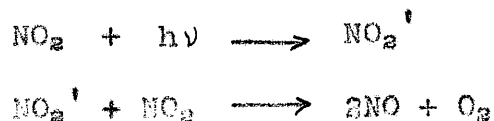
Herzberg had reported trapping ozone out of the afterglow, but Majewska and Bernhardt believed it must have been nitrogen dioxide.

Kaplan²⁵ made spectrographic studies of the oxygen afterglow. He always observed the usual continuum and in addition, since he was using wet gases, the OH bands at $3084 \text{ \AA}$. The absence of other bands indicated to him that there was no active nitrogen in the oxygen afterglow.

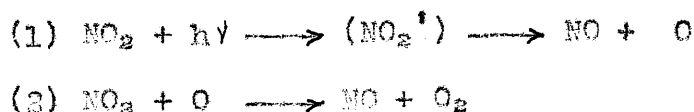
B. Lewis²⁶ made further studies on the wall effects and found that pure (?) oxygen glows when wet, but does not when perfectly dry. He used an electrodeless discharge and a static method. The glowless dry oxygen could be made to glow when a little (10^{-3} mm.) water vapor was introduced. Likewise, paraffin walls were found to favor the afterglow. The conclusion to be drawn is, of course, that certain molecules such as water or paraffin are poor catalysts for oxygen atoms, which are one of the active species in the afterglow.

In a later paper, B. Lewis²⁷ confirmed Herzberg's observation that a mixture of oxygen and nitrogen which gave a nitrogen afterglow at one pressure could often be made to give the oxygen afterglow at higher pressures.

Mecke²⁸ studied the photodissociation of nitrogen dioxide. In agreement with Norrish²⁹, he found that the quantum yield rose from zero at near $4073 \text{ \AA}$ to two at $3650 \text{ \AA}$. Norrish had postulated the following mechanism:



where the prime (') indicates a molecule in an electronically activated state. A study of the absorption spectrum for wave lengths about 3700 Å led Mecke to a different mechanism:



The absorption spectrum consists of diffuse bands which are typical of predissociation.

Mecke's work is especially important since the mechanism proposed for the afterglow involves the reverse of equation (1) and is followed by equation (2) as written.

Baxter³⁰ found a slightly different photochemical threshold for the dissociation of nitrogen dioxide; namely, 4047 Å instead of 3700 Å. The mechanism proposed by Mecke appears to have been satisfactory to him.

Geib and Harteck³¹ carried out the reaction $\text{NO} + \text{O}$ at -183° C. and found a collision efficiency (judged by the amount of nitrogen dioxide formed) of ten per cent. However, they did not put much reliance on their yield because the nitrogen dioxide may have been formed by the low temperature heterogeneous reaction:



For a discussion of the above reaction, reference should be made to the later work of Tenkin and Puizhow^{32,33} who found, at liquid air temperatures and low pressures, a reaction whose half-life was of the order of minutes whereas that of the usual trimolecular process should have been of the order of months.

Stoddart³⁴ has made quite a careful study of the oxygen afterglow with both electrode and electrodeless discharges. He used a static system. Some of his principal conclusions were:

- (1) Pure oxygen is glowless whether wet or dry in either type of discharge.
- (2) Electrode discharges through oxygen contaminated with nitrogen gives an afterglow. Electrodeless discharges do not show this property probably because of the fact that they could not synthesize nitric oxide.
- (3) The addition of a little nitric oxide produces an intense glow in either type of discharge.
- (4) Glowing oxygen is rendered glowless by trapping some active constituent from the gas at -80° C. Nitrogen dioxide is found in the trap. (It must be remembered that this experiment was a static one, and the afterglow probably extended into the trap.)
- (5) The afterglow spectrum consists of a continuum from $4200 \text{ \AA}$ to $6700 \text{ \AA}$. On this there is superposed a series of twenty-eight or thirty diffuse bands.
- (6) The afterglow is due to the oxidation of nitric oxide by ozone.

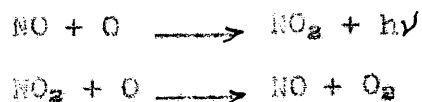
In a later paper³⁵ the same author found that, with a more powerful electrodeless discharge, oxygen containing five per cent nitrogen glowed in a vessel which had been carefully baked out. In the presence of water, such a mixture remained glowless. This

effect is explained by assuming that the formation of nitric oxide will not occur on glass surfaces covered by adsorbed water.

Lord Rayleigh³⁶ pointed out his previous conclusion that pure oxygen gave a white afterglow when an electrodeless discharge was used. Intense drying caused this to disappear. This observation is rather confusing in that, in the experiments to be described, wet or dry oxygen gave little, if any, afterglow. It is wondered if perhaps Lord Rayleigh (Strutt) was not observing the effect of some stray discharge.

Newman³⁷, using an electrode discharge, counted the superposed diffuse bands which Stoddart had mentioned and claimed to have found twenty-nine.

Spealman and Rodebush³ measured the collision efficiency of the reaction between atomic oxygen and nitrogen dioxide and found that the reaction occurred on every 10^6 double collision. A preliminary comparison of the rates of the reactions:



was made and it was found that the latter was apparently only about four times as fast as the former. If the former proceeded by triple collisions and the latter by double collision, it seemed that the difference in rate should be more marked.

III. THEORETICAL

A. Theory of Triple Collisions

The general method to be followed is to calculate efficiencies for each type of collision that is at all probable. That mechanism for which the collision efficiency is most nearly constant would normally be assumed to be the most probable. However, it is evident that there must be several different ways in which an oxygen atom can disappear:

- (1) a gas phase reaction between two atoms and an unreactive third body;
- (2) a gas phase reaction involving one atom, a reactive molecule, and a neutral third body;
- (3) a wall reaction between two atoms;
- (4) a wall reaction between an atom and a reactive molecule.

These simultaneous reactions probably occur at altogether different rates so that the over-all rate will be controlled by the fastest one.

It will be noticed that a third body (either wall or molecule) has been postulated in all cases. This seems necessary to stabilize the molecule produced (e.g. oxygen or nitrogen dioxide). Boltzmann³⁸ pointed out that the total energy of the molecule produced would be the sum of its heat of dissociation and the kinetic energies of the reacting species less the kinetic energy of the molecule. In most cases this would be greater than the heat of dissociation. A collision of the unstable molecule with a third body would transfer the excess energy to the latter.

The quantum theory is even more exacting except in the case of radiation. In radiationless collision, the energy of the reactants is quantized, and it must likewise be quantized in the product. Collisions in which the two quantizations "fit" would indeed be rare. (See Kaplan³⁸)

The classical sort of triple collision is a double collision in which there is a third body within a distance, δ , which is usually much less than 10^{-8} centimeters. Rice³⁹ has concluded that, for instance in the reaction between nitric oxide and molecular oxygen, an association complex such as $(NO)_2$ or $NO \cdot O_2$ is formed and this reacts on subsequent collision with the proper molecule. This seems to be a reversion to the older theory of trimolecular reactions. (Kassel⁴⁰)

Kimball⁴¹ points out that many association reactions appear bimolecular while theory would seem to require stabilization by a triple collision. This is the result of an association complex which is sufficiently long-lived to undergo several stabilizing double collisions before its life period expires. On the other hand, if the average life is short in comparison to the time between collisions, the reaction will appear to be tri-molecular. Only the very simplest molecules have life periods as short as 10^{-13} seconds.

Kimball's work shows that δ can usually be of the order of 10^{-8} cm. or larger, whereas the older treatment of triple collisions required that it be less than 10^{-8} cm.

While the average life of the collision complex, $(O \cdot NO)$, is not listed in his article, comparison indicates that it would have a life of at least 10^{-11} seconds. The steady state concentration

of O.NO can be calculated on this basis.

Number of (O.NO) disappearing/sec. = number formed/sec.

$$N_{(O.NO)} \times 10^{11} \sim \bar{Z}_{O+NO} \sim 5 \times 10^{-10} \frac{N_O N_{NO}}{O NO}$$

$$N_{(O.NO)} \sim 5 \times 10^{-21} \frac{N_O N_{NO}}{O NO}$$

The efficiency of the collision, (O.NO) + W, where W is any third body is:

$$\frac{N_O}{2t_{\frac{1}{2}} \bar{Z}_{(O.NO)} + W} \sim \frac{N_O}{2t_{\frac{1}{2}} 5 \times 10^{10} N_{(O.NO)} N_W}$$

at 300° K, $N_W = 3.2 \times 10^{16}$ p molec. cc.

$$\text{Efficiency} \sim \frac{N_O}{t_{\frac{1}{2}} 150 \times 10^{-15} p N_O N_{NO}} = \frac{[\text{effic. O + NO}] \cdot 10^4}{1.5 p}$$

The symbols here used have the following significance:

- δ - the distance at which two colliding molecules may be considered to be in contact for purposes of triple collision.
- N_i - the number of i particles per cc.
- $t_{\frac{1}{2}}$ - the half-life period in seconds.
- p - the pressure in mm.
- $\bar{Z}_{i+j}$ - the average number of collisions per second per cc. between i and j particles.

B. Collision Calculations.

The collision formulas used are those developed in Kassel:⁴⁰

$$Z_d (\text{unlike}) = 2 N_1 N_2 \sigma_{12}^2 \left(\frac{3\pi kT}{\mu_{12}} \right)^{\frac{1}{2}}$$

$$Z_d (\text{like}) = N_1^2 \sigma^2 \left(\frac{4\pi kT}{m} \right)^{\frac{1}{2}}$$

$$Z_{tr} = N_1 N_2 N_3 (4\pi\sigma_{12}^2) (4\pi\sigma_{23}^2) \delta \left(\sqrt{\frac{kT}{2\pi\mu_{12}}} + \sqrt{\frac{kT}{2\pi\mu_{23}}} \right)$$

where: Z_d and Z_{tr} are the number of double and triple collisions in a cubic centimeter of gas per second;

N_i the number of species i per cubic centimeter;

σ_{ij} the collision diameter, which is the average of the diameters of the two colliding species;

k is the Boltzmann constant;

T , the absolute temperature;

$$\mu_{ij} = \frac{m_i m_j}{m_i + m_j}$$

where: m_i and m_j are the absolute masses of the colliding species;

δ is the distance at which two molecules may be considered to be in contact.

The following rather arbitrary values have been assumed:

$$\sigma_{NO} = 3 \times 10^{-8} \text{ cm.}$$

$$\sigma_O = 1.6 \times 10^{-8} \text{ cm.}$$

$$\sigma_{O_2} = 3 \times 10^{-8} \text{ cm.}$$

where: σ is the radius of the species.

For convenience, the following list of collision formulae are given for various combinations of gaseous species. The values have no absolute significance; the purpose of such calculations is principally to find what type of collision is most nearly proportional to the rate of reaction. The calculated collision frequency should be directly proportional to the actual one.

$O + NO$	$\bar{Z}_d \sim 5 \times 10^{-10} N_O N_{NO}$
$O + O$	$\bar{Z}_d \sim 1 \times 10^{-10} N_O^2$
$O + O_2$	$\bar{Z}_d \sim 5 \times 10^{-10} N_O N_{O_2}$
$O + NO + O_2$	$\bar{Z}_{tr} \sim 3 \times 10^{-23} N_O N_{NO} N_{O_2} \delta$
$O + NO + NO$	$\bar{Z}_{tr} \sim 1 \times 10^{-23} N_O N_{NO}^2 \delta$
$O + O + NO$	$\bar{Z}_{tr} \sim 1 \times 10^{-23} N_O^2 N_{NO} \delta$
$O + O + O_2$	$\bar{Z}_{tr} \sim 1 \times 10^{-23} N_O^2 N_{O_2} \delta$

$$\text{Number of } [O] \text{ reacted per cc. per second} = \frac{N_O}{2t_{\frac{1}{2}}}$$

$$\text{Collision efficiency} = \frac{N_O}{2t_{\frac{1}{2}} \bar{Z}}$$

In this table, N_1 is the original number of 1 particles per cc., and $t_{\frac{1}{2}}$ is the half-life period in seconds.

A series of experiments was carried out using a diffusion method which avoided wall reactions (Figure 10). The apparatus and theory have been described by Polanyi and others in a number of places ^{42, 43, 44}.

The general requirements seem to be that the gas (O and O_2) once out of the nozzle must move away by diffusion and not by mass flow; and the other reacting species (NO) must be in large excess so that its concentration may be considered constant.

In the stationary state, the number of molecules (or atoms) in a given volume is constant. The number disappearing by reaction must be equal to the net increase due to diffusion:

$$k N_O' N_{NO} = \left(\frac{d^2 N_O'}{dr^2} + \frac{2}{r} \frac{dN_O'}{dr} \right) \frac{D}{N_{NO}}$$

where: k is the specific rate constant,
 r is the distance from the nozzle,

D is the diffusion coefficient.

This becomes on integrating and putting in the limits:

$$k = \frac{\left(\ln \frac{N_O}{N_O'} - \ln \frac{R}{r} \right)^2}{(R - r)^2} \cdot \frac{D}{N_{NO}}$$

where R is the radius of the flame where the concentration of oxygen atoms is N_O' and r is the radius of the nozzle.

$$\text{Since } k = \frac{-\frac{dN}{dt}}{N_O' N_{NO}}$$

$$\text{and collision efficiency} \sim \frac{-\frac{dN}{dt}}{5 \times 10^{-10} N_O' N_{NO}} \sim \frac{-\frac{dN}{dt}}{10^{-9} N_O' N_{NO}}$$

$$\text{the collision efficiency} \sim k \times 10^9$$

The diffusion coefficient D can be calculated from Enskog's⁵⁵ equation,

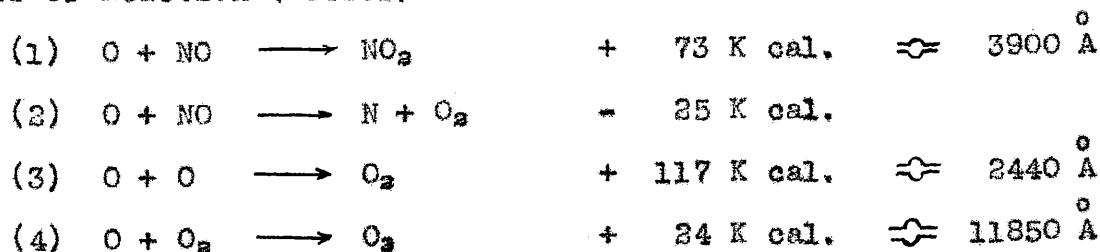
$$D = \frac{3}{8} \sqrt{\frac{RT}{2\pi}} \cdot \frac{1}{\sigma_{12}^2 N} \sqrt{\frac{M_1 + M_2}{M_1 M_2}}$$

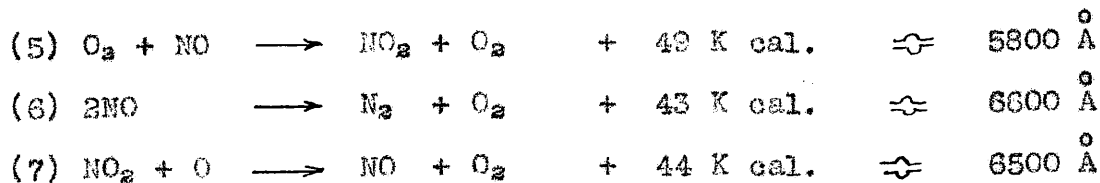
where M_1 is the molecular weight of the 1 particles and N is the number of particles per cc. For the case of oxygen atoms diffusing into nitric oxide:

$$D \sim \frac{90}{p \text{ mm.}} \quad \text{cm}^2/\text{sec.}$$

C. Possible Mechanisms.

Heats of Reaction (Kassel)





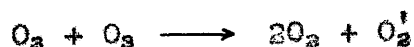
Strutt², Stoddart³⁴, and Newman²⁷ have reported the oxygen afterglow as being a continuum in the region 4200 $\text{\AA}^{\circ}$ to 6700 $\text{\AA}^{\circ}$. In fact, the latter worker has extended it to 4130 $\text{\AA}^{\circ}$. Spealman's plates⁴⁵ show traces of the continuum down to about 4000 $\text{\AA}^{\circ}$. It is difficult to decide just where it does end. However, a short wave length of 4000 $\text{\AA}^{\circ}$ is in good agreement with reaction (1). In fact, (1) appears to be the only reaction, with the possible exception of (3), which would be capable of emitting the proper frequency. (3) can be fairly safely eliminated by the fact that pure oxygen shows no afterglow.

(5) may occur to a slight extent. However, under the conditions of this work ($p \sim 1 \text{ mm.}$), it is doubtful whether ozone could exist in proportions of one ozone molecule per million oxygen atoms. Harteck⁴⁶, using an electrode discharge at considerably higher pressures, finds that the stationary concentration of ozone is about one per million. This would correspond roughly to a reaction (4) at every triple collision and



at every two-thousandth double collision.

Herzberg²³ suggests that the afterglow might come from the reaction:



were there enough ozone present. This, however, neglects the fact that pure partially dissociated oxygen is glowless.

Reaction (6) is altogether improbable since it would

require an enormous heat of activation.

(7), on the other hand, is known to be a fairly rapid reaction and does not emit visible radiation (Spealman and Rodebush³). Presumably, then, the reaction:

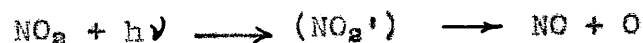


uses up the NO_2 about as fast as it is formed by



Another bit of evidence in favor of the latter reaction is furnished by photochemical studies on nitrogen dioxide.

Norrish²⁹ found the photodissociation of nitrogen dioxide was negligible at $\lambda = 4078 \text{ \AA}$ and rose to a yield of two molecules of nitric oxide per quantum at $3650 \text{ \AA}$. Mecke studied the region $\lambda = 3700 \text{ \AA}$ and found diffuse bands. He concluded that this was a case of predissociation, and that the mechanism can be represented by:



The first of these is the reverse of (1), and the second is identical with (7).

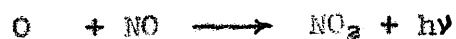
Baxter³⁰ studied the same phenomenon and found some dissociation at $\lambda = 4047 \text{ \AA}$. He agreed with Mecke's mechanism.

More recent work has been done by Franck, Sponer, and Teller⁴⁷. They report that the absorption spectrum of nitrogen dioxide begins at about $6500 \text{ \AA}$ and extends to about $2700 \text{ \AA}$. At about $4000 \text{ \AA}$ a diffuseness of the lines sets in. This is thought to be due to the predissociation of nitrogen dioxide into normal oxygen atoms and nitric oxide. At shorter wave lengths the bands again are resolvable into lines. At still higher frequencies predissociation into ^1D oxygen atoms and normal nitric oxide begins.

The work here described has been carried out with normal oxygen atoms for, while excited (^1D) atoms, electrons, and some electrons must be generated in the discharge itself, these species must be extremely short lived. This may be judged to be so from the fact that the effluent oxygen is glowless in the absence of nitrogen compounds.

Since there are no excited oxygen atoms reacting with nitric oxide, the short wave length limit, if nitrogen dioxide is formed, should be in the neighborhood of $3900 \text{ \AA}^0$.

The mechanism:



is then, supported by energy considerations. It also accounts for the fact that the afterglow persists as long as oxygen atoms are present (nitric oxide is constantly regenerated).

IV. EXPERIMENTAL.

A. Electrical Circuit.(Figure 1)

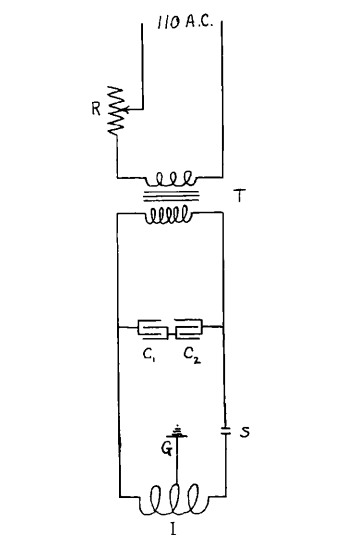


Figure 1. Oscillator

The source of high voltage was a 3 KVA 110 to 25000 General Electric testing transformer. The current through this was regulated by means of lamp bank, R. The two condensers, C_1 and C_2 , of about 0.01 mf. capacity, each consisted of about 18 plates of $8\frac{1}{2}$ " x 10" sheet metal separated by two thicknesses ($\frac{1}{4}$ ") of window glass - all of which was immersed in transformer oil. The spark gap, S, consisted of two circular zinc electrodes about 6 cm. in

diameter. The proper separation (usually about 1.5 cm.) could be obtained by a screw adjustment. The electrodes were cooled by a blast of air between them. The inductance, I, which was wound around the discharge chamber, was made of varying numbers of turns (usually from 8 to 16) of 3 mm. copper tubing and was carefully grounded near the middle. The coil, I, was always cooled by a blast of air. Sometimes, in addition, water was run through the tubing. This did not seem to have much effect on the discharge.

B. Preparation of Gases Used

Oxygen was prepared by the electrolysis of concentrated sodium hydroxide solution in a large water cooled U-tube equipped

with nickel electrodes. It was found necessary to empty and refill the cell every few weeks on account of the density gradient which developed on continued use. After refilling, it required about twenty-four hours to get rid of all traces of nitrogen (or nitrogen compounds) as judged by the absence of the oxygen afterglow. The oxygen was sometimes dried by liquid air or acetone-dry ice, and other times used wet. There was no marked difference except in the higher degree of dissociation in the wet gas.

Nitric oxide was at first made by the action of dilute nitric acid on copper; and, later on, by the reaction of concentrated sulfuric acid on a saturated solution of sodium or potassium nitrite. In either case, the purification consisted of washing the gas with water. Just before the gas passed into the reaction chamber, it was dried in a solid carbon dioxide-acetone cooled trap. In still later experiments, two, two and one-half liter bottles, one of which was filled with water, were so arranged that one could serve as a reservoir for nitric oxide.

Nitrogen dioxide was prepared by blowing a current of tank oxygen through the mixture of nitric oxide and nitrogen dioxide ^{made} by the action of concentrated sulfuric acid on a saturated solution of potassium or sodium nitrite. After passage through a three liter flask, the mixture of nitrogen dioxide and oxygen was run through a trap cooled by solid carbon dioxide-acetone. This trap was then sealed onto the vacuum system through a flowmeter.

C. General Apparatus and Method.

The apparatus was constructed entirely of Pyrex. The vacuum was maintained by a two-stage mercury diffusion pump backed :

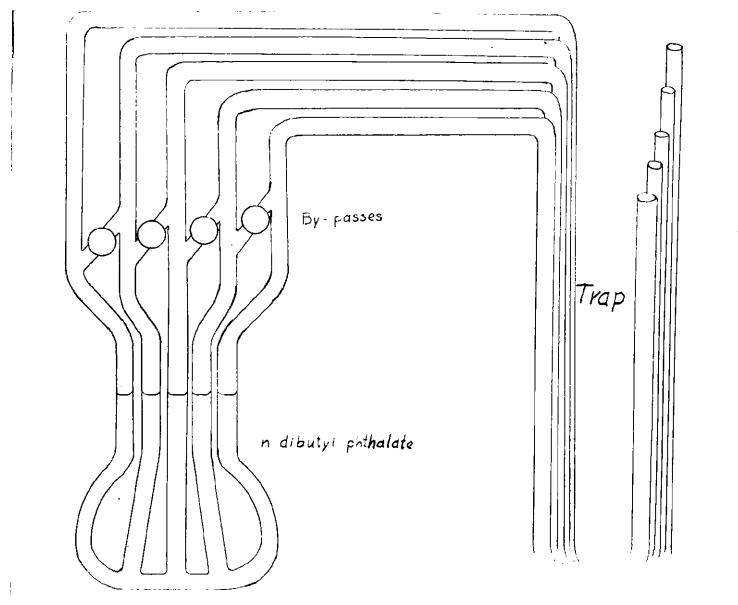


Figure 2. Manometer and trap.

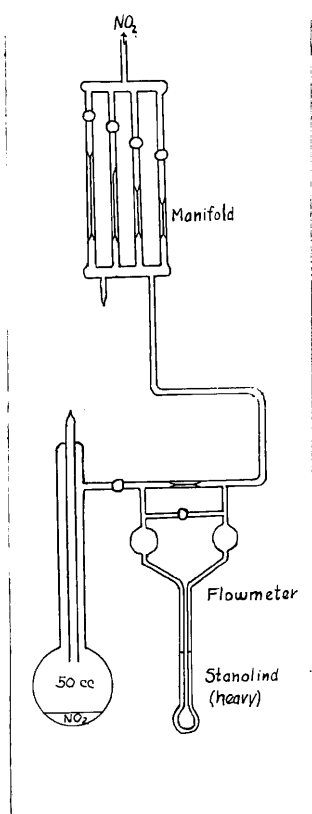


Figure 3. System for regulating flow of nitrogen dioxide.

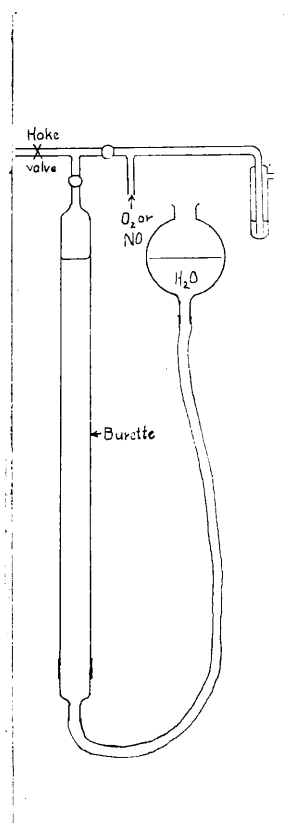


Figure 4. System for regulating flow of oxygen or nitric oxide.

by a Cenco Hyvac Pump (old style).

The pressure was measured by a manometer (Figure 2) filled with n-dibutyl phthalate. The pressure on the reference (zero) arm of the manometer was maintained by a two-stage mercury diffusion pump, which discharged into the low pressure side of the previously described one. The height of the menisci were read to the nearest 0.001 inch by means of a small cathetometer. Taking the density of n-dibutyl phthalate as 1.045₂₁ g./cc., it can be seen that the pressure was measured to the nearest 0.003 mm. of mercury.

The rates of flow of nitric oxide and oxygen were measured directly by gas burettes (Figure 4), and the rates were regulated by means of small Hoke valves. These valves gave considerable trouble, and it was frequently necessary to interrupt a run to clean them. While nitric oxide did not seem to corrode the valve, it was at times impossible to prevent a little air from getting in to form nitrogen dioxide. This gas is highly corrosive.

To measure the rate of flow of nitrogen dioxide, it was necessary to construct and calibrate a flowmeter (Figure 3). The rate of flow was controlled by means of a manifold of four parallel capillaries, each of which was equipped with a stopcock. It happened that the dimensions of these capillaries and the one between the arms of the flowmeter, made the use of a slush of carbon tetrachloride (m.p. = -19.5^o C.) suitable as a refrigerant for the reservoir of nitrogen dioxide.

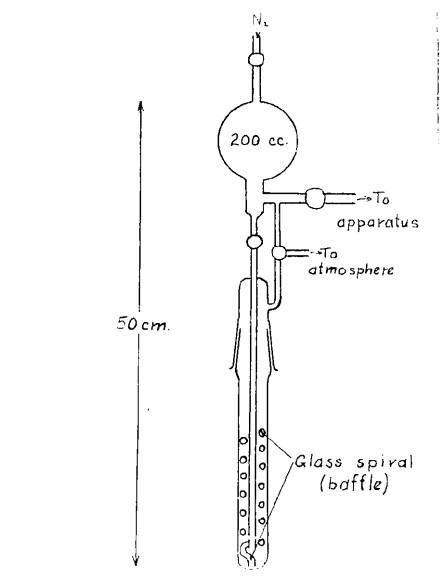


Figure 5. Analytical apparatus.

The analysis of the oxides trapped out from the effluent gases was made according to the procedure described by Burdick⁴⁸ for the analysis of nitric oxide and nitrogen dioxide mixtures. This consisted of bubbling the oxides, diluted in purified nitrogen as suggested in Mellor⁴⁹, through a standard solution of dilute sodium hydroxide, titrating first with standard sulfuric acid and then with standard potassium permanganate in the acid solution (Figure 5).

Mercury and n-dibutyl phthalate vapors were carefully kept out of the reaction and discharge chambers by liquid air traps.

D. Degree of Dissociation.

The degree of dissociation of oxygen into atoms was measured by means of a Wrede⁵⁰ gauge constructed as described by Rodebush and Klingelhoefer⁵¹. With wet oxygen at moderate pressures (ca. 0.4 mm.) dissociation of 30 per cent was usually attainable. With dry oxygen the degree of dissociation was much lower - perhaps about ten per cent. This effect has been noted frequently in the literature and there seem to be two different explanations: dry walls provide a much more efficient catalytic surface for the recombination of atoms; for some reason water makes the dissociation occur more rapidly.

As Wende⁵² has pointed out, the accurate use of the Wrede gauge is pretty well limited to the pressure range of 0.2 to 0.5 mm. This results from the fact that the diameter of the orifice through which diffusion occurs should be considerably less than the mean free path of the molecules present. Using the approximate formula:

$$\text{mean path} \sim \frac{0.1}{P_{\text{mm.}}}$$

it is seen that at a pressure of 0.5 mm. the mean free path is of the order of 0.2 mm. If the diameter be limited to one-tenth the mean free path, the orifice would have to be of the order of 0.02 mm. In practice, it is difficult to prepare an orifice of this size. The lower pressure limit is set by the accuracy with which the pressure difference on the two sides of the opening can be measured. The equation for the degree of dissociation as measured by the Wrede gauge is:

$$\alpha = \frac{\Delta p}{.586 p - \Delta p}$$

where α is the fraction dissociated, p the total pressure of atoms and molecules and Δp is the pressure difference across the film.

In the first experiments (down to 38B), α was measured during the run by a Wrede gauge placed on the discharge side of the constriction to prevent back diffusion of the afterglow into the discharge chamber. It was realized that probably a good many of the atoms would recombine on passage through the constriction. However, a Wrede gauge in the afterglow was worthless (it registered extremely high).

A more convenient and probably just as accurate method

was used in the later experiments. Pure oxygen was pumped through the apparatus, and the degree of dissociation was observed at different pressures by means of a Wrede gauge mounted in the reaction chamber. When plotted, it was found that the degree of dissociation was a function of the pressure and was not greatly affected by the rate of flow of the oxygen (Figure 6). Such a plot (α against p_{mm}) had to be remade when the apparatus was changed.

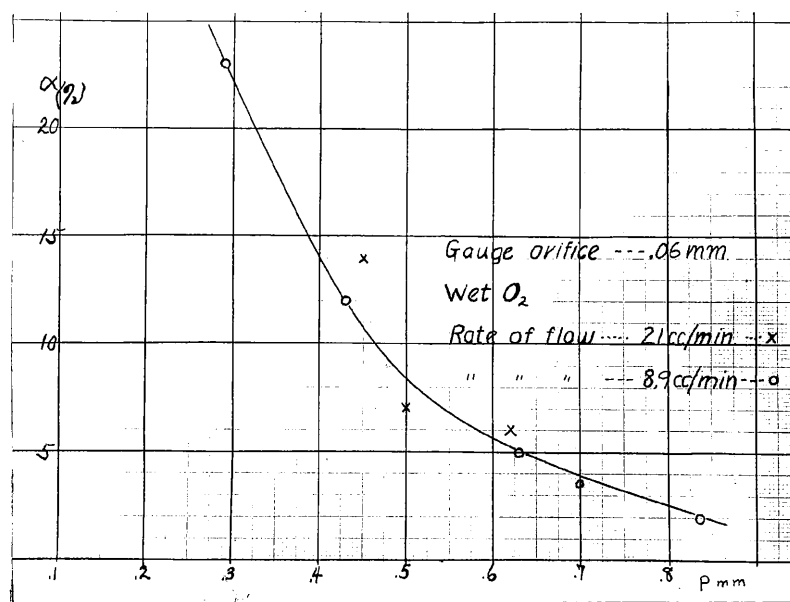


Figure 6. Degree of dissociation of oxygen as a function of pressure and rate of flow.

E. Procedure.

The procedure followed in a typical run was:

1. The evacuated system was flushed with oxygen until it

no longer gave more than a faint afterglow in a darkened room.

2. With enough oxygen flowing through the discharge tube to prevent a back diffusion of the afterglow when it appeared (10 to 25 cc. per minute) the Hoke valve to the nitric oxide was cautiously opened.

3. The volume of the afterglow was regulated by changing the rate of flow of nitric oxide or by varying the pressure in the system by adjusting the stopcock leading to the pumps.

4. The time was noted and a refrigerant was placed around the trap to remove any nitrogen dioxide that might have been formed in the afterglow.

5. The pressure in the reaction vessel was noted and also the volume of the half-decayed afterglow.

6. The rates of flow of nitric oxide and oxygen were measured (sometimes this step followed No. 7).

7. The time was noted ($\sim$ ten minutes) and the trap cut off from the rest of the system by turning the proper stopcocks.

8. The oxides were transferred to a previously evacuated 200 cc. flask by means of a piece of cotton moistened with liquid air.

9. After the oxides had vaporized, they were analyzed as described previously.

F. Experiments

1. With a 3.5 cm. Tubular Reaction Chamber (Figure 7).

The oxide used was nitric oxide. The value of these experiments lies in the fairly accurate estimates of collision efficiencies which they afford. This arises from the fact that

reasonably good estimates of the half-life period could be made since the rate of diffusion was quite slow compared to the rate of flow of the gases. A few analyses of the effluent gases were made, but they were later found to be valueless because the oxides were trapped out in liquid air. It has already been pointed out that a wall reaction between nitric oxide and molecular oxygen occurs at these temperatures. The results of these experiments are given in Table I.

3. With a 5 liter Flask Reaction Chamber (Figure 8).

In these experiments, again, nitric oxide was run into a stream of partially dissociated oxygen. No weight should be attached to the collision efficiencies calculated from these experiments, but they are included for completeness (Tables IIa and IIb). The uncertainty arises from the fact that, in this type of apparatus, it was impossible to make an accurate estimate of half-life periods due to the turbulent flow of the afterglow through the chamber.

That turbulence did play an important part is borne out by the observation that the afterglow appeared to reach maximum intensity and volume within much less than one second after turning on the discharge, whereas the pumping rate indicated that the time for a particle to pass through the afterglow region was of the order of ten seconds. Likewise the rate of decay was perhaps ten times faster than the calculated half life indicated.

In the first group of experiments, no analyses were made. After it had been found that the collision efficiencies were probably not accurate, the same apparatus was used to determine the com-

position of the effluent gases (Table III). It should be noted that nitric oxide should not be stopped in a liquid air trap at the pressures used. At -190°C . the vapor pressure of nitric oxide is about 0.5 mm.⁵³

One method used was to run both nitric oxide and nitrogen dioxide into the stream of oxygen atoms at measured rates for measured times. When liquid air was used to trap out the oxides, it was found that, when nitric oxide and nitrogen dioxide were put in in ratio of 2:1, the effluent oxides had the same composition (Runs 1D to 23D). This ratio seemed to be independent of pressure and did not depend on whether or not the gases were dried. This result would indicate that the reaction



occurs about twice as fast as



In these calculations, a correction was made which, it was hoped, would take care of the nitric oxide which was converted to nitrogen dioxide by the low temperature oxidation reported by Temkin and Puzhow^{52,53}. However, it seemed advisable to try to eliminate this oxidation. This was accomplished by using temperatures of the order of -135°C . (slush of low-boiling petroleum ether). The equation for the vapor pressure of nitrogen dioxide is;⁵³

$$\log_{10} P_{\text{mm}} = \frac{-0.05223}{T} \times 55160 + 13.4$$

This equation holds strictly in the range of -100°C to -40°C . However, it should give the correct order of magnitude at temperatures as low as -135°C . The following pressures have been

calculated:

$$\text{at } -125^{\circ}\text{C} \quad p_{\text{mm.}} = 3 \times 10^{-6}$$

$$\text{at } -125^{\circ}\text{C} \quad p_{\text{mm.}} = 1 \times 10^{-6}$$

As a check on the efficacy of petroleum ether as a refrigerant, nitrogen dioxide flowing through the system at 0.017 mm. was found, within the accuracy of the method, to have been quantitatively trapped out. A number of similar blank runs, some of which were carried out without re-freezing the petroleum ether after a previous run, all gave similar results.

A simple calculation will show the order of the partial pressures of nitrogen dioxide which may be expected at the entrance if $\frac{1}{2}$ of the nitric oxide is converted to nitrogen dioxide.

Let the rate of NO = 3cc. min.

Let the rate of O₂ = 30cc. min.

$$p_{\text{total}} = 0.8$$

$$p_{\text{NO}_2} = 0.8 \times \frac{3}{33} \times 0.01 \sim 10^{-3} \text{ mm.}$$

It is evident (Table III) that the analyses do not check well. This can be explained as being due to the small quantities of nitric oxide or nitrogen dioxide put in (there was always a large excess of oxygen atoms in order to bring the oxides into their "equilibrium" proportions). It was impossible to make a run of longer than about ten minutes duration because of the low heat capacity of the petroleum ether slush. In order to make the slush last longer, the trap was precooled for about ten seconds in a Dewar of liquid air. It is possible that this may have caused varying amounts of nitric oxide to be oxidized by molecular oxygen.

At the start of these experiments, it had been intended

to determine the ratio of concentrations of nitrogen dioxide to nitric oxide in the effluent gases at different pressures in order to throw some light on whether or not the reactions



had the same mechanism.

In all these experiments, care was taken to see that the afterglow was completely decayed before entering the trap. It was often noticed that the use of liquid air around the trap increased the volume of the afterglow. This suggests a possible explanation for the results obtained on running mixtures of nitric oxide and nitrogen dioxide into partially dissociated oxygen (Runs 1D to 28D) and trapping out the resulting oxides with liquid air. It has already been mentioned that such mixtures were unchanged when nitric oxide and nitrogen dioxide were present in the proportion of 2:1. Perhaps the liquid air trap lowered the partial pressure of nitrogen dioxide. This would mean that in the gas the ratio of nitric oxide to nitrogen dioxide would be greater than 2:1, in agreement with the results of experiments with petroleum ether slush as the refrigerant. However, there was a constriction between the reaction chamber and trap (a large stopcock (10 mm.) which was usually partly closed).

3. With 5.8 cm. Tubular Reaction Chamber (Figure 9).

A reaction chamber of this type gives results which are probably a little more dependable than those obtained with the 5 liter flask set-up.

No analyses were made on the effluent gases.

This was the first series of experiments in which the degree of dissociation was determined as a function of the pressure in pure oxygen (Figure 6).

The oxide used in this set of experiments was nitric oxide.

4. With a Diffusion Apparatus (Figure 10).

In these experiments the partially dissociated oxygen entered the reaction chamber through a rather small nozzle (2.2 mm.). There was always a large excess of nitric oxide in the chamber and the rate of flow of the oxygen was slow enough so that the flame produced appeared spherical.

Polanyi's equation is:

$$k = \frac{\left[\ln \left(\frac{N_0}{N_0'} \right) - \ln \left(\frac{R}{r} \right) \right]^2}{(R-r)^2} \times \frac{D}{N_{NO}}$$

and it has been shown (page 19) that

$$\text{Collision efficiency} \sim k \times 10^9$$

The visual determination of the radius, R, at which the intensity is one-half the original $\left(\frac{N_0}{N_0'} = 2 \right)$ was very inaccurate.

A photographic method was tried without much better results. This consisted of making 10-second exposures at f 22 on Eastman Panatomic film and determining the densities by means of a microphotometer (Figure 11).

The data from these runs is collected in Table V.

5. With a Packed Chamber.

This series of experiments was carried out in a packed chamber having a surface: volume ratio of about nine. It was

made by packing a large tube (internal diameter = 6.3 cm.) with sixty-nine 3 x 5 mm. Pyrex tubes.

The degree of dissociation was not measured but can be assumed to be about 10%. Nitric oxide was the only oxide used.

The effluent oxides were trapped out for a measured time (~ 10 min.) in a slush of low-boiling petroleum ether and analyzed.

The collision efficiencies for $O + NO$ are seen to be of the same magnitude as in the 2.5 cm. tubular reaction chamber.

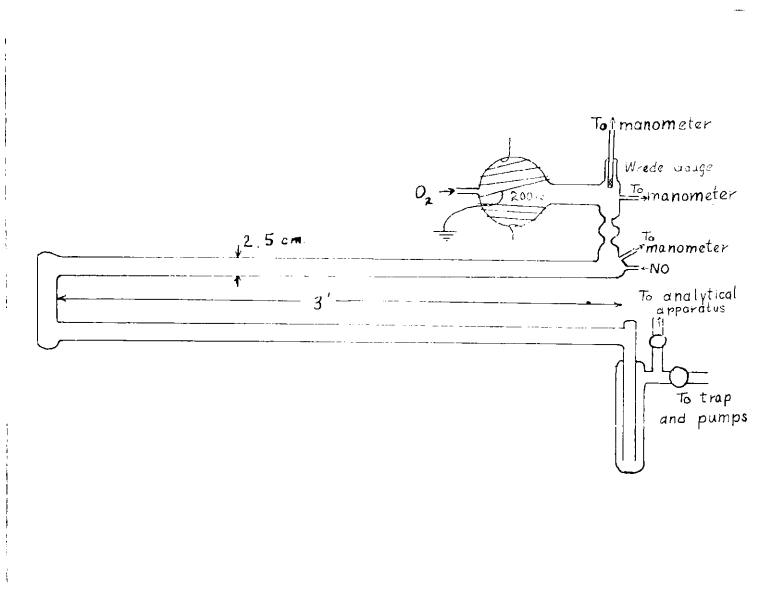


Figure 7. The 2.5 cm. tubular reaction vessel.

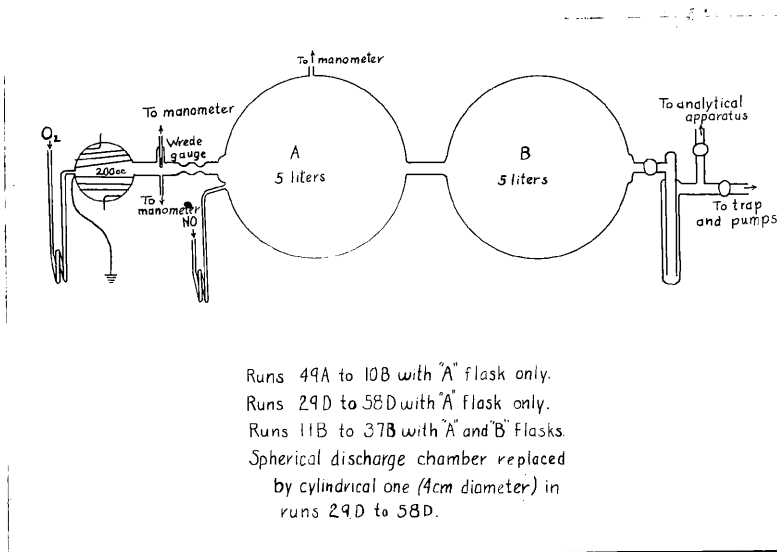


Figure 8. The 5 liter flask reaction vessel.

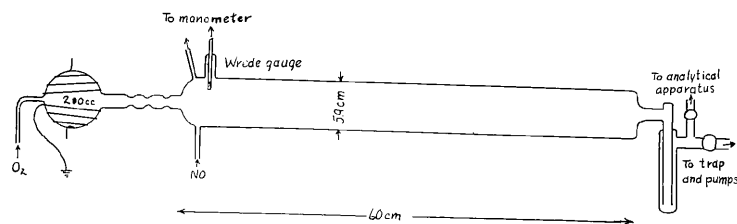


Figure 9. The 5.9 cm. tubular reaction vessel.

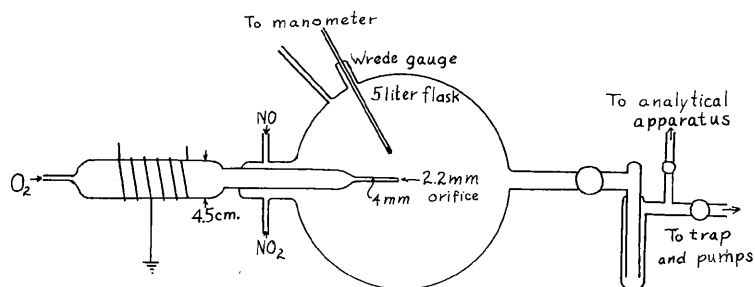


Figure 10. The diffusion apparatus.

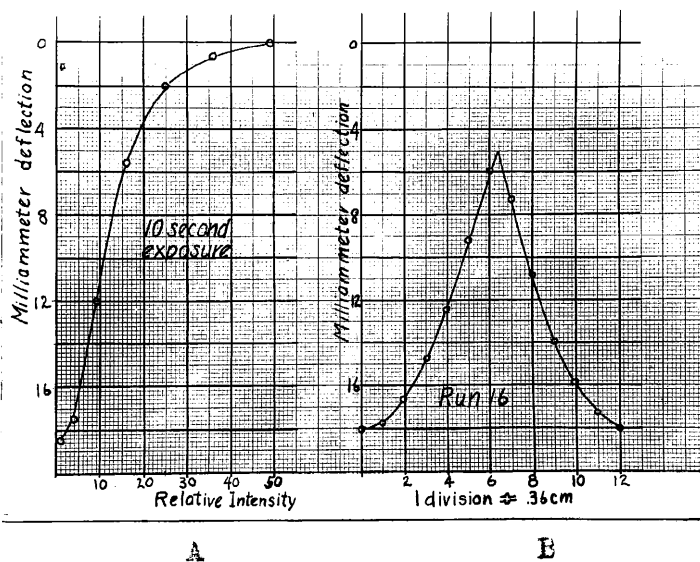


Figure 11. Microphotometer curves.
 A. Panatomic film exposed to various intensities of the afterglow.
 B. Spherical flame of a typical run.

Table Ia 2.5 cm. Tubular Reaction Chamber

-39-

Run	O/NO	Pressure mm.	$t_{1/2}$ sec.	NO molec/cc. $\times 10^{-14}$	NO ₂ molec/cc. $\times 10^{-14}$	NNO molec/cc. $\times 10^{-14}$
16A	0.07	0.114	0.50	2.3	3.2	31
18A	0.11	0.153	0.71	4.1	7.3	38
19A	0.07	0.188	0.64	3.5	9.5	51
20A	0.05	0.221	0.50	5.1	9.5	94
29A	0.19	0.169	0.16	7.5	7.8	39
26A	0.18	0.226	0.14	8.8	13	49
28A	0.37	0.178	0.20	12	19	33
27A	0.26	0.256	0.13	13	18	51
35A	0.27	0.275	0.12	13	26	49
30A	0.38	0.279	0.16	18	25	48
31A	0.36	0.312	0.17	18	37	52
14A	0.42	0.162	0.32	11	13	28
34A	0.50	0.264	0.16	18	38	38
32A	0.42	0.281	0.18	19	37	44
33A	0.43	0.371	0.12	16	33	72
22A	0.85	0.194	0.39	20	19	24
15A	0.77	0.197	0.45	17	23	23
17A	0.72	0.229	0.35	20	25	29
23A	0.65	0.232	0.46	21	20	33
21A	1.4	0.317	0.39	34	44	25
25A	0.80	0.323	0.22	32	36	39
24A	0.72	0.338	0.19	32	32	45

Table Ib Collision Efficiencies (2.5 cm. Tubular Reaction Chamber)

Run	O+NO $\times 10^6$	O+O $\times 10^6$	O+O ₂ $\times 10^6$	O+NO+O ₂ $\times 10^9$	O+2NO $\times 10^9$	2O+NO $\times 10^9$	2O+O ₂ $\times 10^9$	(O+NO)+W $\times 10^2$
16A	0.63	43	6.2	33	10	140	1400	3.7
18A	0.37	17	1.9	8	5	45	240	1.6
19A	0.31	22	1.6	5	3	44	230	1.1
20A	0.21	20	2.1	4	1	21	200	0.63
29A	1.6	42	8.0	34	20	110	530	6.3
26A	1.5	41	5.5	19	15	83	310	4.5
28A	1.5	21	2.6	13	23	63	110	5.6
27A	1.5	29	4.3	14	15	57	160	3.9
35A	1.7	32	3.2	11	17	65	120	4.1
30A	1.3	17	2.5	9	14	36	69	3.1
31A	1.1	16	1.6	5	11	31	43	2.3
14A	1.1	14	2.4	14	20	49	100	4.5
34A	1.6	17	1.6	7	22	46	46	4.0
32A	1.3	15	1.5	6	14	34	40	3.1
33A	1.2	26	2.5	6	8	36	79	2.2
22A	1.1	6.3	1.4	10	23	27	33	3.7
15A	0.95	6.3	1.0	7	20	27	28	3.3
17A	1.0	6.9	1.1	7	17	24	28	2.9
23A	0.67	5	1.1	6	10	15	25	1.9
21A	1.0	3.8	0.6	4	21	15	9	2.1
25A	1.2	7.2	1.2	5	15	18	20	2.5
24A	1.2	8.2	1.6	6	13	18	25	2.4

Table IIa Five liter Flask Reaction Chamber

-41-

Run	O/NO	Pressure mm.	$t_{\frac{1}{2}}$ sec.	NO molec/cc. $\times 10^{-14}$	NO ₂ molec/cc. $\times 10^{-14}$	N ₂ O molec/cc. $\times 10^{-14}$
49A	0.13	0.386	4.0	7.0	63	55
52A	0.11	0.498	3.3	8.6	78	75
10E	0.06	0.525	3.1	2.5	120	38
6E	0.25	0.372	4.9	12	60	50
2E	0.21	0.439	4.6	7.7	97	36
11E	0.34	0.265	4.5	8.1	55	24
22E	0.34	0.320	4.0	20	59	58
3E	0.33	0.379	5.2	12	99	33
12E	0.40	0.382	3.5	12	80	31
4E	0.33	0.402	4.5	17	63	52
9E	0.32	0.442	4.2	16	72	50
1E	0.42	0.405	3.8	26	45	60
26E	0.43	0.522	3.9	37	45	86
50A	0.50	0.523	5.9	14	130	28
17E	1.4	0.145	12.5	8.7	32	6.1
23E	1.3	0.193	11	10	45	7.6
5E	0.95	0.422	5.2	31	84	30
32E	0.73	0.513	2.8	57	30	79
7E	0.82	0.559	3.2	56	85	68
27E	1.4	0.561	5.3	62	73	46
24E	2.9	0.168	11.3	10	39	3.9
13E	1.7	0.199	10.6	12	46	7.0

Table IIa (cont'd) Five liter Flask Reaction Chamber

-42-

Run	O/NO	Pressure mm.	$t_{\frac{1}{2}}$ sec.	NO molec/cc. $\times 10^{-14}$	NO ₂ molec/cc. $\times 10^{-14}$	NO molec/cc. $\times 10^{-14}$
14B	2.0	0.214	10.2	13	50	6.5
18B	5.0	0.215	10.6	13	54	2.5
16B	5.4	0.218	11.9	13	55	2.5
21B	4.4	0.227	10.2	13	58	2.9
28B	31	0.262	5.6	45	39	1.5
19B	11	0.270	9.3	15	71	1.4
25B	20	0.285	7.9	17	74	0.88
36B	5.6	0.295	6.7	54	32	9.6
20B	17	0.295	9.0	14	80	0.87
34B	1.9	0.339	3.6	49	35	26
31B	59	0.377	5.2	91	100	1.5
37B	4.6	0.545	9.8	82	76	18
29B	3.9	0.629	5.2	100	73	27
35B	1.5	0.633	5.8	76	80	49
33B	9.3	0.715	6.0	120	99	13
30B	14	0.853	4.6	130	130	9.4

Table IIB Collision Efficiencies--Five liter Flask Reaction Chamber⁴³

Run	O+NO $\times 10^6$	O+O $\times 10^6$	O+O ₂ $\times 10^6$	O+NO+O ₂ $\times 10^6$	O+2NO $\times 10^6$	2O+NO $\times 10^6$	2O+O ₂ $\times 10^6$	(O+NO)+W $\times 10^2$
49A	0.045	1.8	0.040	0.12	0.41	3.2	2.8	0.08
52A	0.040	1.8	0.039	0.087	0.27	2.3	2.3	0.05
10B	0.085	6.5	0.027	0.12	1.1	17	5.4	0.11
6B	0.041	0.85	0.034	0.11	0.41	1.7	1.4	0.07
2B	0.060	1.4	0.022	0.10	0.84	3.9	1.4	0.09
11B	0.093	1.4	0.040	0.28	1.9	5.7	2.5	0.23
22B	0.043	0.63	0.042	0.12	0.37	1.1	1.1	0.09
3B	0.058	0.80	0.019	0.098	0.88	4.1	0.8	0.10
12B	0.092	1.2	0.036	0.19	1.5	3.8	1.5	0.16
4B	0.043	0.65	0.035	0.088	0.41	1.3	1.0	0.07
9B	0.048	0.74	0.033	0.11	0.48	1.5	1.0	0.07
1B	0.044	0.51	0.059	0.16	0.37	0.84	1.1	0.07
26B	0.030	0.35	0.057	0.11	0.17	0.40	0.77	0.04
50A	0.061	0.60	0.013	0.077	1.1	2.2	0.47	0.08
17B	0.13	0.46	0.025	0.68	11	7.5	1.4	0.60
23B	0.12	0.45	0.020	0.44	7.9	6.0	1.0	0.41
5B	0.064	0.31	0.023	0.13	1.1	1.0	0.37	0.10
32B	0.045	0.31	0.12	0.25	0.29	0.4	1.0	0.06
7B	0.046	0.28	0.037	0.090	0.34	0.41	0.33	0.05
27B	0.041	0.14	0.026	0.093	0.45	0.33	0.21	0.05
24B	0.23	0.44	0.023	1.0	29	11	1.1	0.93
13B	0.13	0.39	0.020	0.49	10	5.6	0.85	0.43

Table IIb Collision Efficiencies--Five liter Flask Reaction Chamber

Run	O+NO $\times 10^6$	O+O $\times 10^6$	O+O ₂ $\times 10^6$	O+NO+O ₂ $\times 10^9$	O+2NO $\times 10^9$	2O+NO $\times 10^9$	2O+O ₂ $\times 10^9$	(O+NO)+W $\times 10^2$
14B	0.15	0.38	0.020	0.50	12	5.8	0.75	0.40
18B	0.38	0.36	0.017	1.2	75	14	0.67	0.12
16B	0.34	0.33	0.015	1.0	68	13	0.61	0.10
21B	0.34	0.38	0.017	0.98	58	13	0.65	0.10
28B	1.2	0.20	0.046	5.1	400	13	0.51	3.0
19B	0.77	0.36	0.015	1.8	270	25	0.50	1.9
25B	1.4	0.37	0.019	3.1	820	42	0.50	3.3
36B	0.16	0.14	0.047	0.81	8.1	0.14	0.43	0.36
20B	1.3	0.40	0.014	2.7	730	45	0.50	0.29
34B	0.11	0.28	0.079	0.20	2.1	1.1	0.81	0.22
31B	1.3	0.11	0.019	2.1	430	7.1	0.11	0.23
37B	0.057	0.062	0.013	0.12	1.6	0.035	0.08	0.07
29B	0.071	0.96	0.026	0.16	1.3	0.36	1.3	0.07
35B	0.035	0.11	0.022	0.073	0.28	0.23	0.14	0.04
33B	0.13	0.070	0.017	0.22	4.9	0.54	0.07	0.12
30B	0.23	0.84	0.017	0.30	12	0.89	0.64	0.18

Table III Experiments with Five liter Flask Reaction Chamber
Analysis of Effluent Oxides

Run	Refrigerant	Pressure mm.	O ₂ cc/min.	NO cc/min.	NO ₂ cc/min.	NO/NO ₂ out
18D	Liquid air	0.22	5.4	7.4	1.2	1.4
17D	" "	0.26	2.2	4.5	1.5	1.2
22D	" "	0.28	7.6	3.5	1.3	1.1
20D	" "	0.30	9.5	2.5	1.5	1.3
26D	" "	0.30	8.2	3.9	1.9	2.1
27D	" "	0.30	9.5	4.0	1.2	3.3
21D	" "	0.35	12	3.5	1.5	1.2
28D	" "	0.36	11	1.1	1.2	1.4
24D	" "	0.39	8.0	5.5	1.6	2.1
29D	" "	0.41	13	0	0.9	1.0
13D	" "	0.45	8.0	4.8	1.2	1.0
3D	" "	0.45	5.9	5.8	1.6	2.0
14D	" "	0.46	9.6	0	3.0	2.1
16D	" "	0.46	9.2	7.6	1.2	1.5
15D	" "	0.47	12	1.8	1.5	1.1
6D	" "	0.47	7.5	4.8	2.9	2.7
11D	" "	0.49	6.0	1.2	0.5	1.1
12D	" "	0.50	6.4	5.4	1.2	2.1
9D	" "	0.53	5.6	4.9	1.5	3.2
10D	" "	0.54	8.1	3.7	2.3	1.8
7D	" "	0.54	5.0	20	0	0.8
2D	" "	0.54	4.8	2.4	2.0	1.8
1D	" "	0.54	5.2	4.6	1.2	2.1
4D	" "	0.55	4.7	4.7	1.3	1.4

Table III Experiments with Five liter Flask Reaction Chamber⁻⁴⁶⁻
Analysis of Effluent Oxides

Run	Refrigerant	Pressure mm.	O ₂ cc/min.	NO cc/min.	NO ₂ cc/min.	NO/NO ₂ out
51D	Pet. ether	0.39	5.8	2.6	0	130
50D	" "	0.40	6.0	2.6	0	72
55D	" "	0.51	20	9.4	0	1000
53D	" "	0.54	20	4.0	0	250
52D	" "	0.56	20	3.0	0	150
54D	" "	0.62	20	16	0	130
58D	" "	0.70	28	4.1	0	300
36D	" "	0.72	9	0	3.1	14
42D	" "	0.73	20	0	2.3	32
35D	" "	0.74	14	0	2.8	8
37D	" "	0.74	12	0	2.3	8
45D	" "	0.74	13	0	2.1	37
47D	" "	0.74	14	7.8	0	49
45D	" "	0.75	10	0	2.0	38
48D	" "	0.76	20	3.5	0	62
57D	" "	0.78	28	8.6	0	150
56D	" "	0.78	28	4.3	0	200
41D	" "	0.78	20	2.6	0	20
38D	" "	0.79	12	1.5	0	20
39D	" "	0.79	18	5.5	0	29
40D	" "	0.79	20	0	2.0	10
46D	" "	0.80	24	6.6	0	34
49D	" "	0.80	20	3.0	0	35
44D	" "	0.82	15	0	2.4	10

Table IVa 5.9 Cm. Tubular Reaction Chamber

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Run	O/NO	Pressure mm.	$t_{1/2}$ sec.	NO molec/cc. $\times 10^{-14}$	NO ₂ molec/cc. $\times 10^{-14}$	NNO molec/cc. $\times 10^{-14}$
62B	0.09	0.62	0.22	9.4	92	100
69B	0.06	0.75	0.28	7.0	110	120
41B	0.07	0.79	0.28	6.4	160	86
42B	0.10	0.90	0.34	6.0	230	60
51B	0.22	0.36	0.35	14	38	63
67B	0.15	0.47	0.27	12	61	79
68B	0.17	0.60	0.33	12	110	72
63B	0.19	0.63	0.40	13	120	70
40B	0.34	0.50	0.36	20	84	58
54B	0.32	0.57	0.61	16	120	49
52B	0.29	0.61	0.26	16	120	56
56B	0.25	0.63	0.33	14	130	56
49B	0.32	0.76	0.40	12	200	38
45B	0.49	0.47	0.99	20	92	41
55B	0.44	0.50	0.36	19	100	43
53B	0.43	0.51	0.85	20	99	47
65B	0.57	0.51	0.60	20	110	35
59B	0.44	0.58	0.70	17	130	39
47B	0.45	0.58	0.78	17	140	38
38B	0.50	0.72	0.78	12	200	24

Table IVa (cont'd) 5.9 cm. Tubular Reaction Chamber

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Run	O ₂ /NO	Pressure mm.	t _{1/2} sec.	NO molec/cc. x 10 ⁻¹⁴	NO ₂ molec/cc/ x 10 ⁻¹⁴	NNO molec/cc. x 10 ⁻¹⁴
57B	1.2	0.19	1.2	24	18	20
44B	1.4	0.25	0.92	27	35	19
50B	1.3	0.27	0.89	27	40	21
58B	1.4	0.33	0.83	28	58	20
64B	1.0	0.37	0.68	24	73	24
48B	1.2	0.44	0.42	24	96	21
43B	0.69	0.47	0.39	22	98	32
66B	0.65	0.49	0.76	22	100	34
46B	1.9	0.29	0.64	29	49	15
39B	2.6	0.36	0.90	29	77	11
61B	5.7	0.42	0.90	28	104	4.9

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Table IVb Collision Efficiencies--5.9 cm. Tubular Reaction Chamber

Run	O+NO $\times 10^6$	O+O $\times 10^6$	O+O ₂ $\times 10^6$	O+NO+O ₂ $\times 10^9$	O+2NO $\times 10^9$	2O+NO $\times 10^9$	2O+O ₂ $\times 10^9$	(O+NO)+W $\times 10^2$
62B	0.46	24	0.49	0.82	2.3	24	26	0.50
69B	0.30	25	0.32	0.45	1.2	21	23	0.27
41B	0.46	2.8	0.22	0.43	2.4	32	17	0.38
42B	0.49	2.5	0.13	0.36	4.1	41	11	0.36
51B	0.45	10	0.75	5.0	3.6	16	27	1.0
67B	0.47	15	0.61	1.3	3.0	19	25	0.65
68B	0.42	13	0.28	0.64	2.9	18	11	0.47
63B	0.36	9.6	0.21	0.50	2.6	14	8	0.38
40B	0.48	7.0	0.23	0.96	4.1	12	8.3	0.64
54B	0.33	5.1	0.14	0.46	3.4	10	2.6	0.38
52B	0.69	12	0.32	0.95	6.1	22	10	0.75
56B	0.54	11	0.23	0.69	4.8	19	8.4	0.57
49B	0.66	10	0.13	0.55	8.7	27	5.2	0.58
45B	0.25	2.5	0.11	0.45	3.0	6.1	2.7	0.35
55B	0.65	7.3	0.28	1.0	7.5	17	7.3	0.87
53B	0.25	2.9	0.12	0.42	2.7	6.3	3.0	0.33
65B	0.48	4.2	0.15	0.72	6.8	12	3.8	0.63
59B	0.37	4.2	0.11	0.47	9.5	11	3.2	0.43
47B	0.34	3.8	0.092	0.40	4.4	10	2.7	0.39
38B	0.33	5.3	0.064	0.45	11	22	2.7	0.46

Table IVb Collision Efficiencies--5.9 cm. Tubular Reaction Chamber

Run	O+NO $\times 10^6$	O+O $\times 10^6$	O+O ₂ $\times 10^6$	O+NO+O ₂ $\times 10^{96}$	O+2NO $\times 10^{96}$	2O+NO $\times 10^{96}$	2O+O ₂ $\times 10^{96}$	(O+NO)+W $\times 10^2$
57B	0.42	1.7	0.46	3.9	9.6	8.7	9.6	1.5
44B	0.57	2.0	0.31	3.7	15	11	5.7	1.5
50B	0.54	2.1	0.28	2.2	13	10	5.2	1.3
58B	0.60	2.2	0.21	1.7	15	11	3.7	1.2
64B	0.61	3.1	0.20	1.4	13	13	4.2	1.1
48B	1.1	5.0	0.25	2.0	27	24	5.2	1.7
43B	0.80	5.8	0.26	1.4	12	18	5.9	1.1
66B	0.39	3.0	0.13	0.64	5.7	9	3.0	0.53
46B	1.0	2.7	0.32	3.5	35	18	5.5	2.2
39B	1.0	1.9	0.14	2.2	46	17	2.5	1.9
61B	2.3	2.0	0.11	3.6	230	25	1.9	3.8

Table V Experiments with Diffusion Apparatus

Run	Pressure mm.	$R_{\frac{1}{2}}$ cm.	NNO molec/cc. $\times 10^{-16}$	D	k $\times 10^{14}$	Collision Efficiencies	
						O+NO $\times 10^5$	(O.NO)+W $\times 10^2$
16	0.43	0.72	1.1	210	7.2	7	110
18	0.49	0.94	1.2	180	4.5	5	68
20	0.54	0.54	1.3	160	5.8	6	74
21	0.56	0.56	1.3	160	6.5	7	83
14	0.57	0.63	1.5	150	4.3	4	47
12	0.61	0.68	1.7	140	2.9	3	33
15	0.62	0.64	1.6	140	3.6	4	43
17	0.66	0.68	1.6	130	4.4	4	40

Table VIa Experiments with Packed Chamber

Run	O/NO	Pressure mm.	$t_{1/2}$ sec.	NO molecc/cc. $\times 10^{-14}$	NO ₂ molecc/cc. $\times 10^{-14}$	HNO molecc/cc. $\times 10^{-14}$
62D	2	0.73	0.30	52	150	34
61D	4	0.80	0.36	63	190	17
59D	4	0.82	0.48	65	190	15
60D	4	0.86	0.37	68	190	15

Table VIb Collision Efficiencies--Experiments with Packed Chamber

Run	O+NO $\times 10^6$	O+O $\times 10^6$	O+O ₂ $\times 10^6$	O+NO+O ₂ $\times 10^9$	O+2NO $\times 10^9$	2O+NO $\times 10^9$	2O+O ₂ $\times 10^9$	(O+NO)+W $\times 10^2$
62D	1.0	3.2	0.22	1.1	14	9.4	2.1	0.91
61D	1.6	2.2	0.15	1.4	48	13	1.2	1.3
59D	1.4	1.6	0.11	1.2	46	11	1.1	1.1
60D	1.8	2.0	0.14	1.6	60	13	1.0	1.4

Note: these calculations are based on the assumption that $\alpha = 15\%$.

Table VII Experiments with Packed Chamber

Analysis of Effluent Oxides

Run	Refrigerant	Pressure mm.	O ₂ cc/min.	NO cc/min.	NO ₂ cc/min.	NO/NO ₂ out
62D	Pet. ether	0.73	30	5.8	0	81
61D	" "	0.80	30	2.5	0	66
59D	" "	0.82	30	2.1	0	81
60D	" "	0.86	30	2.0	0	30

V. DISCUSSION

The collision data are recorded in Tables I, II, IV, V, and VI. For reasons before mentioned, the work summarized in Table II will not be discussed. To facilitate interpretation, runs having approximately the same O/NO ratio have been grouped together. Within these groups, the various runs are arranged in order of increasing pressure.

The experiments, the results of which are recorded in Tables I, IV, and VI, are all very much alike. They can be included in the same discussion.

On first inspection of the "b" tables, one is struck by the reasonable constancy of the efficiency for the collision, $O + NO$. This, however, may be entirely fortuitous since the only experimental quantities involved in calculating this particular efficiency are the half-life period, $t_{\frac{1}{2}}$, and the number of nitric oxide molecules per cc., N_{NO} . The values of $t_{\frac{1}{2}}$ and N_{NO} were generally not greatly changed from run to run. However, the over-all variation of $t_{\frac{1}{2}}$ is about 10, and that of N_{NO} about 20. It should be pointed out that the runs which deviated largely from the usual efficiency are ones in which, as a general rule, either $t_{\frac{1}{2}}$ or N_{NO} was unusually high or low.

As pointed out before, theory would seem to require that the collision complex, $(O \cdot NO)$, formed by O and NO could be stabilized only by subsequent collision or radiation. The latter process would be, in any normal case, very improbable since the time required for an electronically activated molecule to radiate is of the order of 10^{-8} seconds which is a good deal longer than the comparatively long

life assumed for the complex $(\text{NO}\cdot\text{O})$ - namely, 10^{-11} seconds.

As Rodebush⁵⁴ has pointed out, a stabilization of the collision complex by collision would account for the wide range of frequencies emitted since varying amounts of kinetic energy would be assumed by both the nitrogen dioxide molecule and the stabilizing body.

If there were not enough triple collisions to account for the reaction rate, then it might be necessary to assume that the complex were extremely abnormal and ascribe to it an average life of the order of 10^{-6} seconds. Such, however, is not the case as is shown by the calculated efficiencies for the collision, $(\text{O}\cdot\text{NO}) + \text{W}$, (extreme right-hand column of Tables Ib, IVb, and VIb).

These values have been calculated from the formula developed on page 16, and are based on the reasonable assumption that the collision complex, $(\text{O}\cdot\text{NO})$ has a life of the order of 10^{-11} seconds in accord with Kimball's work⁴¹.

While the efficiencies may not possess the constancy which one might wish for, still, in view of the sources of error, the over-all variation of about twenty-fold might be expected. With the elimination of a very few experiments, this could be considerably reduced.

This variation should be compared with that of the efficiency for the collision, $\text{O} + \text{NO}$, (which is eleven-fold) in the light of relative sources of error involved. Among the latter, it may be pointed out that perhaps the molecules present do not all have equal powers of stabilizing the complex. The efficiency then would vary as the relative concentrations changed.

The results of the packed chamber experiments (Tables VIa and VIb) show quite definitely that the rate of the reaction is not greatly affected by the area: volume ratio of the reaction vessel. Consequently, any wall reaction which uses up oxygen atoms in competition with the afterglow-producing reaction cannot be important.

For purposes of comparison, the area : volume ratio of the various reaction vessels is tabulated:

2.5 cm. tubular chamber - - - - -	1.5 cm. ² /cc.
5.8 cm. tubular chamber - - - - -	0.7 "
5 liter spherical chamber - - - - -	0.3 "
packed chamber - - - - -	9. "

On account of the liquid-air temperature oxidation of nitric oxide by molecular oxygen, the data given in the first part of Table III is considered valueless and will not be further discussed. Beginning with run 35D, a slush of low-boiling petroleum ether was used as the refrigerant for trapping out the higher oxides of nitrogen.

When liquid air is used, the oxides are blue provided there is an excess of nitric oxide passing through the trap with the nitrogen dioxide. This is mostly the trioxide. Once in a while a reddish oxide was observed. When petroleum ether was used, the small amount of material in the trap appeared to be colorless.

In these experiments, the initial concentration of oxygen atoms was always a good deal greater than that of the oxide to assure the attainment of the "equilibrium" proportions of nitric oxide and nitrogen dioxide, i.e., the proportions at which the rates of



and



are equal.

The results indicate that the second of these is surely more than ten times faster than the first at any of the pressures used; however, because of the small amounts of oxide which could be trapped out, it is impossible to say just how much faster.

An examination of the results of runs 35D to 58D shows a trend toward large NO/NO₂ ratios in the effluent gases. It was pointed out before that this is presumably due to shortened periods of pre-cooling the trap with liquid air before surrounding it with petroleum ether.

Table VII gives similar data for runs with a packed chamber.

The results of the diffusion experiments are given in Table V. While the efficiencies of the collisions, O + NO and (O.NO) + W, so found are of the order of 10 to 20 times that found by the direct flow method, still this agreement is quite remarkable when one remembers the errors that may be incurred in the calculation of the diffusion coefficient, D, and in the estimation of the radius of the flame at half-life. This latter quantity would have been especially capable of introducing a large error (see equation, page 18).

Spealman and Rodebush³ found that the efficiency of the collision, O + NO₂, was of the order of 10⁻⁵. The efficiency of the collision, O + NO, has been found in this work to be of the order of 10⁻⁶. A simple calculation will show, then, that the rates of the two reactions will be equal when

$$N_{\text{NO}}/N_{\text{NO}_2} \sim 10$$

The direct measurements presented in the last part of Table II and in Table VII indicate that this ratio is probably considerably larger than this in the pressure range studied (~ 0.5 mm.) The direct measurement of the efficiency of $O + NO_2$ is somewhat more difficult than the corresponding measurement with $O + NO$ since the former must be carried out with excess nitrogen dioxide, in which case no afterglow is produced. The extent of the reaction zone must then be estimated by the heat liberated on the walls of the reaction vessel.

It is, therefore, not at all improbable that the combined errors of the two collision efficiencies might result in a total error of five-fold.

Although little of a quantitative nature is known in regard to the Morse curves (potential energy plotted as a function of internuclear distance) for the various electronic levels of nitrogen dioxide, some of their principal relations have been inferred by Herzberg⁵⁶ and Franck, Sponer, and Teller.⁴⁷ The nature of the predissociation spectrum in the region, $\lambda = 3800 \text{ \AA}$ to $\lambda = 4000 \text{ \AA}$, has led them to suppose that the minimum of the potential curve (E) for the excited molecule, dissociation of which gives normal nitric oxide and an excited oxygen atom, lies slightly below the potential of the unassociated nitric oxide and normal oxygen atom.

The equilibrium internuclear distance is thought to be slightly greater for the excited molecule than for the unexcited one. A repulsion curve (R) for normal nitric oxide and atomic oxygen, showing no minimum, intersects the curve (E) once, at a potential slightly above that of the completely dissociated normal products.

The picture for the process producing the afterglow is this:

- (1) A normal oxygen atom approaches a nitric oxide molecule.
- (2) The potential follows curve (R) until the intersection with curve (E) is reached.
- (3) Provided the kinetic energy of the free particles was originally not much greater than the potential at this point, the collision complex, (O·NO), may now change over to curve (E).
- (4) Provided a stabilizing collision does not occur within 10^{-11} seconds (the life assumed for the complex), the system will probably retrace its path to the free particles.
- (5) A complex which has lost a little energy by collision may be unable to get back across the potential hump.
- (6) Such a complex will eventually (10^{-8} seconds) radiate energy.

This picture explains the appearance of bands in the afterglow as being caused by transitions from various vibrational levels in the excited molecules to various levels in the normal molecules. Their diffuse nature may be due to a lack of rotational quantization in the excited state.

The time required for step (6) has been found by fluorescence investigations by Norrish²⁹ and Baxter.³⁷ They found that the fluorescence produced by illuminating nitrogen dioxide with light

of wave lengths $4358 \text{ \AA}$ and $4047 \text{ \AA}$ consisted of broad maxima in the regions $\lambda = 6400 \text{ \AA}$ and $5900 \text{ \AA}$.

Quenching experiments indicated that the life of an excited nitrogen dioxide molecule was of the order of 5×10^{-8} seconds which is extremely short compared to the half-life of afterglow producing reaction as here studied.

Norrish observed that the activated molecule could undergo many collisions without becoming deactivated. This point is not of great importance to the work here described because the time of radiation (5×10^{-8} seconds) is considerably shorter than the time between collisions (10^{-7} seconds or more).

It seems possible that the longer wave lengths in the afterglow may be in part caused by fluorescence.

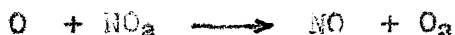
VI. SUMMARY

1. Collision experiments carried out at pressures from 0.1 mm. to 0.9 mm. between atomic oxygen and nitric oxide indicate that one in every 10^8 collisions between O and NO is effective in producing NO_2 . Although this ratio is reasonably constant from run to run, it was decided that the more probable mechanism involved the intermediate formation of a collision complex followed by stabilization by collision, viz.,



where W is a third body. On the assumption that the complex, $(\text{O}\cdot\text{NO})$, has a life of the order of 10^{-11} seconds, one such collision in every one hundred is effective in using up an oxygen atom.

2. In the pressure range 0.4 mm. to 0.8 mm., the reaction,



is certainly more than 10 times as fast as



The difference in rates is probably much greater than this. This conclusion is drawn from analysis of the effluent oxides from the completely decayed oxygen afterglow in which there was originally a large enough excess of oxygen atoms to assure the steady state proportions of NO and NO_2 .

3. It was demonstrated by means of a reaction chamber having a large area : volume ratio that any wall reaction competing with the gas-phase, afterglow-producing one is relatively unimportant.

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VITA

The writer was born December 13, 1911 in Portland, Oregon. He attended grammar school there and in Fairview, Oregon. He completed his secondary education at Jefferson High School, Portland, in 1930, having attended Gorton High School in Yonkers, New York during his junior year. He entered Willamette University at Salem, Oregon in September 1930 and received the degree of Bachelor of Arts in June 1934. During his senior year he was Senior Scholar in Chemistry and was elected to Alpha Kappa Nu, scholastic honorary.

He entered the Graduate School of the University of Illinois in September 1934. During the years 1934-37 he held a teaching assistantship in inorganic chemistry. He is a member of Phi Lambda Upsilon and an associate member of Sigma Xi.

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